Cyano Derivatives of some Organochlorophosphate(v) Ions

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Reaction of excess AgCN with the organochlorophosphate(v) ions $[PRCl_5]^-$ (R = Ph or Me) leads to the formation of $[PPhCl_2(CN)_3]^-$ (all three isomers) and $[PMe(CN)_5]^-$ respectively; salts containing these ions have been isolated, and characterised by elemental analysis and ^{31}P n.m.r. spectroscopy. Several intermediate six-co-ordinate phosphorus complexes have been identified spectroscopically, and isomeric configurations have been assigned by the method of pairwise interactions. The agreement between calculated and observed shift values is less good than in six-co-ordinate phosphorus(v) systems with substituents other than cyanide, possibly because of distortions from regular octahedral geometry.

Few six-co-ordinate phosphate(v) anions containing cyanide ligands have been reported; the complex $[PF_5(CN)]^-$ has been prepared by reaction of PF_5 with cyanide ions,[1] while some cyano derivatives of the hexachlorophosphate ion have been obtained by reaction of $[PCl_6]^-$ salts with AgCN, or by oxidation of phosphorus(III) compounds.[2] Evidence for some bromochlorocyanophosphates(v) was also found from suitable oxidation reactions.[2] Recently, species in the series $[PF_{6-n}(CN)_n]^-$ and $[PF_3Cl_{3-n}(CN)_n]^-$ have been described.[3] The unusual ion $[P_2(CN)_{10}]^{2-}$ has been obtained as its $[CH(PPh_3)_2]^+$ salt, and its crystal structure has been determined.[4] No such derivatives with an organo group on phosphorus have been reported, however.

One of the most striking observations in the chlorocyanophosphate(v) series was the extreme stability of both isomers of the $[PCl_3(CN)_3]^-$ ion, which did not hydrolyse, or undergo substitution reactions with N_3^-, NCS^-, or CN^- ions, except for one fortuitous preparation of *trans*-$[PCl_2(CN)_4]^-$.[2] It was therefore of considerable interest to investigate the reactions of organochlorophosphates with cyanide ions, to see whether their behaviour parallelled that of $[PCl_6]^-$, and whether particular stability was associated with a certain number of cyano groups.

We report the first preparation of cyano derivatives of the ions $[PRCl_5]^-$ (R = Ph[5] or Me[6]). Salts containing the ions $[PPhCl_2(CN)_3]^-$ (a mixture of the three possible isomers) and $[PMe(CN)_5]^-$ have been isolated, and characterised by elemental analysis and ^{31}P n.m.r. spectroscopy. Several intermediate chlorocyanophosphates have been identified spectroscopically in solution, and their isomeric configurations assigned by the method of pairwise interactions,[2,3,7–13] although this procedure did not give such good numerical agreement as in some other six-co-ordinate phosphorus(v) systems. Possible explanations for the observed behaviour are discussed. A preliminary account of this work[14] was presented at the International Conference on Phosphorus Chemistry (Nice, September, 1983).

Experimental

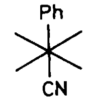
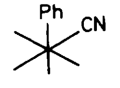
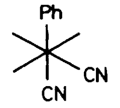
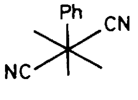
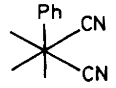
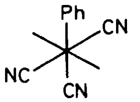
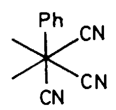
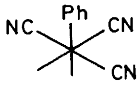
All manipulations including n.m.r. sample preparation were carried out either *in vacuo* or under an inert atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used, in general without further purification except for tetraalkylammonium chlorides, which were dried as in earlier work.[2] The compounds $PPhCl_4$ and $PMeCl_4$ were obtained by chlorination of $PPhCl_2$ and $PMeCl_2$ respectively,[15] $[NEt_4][PMeCl_5]$ was prepared as described previously,[6] and $[NEt_4][PPhCl_5]$ was prepared by a similar procedure to that used for the $[NPr^n{}_4]^+$ and $[N(n\text{-}C_5H_{11})_4]^+$ salts (Found: C, 39.9; H, 6.3; Cl, 42.5; N, 3.1; P, 7.3. $C_9H_{23}Cl_5NP$ requires C, 40.5; H, 6.1; Cl, 42.7; N, 3.4; P, 7.5%).

Tetraethylammonium Dichlorotricyano(phenyl)phosphate, $[NEt_4][PPhCl_2(CN)_3]$.—$[NEt_4][PPhCl_5]$ (3.848 g, 9.26 mmol) was dissolved in CH_2Cl_2, and an excess of silver cyanide (6.204 g, 46.3 mmol) was added, with stirring. The mixture was left to stir for *ca.* 2 h, and the silver salts were removed by filtration. The volume of solvent was reduced *in vacuo*, and the solution then placed in the refrigerator. The fine white crystals which formed were filtered off and washed with low-boiling (303—313 K) light petroleum (Found: C, 52.0; H, 7.5; Cl, 16.5; N, 14.6; P, 8.1. $C_{17}H_{25}Cl_2N_4P$ requires C, 52.7; H, 6.5; Cl, 18.3; N, 14.5; P, 8.0%). The ^{31}P n.m.r. spectrum of a solution of the product in CH_2Cl_2 showed that all three of the possible isomers were present.

Attempted Preparation of Tetraethylammonium Trichlorodicyano(phenyl)phosphate, $[NEt_4][PPhCl_3(CN)_2]$.—The compound $[NEt_4][PPhCl_5]$ (1.651 g, 3.97 mmol) was dissolved in a small amount of CH_2Cl_2, and AgCN (1.081 g, 8.07 mmol) was added, with stirring. The mixture was left to stir for 1 h, the silver salts were removed by filtration, and the volume of solvent was reduced *in vacuo*. The solution deposited fine white crystals when left in the refrigerator. These were separated and washed with low-boiling light petroleum (Found: C, 48.0; H, 6.8; Cl, 25.8; N, 10.0; P, 8.2. $C_{16}H_{25}Cl_3N_3P$ requires C, 48.4; H, 6.4; Cl, 26.8; N, 10.6; P, 7.8%). When some of the crystals were dissolved in CH_2Cl_2 and their ^{31}P n.m.r. spectrum recorded, however, the presence of *cis*-$[PPhCl_4(CN)]^-$ and the isomers of $[PPhCl_2(CN)_3]^-$, as well as the three isomers of $[PPhCl_3(CN)_2]^-$, showed that a pure compound had not been obtained.

Tetraethylammonium Pentacyano(methyl)phosphate, $[NEt_4][PMe(CN)_5]$.—The compound $[NEt_4][PMeCl_5]$ (3.318 g, 9.39 mmol) was dissolved in $MeNO_2$, and a slight excess of AgCN relative to a 5:1 molar ratio (6.484 g, 48.4 mmol) was added, with stirring. The solution was left to stir for 1 h, the silver salts were removed by filtration from the orange solution, and the solvent was removed *in vacuo* to yield an orange solid (Found: C, 47.3; H, 7.7; Cl, 0.0; N, 20.2; P, 9.1. $C_{14}H_{23}N_6P$ requires C, 54.9; H, 7.6; Cl, 0.0; N, 27.4; P, 10.1%). Carbon and nitrogen analyses were consistently low from several preparations of this compound, and it appeared that difficulty was being encountered in obtaining complete combustion of the cyano groups. The complete absence of chlorine was considered

Table 1. Calculated and experimental ^{31}P n.m.r. shifts (p.p.m.) for $[PPhCl_{5-n}(CN)_n]^-$

		Calculated $\delta(^{31}P)$		Experimental
Ion	Isomer	A	B	$\delta(^{31}P)$
	(I)	−212.4	−212.4	Not seen
	(II)	−235.2	−237.9	−224.4
	(I)	−251.9	−254.6	−259.5
	(II)	−267.3	−272.7	−277.3
	(III)	−274.7	−280.1	−285.3
	(I)	−291.4	−296.8	−299.8
	(II)	−298.8	−304.2	−309.5
	(III)	−314.2	−322.3	−314.2

conclusive, however. The ^{31}P n.m.r. spectrum of the compound redissolved in CH_2Cl_2 showed only one major peak at −333.7 p.p.m., assigned to the $[PMe(CN)_5]^-$ ion, together with a minor impurity signal at 17.8 p.p.m.

Phosphorus-31 n.m.r. spectra were recorded at 307.2 K on a Fourier-transform spectrometer, as described previously.[10] Chemical shifts were measured relative to external H_3PO_4, with the downfield direction taken as positive. Elemental micro-analyses were also obtained as indicated in earlier papers.[10,15]

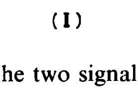
Results and Discussion

(*a*) *Substitution into the* $[PPhCl_5]^-$ *Ion by* CN^-.—When small amounts of AgCN were added to a solution of $[NEt_4][PPhCl_5]$ in CH_2Cl_2, with excess NEt_4Cl present to suppress the dissociation of the six-co-ordinate species,[5] new n.m.r. signals were observed upfield from that of the starting material (Table 1). These peaks were assigned to particular ions in the series $[PPhCl_{5-n}(CN)_n]^-$ from the changes in their relative intensities with amount of added AgCN. In solutions with a small amount of AgCN present, the resonance at −259.5 p.p.m. was more intense than that at −285.3 p.p.m., but the latter became relatively more intense with addition of more cyanide, as the intensity of the signal at −224.4 p.p.m. declined. Even so, both signals are attributed to isomers of $[PPhCl_3(CN)_2]^-$, and a possible rationalisation of this behaviour is discussed below.

The anions were quite stable in solution, and attempts were made to isolate some of the complexes. A 1:2 molar ratio reaction of $[NEt_4][PPhCl_5]$ with AgCN led to the isolation of crystals which analysed approximately as $[NEt_4][PPhCl_3(CN)_2]$ (Experimental section). When they were redissolved in CH_2Cl_2, several ^{31}P resonances were seen, at −227.3(m), −262.8 (s), −277.3 (mw), −288.6 (w), −302.9 (s), −311.1 (ms), and −314.1 (ms) p.p.m., assigned sequentially to *cis*-$[PPhCl_4(CN)]^-$, the three isomers of $[PPhCl_3(CN)_2]^-$, and the three isomers of $[PPhCl_2(CN)_3]^-$. Hence a mixture of ions rather than a pure product was obtained. A 1:3 molar ratio reaction also gave white crystals, which analysed as $[NEt_4][PPhCl_2(CN)_3]$ and on dissolution gave signals at −301.5 (s), −309.5 (vs), and −314.2 (s) p.p.m. These signals were assigned to the three possible isomers of the anion. Very similar results were obtained from a 1:5 molar ratio reaction; the product analysed as the trisubstituted compound, and gave signals when redissolved at −301.5 (vs), −309.5 (s), and −314.2 (s) p.p.m. The shifts were identical to those from the 1:3 reaction, and the only difference was a change in their relative intensities, as indicated. Hence substitution stops at the tricyanophosphate stage in this system, parallel to the behaviour of $[PCl_6]^-$ towards AgCN, where the $[PCl_3(CN)_3]^-$ ion (both isomers) is very resistant to further substitution.[2] Like $[PCl_3(CN)_3]^-$, the $[PPhCl_2(CN)_3]^-$ ion proved to be resistant to hydrolysis, and its ^{31}P n.m.r. spectrum was unchanged by exposure to the laboratory atmosphere for 4 h. It also did not react with tosylamine, unlike the isomers of $[PPhCl_3(CN)_2]^-$.[16]

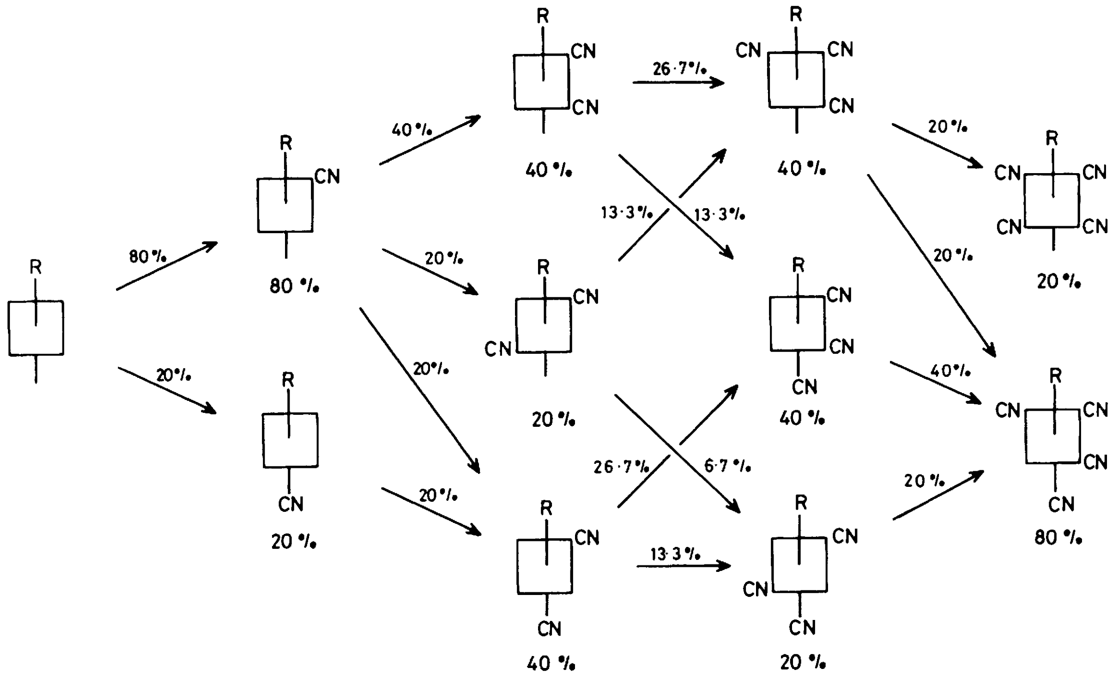
To apply the method of pairwise interactions[7] to this system, the Ph:Cl term was taken as −1.05 p.p.m. from the limiting shift of the $[PPhCl_5]^-$ ion,[5] while the Ph:CN term was derived as −26.2 p.p.m. from the highest field chemical shift (−314.2 p.p.m.) for an isomer of $[PPhCl_2(CN)_3]^-$, which was assumed to have the structure with three coplanar CN groups and Cl *trans* to Ph. (Calculations always gave the most negative numerical shift value for this isomer.) Other terms were taken from the $[PCl_{6-n}(CN)_n]^-$ system.[2] The results are shown in column A of Table 1. A second set of values was derived by taking the weighted average for the Ph:CN term from the shifts of the three isomers of $[PPhCl_2(CN)_3]^-$, and these are given in column B. Although the numerical agreement is only moderate, some isomeric configurations may be deduced, as shown in Table 1.

The single isomer detected for $[PPhCl_4(CN)]^-$ is assigned a *cis* configuration since statistically this is the most probable product, although the experimental shift is between the calculated values for the *cis* and *trans* isomers. The experimental value could be rather low if the $[PPhCl_4(CN)]^-$ ion dissociates to any extent, like $[PPhCl_5]^-$ in CH_2Cl_2,[5] so the experiment was repeated in $PhNO_2$ as solvent. When AgCN was added, resonances at −225.7 (s), −262.8 (mw), −286.9 (m), −302.9 (s), −309.5 (s), and −314.2 (ms) p.p.m. were observed in the six-co-ordinate region, generally in good agreement within experimental error with the shift values in CH_2Cl_2. No substantial difference in the extent of dissociation in these solvents was therefore apparent.



(I)

As mentioned above, the two signals assigned to isomers of $[PPhCl_3(CN)_2]^-$ from the substitution reaction in CH_2Cl_2 are interesting in that the peak at −259.5 p.p.m. was initially more intense, but the one at −285.3 p.p.m. increased rapidly in



Scheme 1. Statistical pattern of substitution in the $[PRCl_5]^-$–CN^- system

Table 2. $\delta(^{31}P)$ for $[PMeCl_{5-n}(CN)_n]^-$ ions in CH_2Cl_2 solution

n	0	1	2	3	4	5
$\delta(^{31}P)$/ p.p.m.	-204.7	-224.0 -217.7	-267.5	-296.6	-325.5 -315.9	-333.7

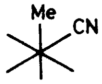
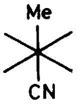
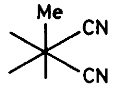
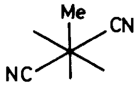
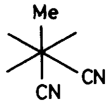
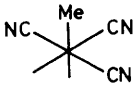
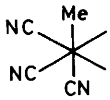
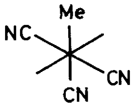
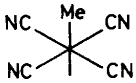
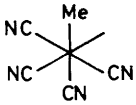
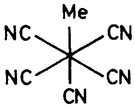
intensity with the addition of more cyanide, as the intensity of the signal at -224.4 p.p.m. decreased. A possible explanation is that both isomers of $[PPhCl_4(CN)]^-$ are initially formed, but the *trans* isomer is not detected in solution because it is rapidly substituted by more CN^- to give the isomer (I) of $[PPhCl_3(CN)_2]^-$, with a shift of -259.5 p.p.m. Substitution into *cis*-$[PPhCl_4(CN)]^-$ then leads predominantly to isomer (III) of $[PPhCl_3(CN)_2]^-$, with two *cis* CN groups and Cl *trans* to phenyl (δ -285.3 p.p.m.), as shown by the statistical treatment, which is given in Scheme 1 for reaction of $[PRCl_5]^-$ with CN^-. Some support for this hypothesis is provided by the pairwise calculations, which give the nearest value to -259.5 p.p.m. for isomer (I) and the nearest value to -285.3 p.p.m. for isomer (III). A small peak at -277.3 p.p.m. observed in the spectrum of the re-dissolved 1:2 reaction product is assigned to the third isomer (II) of $[PPhCl_3(CN)_2]^-$, in keeping with the intermediate shift value calculated from pairwise additivity. All three isomers of $[PPhCl_2(CN)_3]^-$ were observed, and the structures are assigned as shown in Table 1 on the basis of the pairwise calculations.

(*b*) *Substitution into the* $[PMeCl_5]^-$ *Ion by* CN^-.—Successive small amounts of AgCN were similarly added to a concentrated solution of $[NEt_4][PMeCl_5]$[6] (prepared by adding excess $[NEt_4]Cl$ to a solution of $PMeCl_4$ in CH_2Cl_2, and the ^{31}P n.m.r. spectrum was recorded after each addition. New signals upfield from the $[PMeCl_5]^-$ resonance were found, as well as some weak peaks from hydrolysis $[PMe(O)Cl_2]$ or decomposition products. From the changes in the relative intensities of the peaks in the six-co-ordinate region with amount of added AgCN, it was possible to assign them to particular species in the series $[PMeCl_{5-n}(CN)_n]^-$ as shown in Table 2. The initial spectrum of the mixture with a small amount of AgCN added did not show the peak at -217.7 p.p.m., but this was observed as a minor signal in one of the later spectra. There was some doubt as to whether it was genuine, but it could be due to the less abundant isomer of $[PMeCl_4(CN)]^-$. Only one isomer was observed for $n = 2$ and 3, although there are three possible configurations in each instance.

Reactions of various molar ratios of $[PMeCl_5]^-$ with AgCN did not give a single anionic product. For example a 1 : 2 reaction in $MeNO_2$ gave a number of peaks at -225.7 (m), -269.1 (vs), -298.2 (m), -319.5 (w), and -327.2 (m) p.p.m., as well as some impurity signals. A 1:4 reaction in MeCN showed resonances at -267.5 (vs), -296.6 (vs), -317.5 (w), and -325.5 (m) p.p.m., whereas a 1:5 reaction in this solvent gave peaks at -315.9 (vs), -327.1 (s), and -333.7 (m) p.p.m., ascribed to the two isomers of $[PMeCl(CN)_4]^-$ and to $[PMe(CN)_5]^-$ respectively. No attempt was made to isolate the mixed chlorocyanophosphates in view of these results, but the reaction of $[NEt_4][PMeCl_5]$ with excess (>5:1) AgCN in CH_2Cl_2 gave an orange solid, analysis of which showed the absence of chlorine. When redissolved in CH_2Cl_2 it yielded a major peak at -333.7 p.p.m., assigned to the anion $[PMe(CN)_5]^-$, and a minor impurity peak at 17.8 p.p.m. Its i.r. spectrum showed absorption bands at 2 200s, 2 166w, and 2 060m cm^{-1}, characteristic of the C≡N group.

The pairwise additivity method[7] was also applied to this system, by taking the Me:Cl term as -1.48 p.p.m. from the limiting shift of the $[PMeCl_5]^-$ ion[6] and the CN:Cl, CN:CN, and Cl:Cl terms from the $[PCl_{6-n}(CN)_n]^-$ system.[2] This leaves only the Me:CN term as an unknown. The $[PMeCl_4(CN)]^-$ ion can exist in two isomeric forms, with the CN group either *trans* or *cis* to the methyl. For the *trans* isomer there are no Me:CN interactions, and its chemical shift can be calculated as -214.1 p.p.m., in reasonable agreement with the minor peak observed at -217.7 p.p.m. The resonance at -224.0 p.p.m. is therefore assigned to *cis*-$[PMeCl_4(CN)]^-$, enabling the

Table 3. Calculated and experimental ^{31}P n.m.r. shifts (p.p.m.) for $[PMeCl_{5-n}(CN)_n]^-$

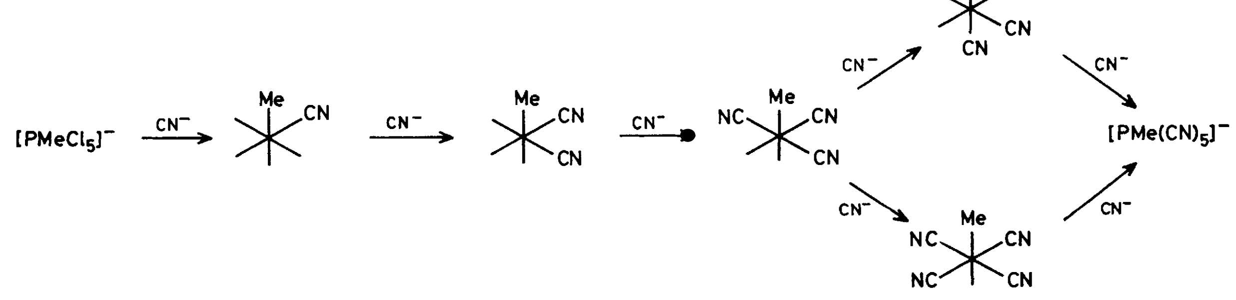
Ion	Calculated $\delta(^{31}P)$			Experimental
	A	B	C	$\delta(^{31}P)$
	−224.0	−225.7	−224.0	−224.0
	−214.1	−214.1	−214.1	−217.7
	−250.6	−254.0	−248.6	−267.5
	−243.3	−246.7	−243.3	
	−240.7	−242.4	−238.7	
	−277.3	−282.4	−273.2	−296.6
	−274.7	−278.1	−268.6	
	−267.3	−270.7	−263.3	
	−311.2	−318.0	−303.1	−325.5
	−308.7	−313.8	−298.5	−315.9
	−350.0	−356.8	−333.5	−333.7

Me:CN term to be evaluated as −13.74 p.p.m. The shifts for all the other possible isomers may then be calculated, as shown in column A of Table 3, and clearly are not in good numerical agreement with the experimental shifts for n = 2—5. The breakdown of this approach is perhaps not surprising, having been observed previously in the $[PCl_{6-n}(CN)_n]^-$ series[2] and in related fluoro systems with cyano groups present,[3] and may arise from distortion of the (assumed) regular octahedral structure, particularly as the number of cyano groups increases.

Since the $[PMeCl_5]^-$ ion is not completely associated in CH_2Cl_2 even in the presence of excess chloride ions,[6] the chemical shift of the first substitute was checked in $PhNO_2$ also, in case the $[PMeCl_4(CN)]^-$ ion dissociated to any extent in CH_2Cl_2, thus giving a lower field shift and a low value for the Me:CN term. $[N(n\text{-}C_5H_{11})_4]Cl$ was added to a solution of $PMeCl_4$ in $PhNO_2$ until the limiting shift of −204.7 p.p.m.[6] was attained, and AgCN was then added. The ^{31}P solution spectrum contained peaks at −198.2 (s) ($[PMeCl_5]^-$), −225.7 (s), ascribed to *cis*-$[PMeCl_4(CN)]^-$, −267.5 (m), −298.2 (ms), −317.5 (s), and −335.3 (m) p.p.m. The values are very similar for the two solvents within experimental error, suggesting that the cyano complexes are predominantly associated in solution. If the Me:CN value of −15.44 p.p.m. from the shift of *cis*-$[PMeCl_4(CN)]^-$ in $PhNO_2$ is used, the calculated values in column B of Table 3 are obtained. This gives marginally better agreement for n = 2, 3, or 4, but even poorer agreement than before for n = 5. Alternatively if the Me:CN term is taken as −13.74 p.p.m. and the experimental shift for $[PMe(CN)_5]^-$ then used to obtain a revised value for the CN:CN term of −34.84 p.p.m., the values in column C result, which gave a poorer fit than column A for n = 2, 3, and 4.

Despite these limitations, some deductions can be made from the data. The results suggest that $[PMeCl_3(CN)_2]^-$ probably has the first structure shown in Table 3, with *cis* cyano groups and a chlorine *trans* to the methyl, since this isomer has the highest calculated shift. Similarly, the most probable isomer for $[PMeCl_2(CN)_3]^-$ is the one with three cyano groups *cis* to the methyl. Both isomers of $[PMeCl(CN)_4]^-$ were detected, and the initially more abundant isomer (δ −315.9 p.p.m.) may be the one with the additional CN *trans* to the methyl group, although the values calculated from pairwise interactions are quite close in this instance.

These conclusions are supported by a statistical consideration of the system (Scheme 1). The *cis* isomer of $[PMeCl_4(CN)]^-$ is four times more likely to be formed than the *trans* isomer, and the experimental results confirm that one isomer is formed almost exclusively. Only one isomer was detected for $[PMeCl_3(CN)_2]^-$ and the statistically more probable configuration by substitution into *cis*-$[PMeCl_4(CN)]^-$ is with both cyano groups *cis* and Cl *trans* to methyl. Substitution into this isomer leads preferentially to the isomer of $[PMeCl_2(CN)_3]^-$ with



Scheme 2. Pattern of substitution by CN^- in $[PMeCl_5]^-$

three coplanar cyano groups. Both isomers of $[PMeCl(CN)_4]^-$ are now equally likely to be formed from this starting material and both were observed, although not in equal quantities. While the results indicate that the statistical predictions are not followed exactly, since all isomers would then be seen, and that the methyl and/or cyano groups may therefore exert directive effects leading to the preferential formation of particular isomers, the structural deductions are entirely compatible from the two approaches. The suggested pattern of substitution is thus as shown in Scheme 2.

The difference in behaviour between the ions $[PPhCl_5]^-$ and $[PMeCl_5]^-$ towards AgCN is quite striking; while the presence of three CN groups appears to confer a particular stability on $[PPhCl_2(CN)_3]^-$, similar to that shown by $[PCl_3(CN)_3]^-$, there is no such stability associated with $[PMeCl_2(CN)_3]^-$. It was suggested previously that the stability of $[PCl_3(CN)_3]^-$ (both isomers) could be due to P–Cl π bonding by donation from filled chlorine orbitals to the unoccupied $3d\ t_{2g}$ orbitals on phosphorus, which may be lowered in energy by the presence of the CN groups.[2] This process seems therefore to be aided by the presence of the phenyl group, which can participate in π bonding, but not by the electron-supplying methyl group which has no such possibility.

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