# Adducts of Phosphorus(v) Chloride with Pyridine Bases

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Complex formation between $PCl_5$ and a variety of pyridine bases has been investigated in solution by means of $^{31}P$ n.m.r. spectroscopy. Most unidentate pyridines form molecular 1 : 1 adducts co-ordinated *via* the pyridine nitrogen, although 2-cyanopyridine may be attached *via* the cyano-group. Complex formation appears to be inhibited by both steric and electronic effects, but steric hindrance seems to be more important. Some methyl-substituted pyridines are chlorinated by $PCl_5$ with formation of $PCl_3$. Bidentate pyridines form ionic derivatives $[PCl_4L][PCl_6]$ (2 : 1), $[PCl_4L]Cl$ (1 : 1), or mixtures of these, but the stable species in concentrated solution is the 2 : 1 adduct. Some of the adducts have been isolated and characterised by a number of physical techniques. The solid-state structures appear to correspond with those in solution, except for derivatives of bidentate pyridines mentioned above.

SEVERAL reports have appeared in the literature concerning pyridine adducts of phosphorus(v) chloride, but the data are far from consistent. A 1 : 1 adduct was mentioned independently by Holmes[1] and Gutmann,[2] but the first detailed account was given by Beattie and Webster,[3] who isolated the moisture-sensitive compound from carbon disulphide solution. They recorded its i.r. and Raman spectra and found it to be undissociated in benzene and acetonitrile.[4,5] The heat of reaction in nitrobenzene was measured by Holmes and his co-workers[6,7] who suggested that the adduct was molecular from cryoscopic and conductivity measurements. Ultraviolet data for a series of pyridine (py) adducts also supported a molecular structure.[8] Independent measurements of the $^{31}P$ n.m.r. chemical shift of $PCl_5$ in liquid pyridine (234 and 233.2 p.p.m.)[9,10] and of a mixture of $PCl_5$ and pyridine in 1,2-dichloroethane[10] (232.6 p.p.m.) have been interpreted in terms of the molecular adduct $PCl_5{\cdot}py$, as have the results for the similar $PCl_5{\cdot}3Me\text{-}py$ system.[10] The shifts of 296 (solid) and 310 p.p.m. (acetonitrile) reported by Wieker *et al.*[11] for the $PCl_5{\cdot}py$ adduct are almost certainly due to a hexachlorophosphate,[12] probably the pyridinium salt formed by partial hydrolysis.

Paul and his co-workers[13,14] concluded from conductivity measurements in nitrobenzene that 1 : 1 adducts of $PCl_5$ with py, quinoline, 3Me-py, and 4Me-py were ionic, in contrast to the work of Holmes *et al.*[6] Their i.r. spectrum for $PCl_5{\cdot}py$, moreover, differs from that of Beattie and Webster.[3] Conflicting conclusions have also been reached from the reactivity of $PCl_5$ and its pyridine adduct towards ammonium chloride. Lehr and Schwarz[15] found that reactivity decreased along the series $[PCl_6]^- < PCl_5{\cdot}py < PCl_5 < [PCl_4]^+$, in agreement with a molecular structure, but Zhivukhin *et al.*[16] reported increased reactivity of $PCl_5$ towards $[NH_4]Cl$ on addition of pyridine, supporting an ionic formulation $[PCl_4(py)]Cl$ for the 1 : 1 adduct. Very recently a 1 : 1 adduct of pyrazine (pyz) with $PCl_5$ has been isolated,[17] for which an ionic structure $[PCl_4(pyz)]Cl$ was suggested, with possible $\pi$ bonding between the ring and phosphorus as in metal sandwich compounds.

In addition, some co-ordination compounds of $PCl_5$ with bidentate pyridines are known. Deveney and Webster[18,19] isolated a 1 : 1 adduct of $PCl_5$ and 1,10-phenanthroline, formulated as $[PCl_4(phen)]Cl$ from cryoscopy, conductivity, and comparison of its i.r. spectrum with that of $[PCl_4(phen)][SbCl_6]$.[20] A 1.33 : 1 adduct of $PCl_5$ with 2,2′-bipyridyl has been prepared,[10] which shows $^{31}P$ n.m.r. peaks in nitrobenzene solution of approximately equal intensity at 191.3 and 299.0 p.p.m., assigned to $[PCl_4(bipy)]^+$ and $[PCl_6]^-$ respectively. The solid 'compound' is thus probably a mixture of $[PCl_4(bipy)][PCl_6]$ and $[PCl_4(bipy)]Cl$,[2] but the solution-stable species seems to be the 2 : 1 adduct; $[PCl_4(bipy)]^+$ has also been mentioned as a personal communication in ref. 5.

We report the results of a solution investigation into adducts of $PCl_5$ with a large number of pyridine bases by means of $^{31}P$ n.m.r. spectroscopy, which has established the structures assumed therein. The effect on adduct formation of the basicity of the pyridine, and of large ring substituents in the 2 position, has been studied. Several of the compounds have been isolated and charac-

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[1] R. R. Holmes, *Diss. Abs.*, 1954, **14**, 452.

[2] V. Gutmann, *Monatsh.*, 1954, **85**, 1077.

[3] I. R. Beattie and M. Webster, *J. Chem. Soc.*, 1961, 1731.

[4] I. R. Beattie and M. Webster, *J. Chem. Soc.*, 1963, 38.

[5] I. R. Beattie, T. R. Gilson, and G. A. Ozin, *J. Chem. Soc.* (*A*), 1968, 2772.

[6] R. R. Holmes, W. P. Gallagher, and R. P. Carter, jun., *Inorg. Chem.*, 1963, **2**, 437.

[7] R. R. Holmes, *Abs. 142nd Ann. Meeting Amer. Chem. Soc.*, New Jersey, September 1962, p. 29N.

[8] K. Hensen and W. Sarholtz, *Theor. Chim. Acta*, 1968, **12**, 206.

[9] H. P. Latscha, *Z. Naturforsch.*, 1968, **B23**, 139.

[10] K. B. Dillon, unpublished work.

[11] W. Wieker, A-R. Grimmer, and L. Kolditz, *Z. Chem.*, 1967, **7**, 434.

[12] K. B. Dillon, R. J. Lynch, R. N. Reeve, and T. C. Waddington, *J. Inorg. Nuclear Chem.*, 1974, **36**, 815.

[13] R. C. Paul and S. L. Chanda, *Indian J. Chem.*, 1968, **6**, 754.

[14] R. C. Paul, M. L. Sehgal, and S. L. Chanda, *J. Indian Chem. Soc.*, 1970, **47**, 1071.

[15] W. Lehr and M. Schwarz, *Z. anorg. Chem.*, 1968, **363**, 43.

[16] S. M. Zhivukhin, V. V. Kireev, V. P. Popilin, and G. S. Kolesnikov, *Russ. J. Inorg. Chem.*, 1970, **15**, 630.

[17] J. N. Ishley and H. C. Knachel, *Inorg. Chem.*, 1975, **14**, 2558.

[18] M. J. Deveney and M. Webster, *Inorg. Nuclear Chem. Letters*, 1967, **3**, 195.

[19] M. Webster and M. J. Deveney, *J. Chem. Soc.* (*A*), 1968, 2166.

[20] I. R. Beattie, K. Livingston, and M. Webster, *J. Chem. Soc.*, 1965, 7421.

terised in the solid state by analysis and $^{31}P$ n.m.r. and i.r. spectroscopy.

## EXPERIMENTAL

All the manipulations were carried out either *in vacuo* or under an inert atmosphere of dry nitrogen. Chemicals were of the best available commercial grade, including pyridine for Karl Fischer analysis, and were used without further purification except as indicated below. 1,10-Phenanthroline (anhydrous) was dried and stored over concentrated sulphuric acid in a desiccator. 2-Methyl-, 3-methyl-, 2,4,6-trimethyl-, and 2-chloro-pyridine were redistilled from potassium hydroxide pellets and stored under nitrogen. The absence of excessive amounts of water in the pyridines was checked by recording their i.r. spectra.

Phosphorus-31 n.m.r. spectra were recorded at 307.2 K on a Perkin-Elmer R10 spectrometer operating at 24.29 MHz, with a Digiac signal-averaging accessory. Solid and liquid samples were contained in stationary sample tubes (outside diameter, 8.4 mm). The technique of recording solid-state spectra on a high-resolution machine has been described previously.[21] Deconvolution of overlapping solid-state signals was accomplished by means of a Dupont 310 curve resolver. Chemical shifts were measured relative to external $P_4O_6$, but are expressed relative to 85% phosphoric acid to facilitate comparison with literature data.

TABLE 1

Analytical data for adducts of $PCl_5$ and pyridines

| | | Analysis (%) | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Found | | | | | | Calc. | | | | | |
| Compound | Solvent | C | H | N | P | Cl | X * | C | H | N | P | Cl | X * |
| $PCl_5\cdot py$ | $MeNO_2$ | 20.75 | 2.10 | 4.55 | 10.35 | 60.4 | | 20.85 | 1.75 | 4.85 | 10.75 | 61.7 | |
| $PCl_5\cdot py\cdot 2PhNO_2$ | $PhNO_2$ | 35.55 | 2.65 | 7.85 | 5.95 | 35.8 | | 37.9 | 2.80 | 7.80 | 5.75 | 33.0 | |
| $PCl_5\cdot 3,5Me_2$-py | $PhNO_2$ | 28.05 | 3.40 | 4.85 | 9.85 | 55.7 | | 26.65 | 2.90 | 4.45 | 9.80 | 55.7 | |
| $PCl_5\cdot 3Me$-py | $PhNO_2$ | 24.9 | 3.15 | 5.30 | 9.70 | 59.6 | | 23.9 | 2.30 | 4.65 | 10.3 | 58.9 | |
| $PCl_5\cdot 3Cl$-py | $EtNO_2$ | 18.7 | 1.40 | 4.35 | 9.60 | 65.5 | | 18.65 | 1.25 | 4.35 | 9.65 | 66.1 | |
| $PCl_5\cdot 3Br$-py | $EtNO_2$ | 17.15 | 1.60 | 3.90 | 8.20 | 49.3 | 22.1 | 16.4 | 1.10 | 3.80 | 8.50 | 48.4 | 21.8 |
| $PCl_5\cdot 3I$-py | $MeNO_2$ | 14.8 | 1.25 | 3.35 | 7.40 | 42.4 | 30.5 | 14.55 | 1.00 | 3.40 | 7.50 | 42.9 | 30.7 |

* X = Br or I.

Carbon, hydrogen, and nitrogen microanalyses were obtained by combusion using a Perkin-Elmer 240 Elemental Analyser. The results were often very variable, and analyses for phosphorus and halogen were considered to be more reliable. Phosphorus was determined colorimetrically as the molybdovanadophosphate complex after decomposition of the adduct by heating with sodium peroxide in a nickel Parr bomb. Chlorine was analysed by potentiometric titration against silver nitrate in an aqueous acetone medium. Bromine and iodine were determined iodimetrically following a Schoniger oxygen flask combustion of the compound as described by Ingram.[22] Infrared spectra of solids were run as Nujol mulls in the range 250—4 000 $cm^{-1}$ on a Perkin-Elmer 457 instrument. Caesium iodide plates for the range below 650 $cm^{-1}$ were protected with Polythene discs to prevent attack by chlorine-containing compounds.

The preparation of solid complexes is described below.

(*a*) *Unidentate pyridines*. The general procedure adopted was to add the stoicheiometric quantity of base slowly, either as a neat liquid or as a solution in the minimum volume of solvent (Table 1), to $PCl_5$ dissolved or suspended in the same solvent. The mixtures were stirred for a few minutes to ensure homogeneity. Rapid precipitation of the adduct occurred for all but 3Me-py, where the solid which formed initially redissolved on stirring; in this instance the solvent ($PhNO_2$) was immediately distilled off *in vacuo*. The solids were isolated, washed with benzene for $MeNO_2$ as solvent or (sometimes) with $CH_2Cl_2$ for other solvents, and then with low-boiling light petroleum. Drying was completed at the pump where necessary. Solvents used and elemental analyses of the adducts are given in Table 1. The absence of unchanged $PCl_5$ in the products was shown by the lack of the characteristic band due to $[PCl_4]^+$ at 654 $cm^{-1}$ (i.r.).

(*b*) *Bidentate pyridines*. $[PCl_4(phen)][PCl_6]$. Phosphorus(V) chloride (3.87 g, 18.6 mmol) and 1,10-phenanthroline (1.72 g, 9.5 mmol) were dissolved separately in the minimum quantity of nitroethane. The $PCl_5$ solution was added quickly to the phen solution with stirring, and the mixture was allowed to stand for a few minutes. The crystals which appeared were separated, washed with methylene chloride and light petroleum, and dried *in vacuo* {Found: C, 23.9; H, 1.35; Cl, 59.35; N, 5.10; P, 10.2. $[PCl_4(phen)][PCl_6]$ requires C, 24.15; H, 1.35; Cl, 59.4; N, 4.70; P, 10.4%}.

$[PCl_4(phen)][PCl_6]_xCl_{1-x}$. (*i*) A solution of phen (2.43 g, 13.5 mmol) in a few millilitres of dry benzene was added slowly, with stirring, to a solution of $PCl_5$ (2.81 g, 13.5 mmol) in dry benzene (100 $cm^3$). A yellowish white suspension was formed. The solid was filtered off, washed with light petroleum, and dried *in vacuo* to yield an off-white powder (Found: C, 32.65; H, 2.60; Cl, 53.75; N, 6.50; P, 9.20%). The analyses correspond approximately to the composition $[PCl_4(phen)][PCl_6]_{0.324}Cl_{0.676}$.

(*ii*) {This method was used by Webster and Deveney [19] to prepare $[PCl_4(phen)]Cl$.} Phosphorus(V) chloride (2.78 g, 13.3 mmol) dissolved in benzene (79 $cm^3$) was added to phen (2.42 g, 13.4 mmol) dissolved in the minimum quantity of benzene. The off-white powder produced was isolated as in (*i*) (Found: C, 34.25; H, 1.85 ; Cl, 51.6; N, 5.85; P, 8.85%). The analyses correspond to an approximate composition $[PCl_4(phen)][PCl_6]_{0.214}Cl_{0.786}$.

$[PCl_4(bipy)][PCl_6]$. A saturated solution of 2,2′-bipyridyl (2.11 g, 13.5 mmol) in nitromethane was added to a saturated solution of $PCl_5$ (5.65 g, 27.1 mmol) in nitromethane, with stirring. The crystals which rapidly formed were separated, washed with light petroleum, and dried *in vacuo* {Found: C, 19.25; H, 1.60; Cl, 60.7; N, 4.60; P, 10.3. $[PCl_4(bipy)][PCl_6]$ requires C, 20.95; H, 1.40; Cl, 61.9; N, 4.90; P, 10.8%}.

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[21] K. B. Dillon and T. C. Waddington, *Spectrochim. Acta*, 1971, **A27**, 1381.

[22] G. Ingram, 'Organic Elemental Analysis,' Chapman Hall, London, 1963.

## RESULTS AND DISCUSSION

(*a*) *Solution Investigations.*—The behaviour of a variety of substituted pyridines towards $PCl_5$ was investigated in solution by means of $^{31}P$ n.m.r. spectroscopy. Samples were usually prepared with a large excess of the pyridine, often with the base as solvent in the case of liquid pyridines, to increase the extent of complex formation with weak ligands. Some solutions containing a 1 : 1 molar ratio of base to $PCl_5$ in nitrobenzene were also made up. The results are shown in Table 2, in the order of the $pK_a$ values for the conjugate acids of the pyridines.[23,24] Chemical shifts agree well with previous determinations,[9,10] except for those reported by Wieker *et al.*[11] for $PCl_5{\cdot}py$ as mentioned in the introduction. The results for different types of pyridines are discussed in more detail below.

TABLE 2

Phosphorus-31 n.m.r. solution studies of $PCl_5$–pyridine reactions

| Base | $pK_a$ [23,24] | $\delta(^{31}P)$/ p.p.m. | Solvent [a] |
|---|---|---|---|
| $2,4,6Me_3$-py | 7.4 | −217.0, 297.3 | 1 : 1 in $PhNO_2$ |
| $3,5Me_2$-py | 6.2 | Adduct insoluble | $PhNO_2$ (saturated) |
| 2Me-py | 5.9 | −217.3 | 1 : 1 in $PhNO_2$ |
| 3Me-py | 5.6 | 228.0 [b] | Neat |
| py | 5.2 | 228.0 | Neat |
| phen | 4.9 [c] | 190.6, 299.0 | $PhNO_2$ (saturated) |
| | | 193.3, 298.6 | 1 : 1 in $PhNO_2$ |
| 3I-py | 3.3 | 229.7 | $PhNO_2$ (saturated) |
| 3F-py | 3.0 | 229.3 | Neat |
| 3Br-py | 2.9 | 228.3 | Neat |
| 3Cl-py | 2.8 | 228.6 | Neat |
| 4CN-py | 1.9 | 227.5 | $PhNO_2$ (saturated) |
| 3CN-py | 1.4 | 228.1 | $PhNO_2$ (saturated) |
| pyz | 0.8 | 224.9 | $PhNO_2$ (saturated) |
| | | 219.1 | 1 : 1 in $PhNO_2$ |
| $3,5Cl_2$-py | 0.7 | 222.7 | $PhNO_2$ (saturated) |
| | | 170.2 | 1 : 1 in $PhNO_2$ |
| 2Br-py | 0.8 | 83.0 | Neat |
| 2Cl-py | 0.6 | 109.1 | Neat |
| | | 84.8 | 1 : 1 in $PhNO_2$ |
| 2CN-py | −0.3 | 170.8 | Neat |
| | | 171.3 | 1 : 1 in $PhNO_2$ |
| 2F-py | −0.4 | 184.7 | Neat |
| | | 77.8 | 1 : 1 in $PhNO_2$ |

[a] Either neat base, nitrobenzene saturated with base, or nitrobenzene (for 1 : 1 mixtures). [b] A signal at −203.3 p.p.m. slowly appears. [c] $pK_1$.

*Pyridine,* 3X-py (X = F, Cl, Br, I, *or* CN), *and* 4CN-py. With an excess of these ligands, which provide no steric barriers to complex formation, $PCl_5$ gave a single $^{31}P$ resonance between 227 and 230 p.p.m. The large upfield shift relative to $PCl_5$ shows the formation of a six-co-ordinate species in each case, while the shift difference from cationic derivatives such as $[PCl_4(phen)]^+$ or $[PCl_4(py)_2]^+$ (ref. 25) is compatible with formulation as a molecular adduct $PCl_5{\cdot}py$. This conclusion is supported by the solid-state results and is in agreement with the deductions of most previous workers for the phosphorous(V) chloride–pyridine system.[3-10] The compounds have been shown not to exchange on the n.m.r. time scale with the corresponding $[PCl_4(py)_2]^+$ ions,[25] confirming that the signals do not arise from mixtures of $[PCl_4(py)_2]^+$ and $[PCl_6]^-$ ions with a single averaged shift, but are due to distinct chemical species.

The chemical shift does not seem to be affected by the basicity of the pyridine, the values all being within the range of solvent effects and experimental uncertainty. The complexes also appear to be completely associated under the experimental conditions, since neither a free $PCl_5$ resonance nor a shift of a possible averaged $PCl_5$–$PCl_5{\cdot}py$ peak was detected. The similarity of the results for complexes of 3- and 4-cyanopyridine with those for the other ligands in this group suggests that the mode of co-ordination is identical, *via* the ring nitrogen rather than the cyano-group. This is the usual form of co-ordination for these bases because of the greater nucleophilicity of the pyridine nitrogen,[26,27] althought bridging cyanopyridines have been reported for stronger acceptors such as tin(IV) chloride with no excess of base present.[26]

*Pyrazine and* 3,5-*dichloropyridine.* These weaker bases when in excess gave slightly lower shifts with $PCl_5$ than the previous group, as shown in Table 2. Accordingly, solutions containing equimolar quantities of base and $PCl_5$ were prepared, to check whether complex formation was incomplete, with the shift representing an average between free and bound $PCl_5$. The value of 170.2 p.p.m. for the 1 : 1 mixture of $PCl_5$ and $3,5Cl_2$-py confirms this hypothesis, and corresponds to *ca.* 60% association. Steric interference with complex formation is not expected for this ligand, and the incompleteness of the process appears to be electronic in origin, caused by the low basicity of the pyridine. Conversely, pyrazine (pyz) gave very similar shifts for the 1 : 1 mixture and the solution with excess of base present, any difference probably being due to impurities in the pyz which make the base : $PCl_5$ ratio less than 1 : 1. The slightly lower shift for the pyrazine system than for 3X-py complexes thus probably reflects the rather different type of ligand involved, and complex formation appears to be essentially complete. No evidence was found for the formation of an ionic, possibly π-bonded, adduct $[PCl_4(pyz)]Cl$ in solution, as suggested by Ishley and Knachel.[17] Such a species is expected to have a much lower $^{31}P$ chemical shift, as shown by the results for adducts of $PCl_5$ with bidentate pyridines which are discussed below.

2X-py (X = F, Cl, Br, *or* CN). Phosphorus(V) chloride dissolved in these weakly basic pyridines to give solution $^{31}P$ chemical shifts of between 83 and 185 p.p.m. (Table 2). Indeed the value in 2-bromopyridine lies close to that of free $PCl_5$ in non-polar solvents,[28] but the peak

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[23] D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965.

[24] K. Schofield, 'Heteroaromatic Nitrogen Compounds,' Butterworths, London, 1967.

[25] K. B. Dillon, R. N. Reeve, and T. C. Waddington, *J.C.S. Dalton*, submitted for publication.

[26] S. C. Chan and F. T. Wong, *Austral. J. Chem.*, 1971, **24**, 1519.

[27] S. C. Jain, *J. Inorg. Nuclear Chem.*, 1973, **35**, 505.

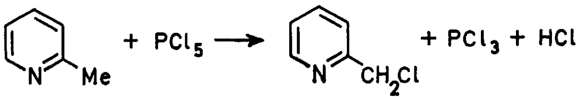
[28] V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 227.

was very broad suggesting an exchange process. 1 : 1 Mixtures of 2-chloro- and 2-fluoro-pyridines with $PCl_5$ in nitrobenzene gave broad signals at *ca.* 80 p.p.m., indicating exchange between free and complexed $PCl_5$ but with the equilibrium $PCl_5 + py \rightleftharpoons PCl_5{\cdot}py$ lying very much to the left. We therefore conclude that the 2-halogenopyridines complex much less strongly than the bases discussed previously. It is noteworthy that the order of complexing ability appears to be 2F-py > 2Cl-py > 2Br-py, the reverse order of their basicities, indicating that steric hindrance from the bulkier 2 substituents is more important than electronic effects in this series.

The formation of ionic adducts $[PCl_4(2X\text{-}py)_2]Cl$ (ref. 25) in equilibrium with $[PCl_4]Cl$ cannot be entirely discounted from the shift values. This possibility seems remote, however, in view of the general chemical similarities of the pyridine bases, and of the results for 1 : 1 mixtures of $PCl_5$ and 2-chloro- or 2-fluoro-pyridine which are much closer to the $PCl_5$ position than to $[PCl_4]^+$. Moreover, 2-halogenopyridines have been shown not to co-ordinate when added in a 2 : 1 molar ratio to a nitrobenzene solution of $[PCl_4][SbCl_6]$, since the shift observed is identical with that of $[PCl_4]^+$ in each case.[25]

2-Cyanopyridine gives almost identical shifts for the 1 : 1 mixture with $PCl_5$ and for the solution with excess of base present, suggesting that complex formation is virtually complete but that the adduct is of a different type to those discussed previously. This ligand is known to co-ordinate to transition metals through either the ring nitrogen [29] or the cyano-group,[26,30] the latter mode being ascribed to more favourable steric factors despite the greater nucleophilicity of the pyridine nitrogen. It is thus possible that complex formation with $PCl_5$ takes place *via* the cyano-group. Aliphatic nitriles with hydrogens on the 2-carbon are known to react in a complex way with $PCl_5$ at room temperature, giving ionic products including $[PCl_6]^-$,[31] but this course of reaction is not open to 2CN-py. Acetonitrile is also reported not to react with $PCl_5$ at 233 K,[32] but a six-co-ordinate species has clearly been formed in our system. A 1 : 1 mixture of $PCl_5$ and benzonitrile in nitrobenzene showed only a $^{31}P$ resonance due to molecular $PCl_5$ at 82 p.p.m., however, with no adduct apparently present. It thus appears that the presence of a cyano-group alone is not sufficient to cause complex formation.

*Methylpyridines.* These ligands behave differently towards $PCl_5$ than those discussed above. With 1 : 1 mixtures of $PCl_5$ and 2-methyl-substituted pyridines, rapid darkening of the solution was observed. When the samples were stable enough for their $^{31}P$ n.m.r. spectra to be recorded, signals due to $PCl_3$ were apparent, together with a signal for $[PCl_6]^-$ from 2,4,6-trimethylpyridine.[12] The formation of $PCl_3$ suggests that $PCl_5$ acts as a chlorinating agent towards these bases, probably attacking a methyl group, *e.g.* as in (1). The HCl formed as a by-product may then produce a hexachlorophosphate by reaction with more $PCl_5$ and base [equation (2)]. No evidence for formation of six-co-ordinate species other than $[PCl_6]^-$ was found.



(1)

The results for pyridines with methyl groups in the 3 or 5 positions differed. 3,5-Dimethylpyridine formed an insoluble stable 1 : 1 adduct with $PCl_5$ (Experimental and solid-state sections), and no solution spectra could be obtained. 3-Methylpyridine dissolved $PCl_5$ to give a clear yellow solution which darkened slowly. The solution showed a six-co-ordinate adduct peak at 228 p.p.m., but a low-field peak appeared slowly at —203.3 p.p.m., attributed to $PCl_3$ complexed weakly by the excess of pyridine. Solid adducts of $PCl_3$ with pyridines have been reported,[33-35] but their solution behaviour has been little investigated.[36] The $^{31}P$ n.m.r. spectrum of a solution of $PCl_3$ in excess of pyridine showed a single peak with a concentration-dependent shift of a similar order of magnitude to that observed with 3Me-py.

$$py + PCl_5 + HCl \longrightarrow [Hpy][PCl_6] \qquad (2)$$

There are thus two competing reactions in these systems, complex formation and chlorination. The 2-methylpyridines may well be sufficiently sterically hindered to inhibit adduct formation, thus favouring the chlorination reaction, whereas complex formation occurs preferentially with 3-methylpyridines, the adduct being stable if isolated at this stage. It is noteworthy that $PF_5$ is only partially associated with 2,4,6Me$_3$-py at 298 K, although it forms a stable adduct with py.[37]

*Bidentate pyridines.* 1,10-Phenanthroline gives two equally intense peaks with $PCl_5$, both of which lie in the six-co-ordinate region, when present either in an equimolar amount or in excess (Table 2). The high-field peak is readily assignable to $[PCl_6]^-$,[12] and the signal at *ca.* 192 p.p.m. is ascribed to the cationic species $[PCl_4(phen)]^+$. This deduction accords with the co-ordinating properties of the ligand, the rigid structure of which makes unidentate co-ordination highly unlikely. The chemical shifts are very similar to those observed on dissolving a 1.33 : 1 adduct of $PCl_5$ with 2,2′-bipyridyl in nitrobenzene.[10] Thus under our conditions the solution-stable species appears to be the 2 : 1 adduct $[PCl_4L][PCl_6]$. The 1 : 1 adduct $[PCl_4L]Cl$ appears not to be present even when excess of ligand is available. This conclusion contrasts

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[29] I. Piljac and T. Reynolds, *Inorg. Chim. Acta*, 1969, **3**, 49.

[30] F. Farha and R. T. Iwamoto, *Inorg. Chem.*, 1965, **4**, 844.

[31] H. P. Latscha, W. Weber, and M. Becke-Goehring, *Z. anorg. Chem.*, 1969, **367**, 40.

[32] C. D. Schmulbach and I. Y. Ahmed, *J. Chem. Soc.* (*A*), 1968, 3008.

[33] R. C. Paul, M. L. Sehgal, and S. L. Chanda, *J. Indian Chem. Soc.*, 1970, **47**, 1071.

[34] D. H. Boal and G. A. Ozin, *J.C.S. Dalton*, 1972, 1824.

[35] R. G. Makitra, M. S. Makuruk, and M. N. Didych, *J. Gen. Chem.* (*U.S.S.R.*), 1972, **42**, 1872.

[36] A. R. Katritzky, F. J. Swinbourne, and B. Ternai, *J. Chem. Soc.* (*B*), 1966, 235.

[37] E. L. Muetterties, T. A. Bither, M. W. Farlow, and D. D. Coffman, *J. Inorg. Nuclear Chem.*, 1960, **16**, 52.

with that of Webster and Deveney,[19] who deduced the solution structure [$PCl_4$(phen)]Cl from molecular-weight and cryoscopic measurements in nitrobenzene. The explanation of this discrepancy may lie in the much more dilute solutions which they used, by analogy with $PCl_5$ itself where the dominant equilibrium at very low concentrations is (3) and at higher concentrations is (4).

$$PCl_5 \rightleftharpoons [PCl_4]^+ + Cl^- \qquad (3)$$

$$2PCl_5 \rightleftharpoons [PCl_4]^+ + [PCl_6]^- \text{ (ref. 38)} \qquad (4)$$

It is noteworthy that chloride ion appears to be a stronger ligand than py towards $PCl_5$ in solution. When a less than equimolar amount of dry tetra-n-pentylammonium chloride was added to a nitrobenzene solution of $PCl_5$·py the $^{31}P$ n.m.r. spectrum indicated the presence of two six-co-ordinate species, $PCl_5$·py and $[PCl_6]^-$, the latter being present in higher concentration. This experiment shows that the two species do not exchange rapidly on the n.m.r. time scale, and that equilibrium (5) lies to the right under these conditions.

$$PCl_5\cdot py + Cl^- \rightleftharpoons [PCl_6]^- + py \qquad (5)$$

(*b*) *Solid-state Studies.*—(*i*) *Adducts of unidentate pyridines.* The similarity of the solid-state and solution i.r. spectra of $PCl_5$·py [4,5] suggests that the adduct retains a molecular structure in both phases. To extend the structural information, some solid adducts were isolated, as described in the Experimental section, and studied by various physical techniques. The adducts of unidentate pyridines analysed as 1 : 1 species, as shown. In addition, the bis(nitrobenzene) solvate of $PCl_5$·py was prepared from nitrobenzene solution. These adducts were all white or off-white solids, stable in the absence of moisture. Their $^{31}P$ n.m.r. spectra consisted of single broad symmetrical peaks; the chemical shifts obtained are shown in Table 3. Considerable experimental difficulty was experienced with the 3-halogenopyridine adducts, since the baseline tended to drift during spectrum accumulation; indeed no reliable value for the 3-iodopyridine adduct could be determined. Within experimental uncertainty the values are in good agreement with the solution results given previously, and confirm the molecular structure of the solid compounds. The linewidths are larger than those in more symmetrical six-co-ordinate species such as $[PCl_6]^-$,[12] possibly because of lower symmetry, the presence of the nitrogen quadrupole, or variations in interdipolar distances. The similarity of the shifts for $PCl_5$·py and $PCl_5$·py·2$PhNO_2$ suggests the same mode of co-ordination in each case, *i.e.* with the pyridine attached to phosphorus and the nitrobenzene loosely held in the lattice as solvent of crystallisation. This was confirmed by the i.r. spectra discussed below.

TABLE 3

Phosphorus-31 n.m.r. solid-state shifts for adducts of $PCl_5$ and pyridines

| Compound | $\delta(^{31}P)$/p.p.m. |
|---|---|
| $PCl_5$·py | 224.7 ± 4.1 |
| $PCl_5$·py·2$PhNO_2$ | 228.5 ± 2 |
| $PCl_5$·3,5$Me_2$-py | 216 ± 13 |
| $PCl_5$·3Me-py | 237 ± 7 |
| $PCl_5$·3Cl-py | 235.8 ± 7.3 |
| $PCl_5$·3Br-py | 236 ± 10 |

TABLE 4

Infrared bands ($cm^{-1}$) for adducts between $PCl_5$ and pyridines

| Compound | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $PCl_5$·py | 642m | 610w | 588w [a] | 484s, br | 440s | 352w | 312w | 292w | 268w | 253w | | |
| $PCl_5$·py·2$PhNO_2$ | 642m | 612w | 591w [a] | 485s, br | 432s, br | 398w [b] | 349w | 312w | | | | |
| $PCl_5$·3,5$Me_2$-py | 638w | 615w | 588w [a] | 538m | 527m | 496s | 470s, br | 438s, br | 348m | 299w | 278w | |
| $PCl_5$·3Me-py | 637w | | 593m [a] | 531m | 527 (sh) | 494s | 448s, br | 392m | 353w | 345w | 300vw | 292w |
| $PCl_5$·3I-py | 654w | 620w | 591m [a] | 518m | 508m | 488s | 450s, br | | | | | |
| $PCl_5$·3Br-py | 650m | 618w | 589m [a] | 521m | 512m | 488s | 448s, br | 402s | 362m | 350w | 327w | 290w |
| $PCl_5$·3Cl-py | 652w | 622w | 592m [a] | 532m | 526m | 492s | 448s, br | | | | | |

[a] $POCl_3$ hydrolysis impurity. [b] $PhNO_2$ band.

The bands observed in the i.r. spectra (Nujol mulls) of these adducts within the range 350—660 $cm^{-1}$ (in some cases 250 $cm^{-1}$) are listed in Table 4. The frequencies for both $PCl_5$·py and its bis(nitrobenzene) solvate are very similar to those reported by Beattie and his co-workers [4,5] with the exception of a weak band at 398 $cm^{-1}$ in the latter ascribed to free nitrobenzene.[39] The same mode of co-ordination is thus indicated in both adducts. Marked frequency shifts of this band have been reported for co-ordinated nitrobenzene in transition-metal complexes,[39] and a smaller shift (to 387 $cm^{-1}$) for the $AlCl_3$·$PhNO_2$ adduct.[40] The bands between 350 and 520 $cm^{-1}$ in the spectra of $PCl_5$·py were considered as mainly due to P–Cl vibrations, with little or no contribution from the P–N bond.[4,5] This is the lower end of the P–Cl frequency range, showing that the P–Cl bonds are weakened by co-ordination of the base. These absorptions are broad and largely unresolved, but greater resolution was possible in the substituted-pyridine adducts where the bands are appreciably sharper. Nevertheless the spectra are all essentially similar, and differ considerably from that of $[PCl_4][PCl_6]$.[41] They thus confirm the molecular structure for the solids deduced previously from the n.m.r. data. The strong broad band at *ca.* 450 $cm^{-1}$ in $PCl_5$·py was assigned tentatively by Beattie *et al.*[5] to $a_1$ $\nu(PCl_{ax.})$, and the absorptions between 480 and 510 $cm^{-1}$ to $e$ $\nu(PCl_{eq.})$.

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[38] R. W. Suter, H. C. Knachel, V. P. Petro, J. H. Howatson, and S. G. Shore, *J. Amer. Chem. Soc.*, 1973, **95**, 1474.

[39] W. L. Driessen, L. M. van Geldrop, and W. L. Groeneveld, *Rec. Trav. chim.*, 1970, **89**, 1271.

[40] D. E. H. Jones and J. L. Wood, *J. Chem. Soc.* (*A*), 1966, 1448.

[41] G. L. Carlson, *Spectrochim. Acta*, 1963, **19**, 1291.

As Table 4 shows, these frequencies do not vary markedly with the basicity of the pyridine, suggesting that the strength of the co-ordinate bond is similar in all cases. This is also in agreement with the solution n.m.r. results. The medium-to-weak vibration found in all the systems in the range 638—654 cm$^{-1}$ appears to be genuine and not due to $[PCl_4]^+$ impurity; a similar band was reported for $PCl_5{\cdot}py$.[4]

(*ii*) *Adducts of bidentate pyridines.* The preparation of $[PCl_4(phen)][PCl_6]$ is described in the Experimental section. Its $^{31}P$ n.m.r. spectrum showed a broad asymmetric peak, which was deconvoluted (on the assumption of a 1 : 1 area ratio) to give signals at 199 ± 10 and 298 ± 2 p.p.m. These values are in excellent agreement with the solution data and fully support the proposed structure. The hexachlorophosphate peak is much narrower than the cation signal, accounting for the asymmetric appearance. When the literature preparation of the 1 : 1 complex[19] was repeated, non-stoicheiometric products were obtained, the composition of which depended on the order of addition of the components (Experimental section). This behaviour is probably due to the immediate formation of the 1 : 1 adduct $[PCl_4(phen)]Cl$, which then disproportionates to the 2 : 1 species and the free base. Precipitation occurs before this process is complete. Rapid isolation could thus give the 1 : 1 adduct, as presumably accomplished by Webster and Deveney.[19] The solid-state $^{31}P$ n.m.r. spectrum of the adduct of approximate composition $[PCl_4(phen)][PCl_6]_{0.214}Cl_{0.786}$ showed the expected peak for $[PCl_6]^-$, with a broad shoulder at lower field due to the cation. All the three solids isolated were dissolved in nitrobenzene and their $^{31}P$ n.m.r. solution spectra were recorded (Table 5). Each showed two peaks of equal area within experimental uncertainty, confirming that the solution-stable species is the 2 : 1 adduct $[PCl_4(phen)][PCl_6]$, at least under the conditions used in this work. The difference from the conclusions of Webster and Deveney, who identified the species in solution as the 1 : 1 adduct,[19] has been discussed in the previous section.

TABLE 5

Phosphorus-31 n.m.r. data for adducts between $PCl_5$ and 1,10-phenanthroline in $PhNO_2$

| Compound | $\delta(^{31}P)$/p.p.m. |
|---|---|
| $[PCl_4(phen)][PCl_6]$ | 192.7, 299.1 |
| $[PCl_4(phen)][PCl_6]_{0.324}Cl_{0.676}$ | 193.4, 302.2 |
| $[PCl_4(phen)][PCl_6]_{0.214}Cl_{0.786}$ | 192.4, 299.2 |

TABLE 6

Infrared bands (350—550 cm$^{-1}$) for adducts between $PCl_5$ and 1,10-phenanthroline

| Compound | | | | | | | |
|---|---|---|---|---|---|---|---|
| $[PCl_4(phen)][PCl_6]_{0.324}Cl_{0.676}$ | 542s | 527m | 511s | 488s | 467s | 452s | 438s |
| $[PCl_4(phen)][PCl_6]_{0.214}Cl_{0.786}$ | 541s | 525m | 509s | 488s | 466s | 449s | 437s |
| $[PCl_4(phen)][PCl_6]$ | 539s | 525 (sh) | 508s | 482s | 452 (sh) | 438s | 422 (sh) |

The i.r. bands observed in the range 350—550 cm$^{-1}$ for the solids isolated are given in Table 6. The spectra consist of a broad absorption at *ca.* 438 cm$^{-1}$ due to $[PCl_6]^-$,[41] together with other lines at higher frequency ascribed to the cation. The bands closer to the $[PCl_6]^-$ absorption are better resolved in the non-stoicheiometric adducts, where the concentration of this anion is lower. The similarity of the cation spectra to each other and to those for $[PCl_4(phen)]Cl$[19] and $[PCl_4(phen)][SbCl_6]$[20] confirms that the ligand is similarly co-ordinated in all cases.

The hydrolysis behaviour of the 2 : 1 adduct was investigated by exposing it to the laboratory atmosphere. There was a limited evolution of hydrogen chloride, but a white powder remained even after overnight exposure, rather than a viscous liquid as usually found on hydrolysis of phosphorus(V) chloro-compounds. The i.r. spectrum of the powder showed little difference from that of the starting material below 650 cm$^{-1}$, except for the disappearance of the $[PCl_6]^-$ absorption. Some broadening of higher-frequency peaks was noticed, suggesting that the cation is attacked slowly by moist air, but the six-co-ordinate species $[PCl_4(phen)]^+$ is clearly considerably more resistant to hydrolysis than uncomplexed $[PCl_4]^+$. This agrees with the report that $[PCl_4(phen)][SbCl_6]$ does not hydrolyse readily.[20]

The isolation of the 2 : 1 adduct of $PCl_5$ with 2,2′-bipyridyl has been described (Experimental section). The solid-state $^{31}P$ n.m.r. spectrum was deconvoluted, assuming two signals of equal intensity, to give a sharp peak at 292 ± 5 p.p.m. with a broad shoulder at 181.5 ± 7 p.p.m., as expected for the structure $[PCl_4(bipy)][PCl_6]$. The results are in good agreement with solution shifts found previously for the adduct of approximate composition $[PCl_4(bipy)][PCl_6]_{0.33}Cl_{0.67}$.[10] The i.r. spectrum of the 2 : 1 adduct below 600 cm$^{-1}$ consisted of a broad absorption at 437 cm$^{-1}$ assigned mainly to $[PCl_6]^-$,[41] and a partially split band at 517 and 510 cm$^{-1}$ assigned to the cation. Other cation vibrations are probably obscured by the $[PCl_6]^-$ band.

Our main conclusions are that most unidentate pyridines co-ordinate to $PCl_5$ *via* the pyridine nitrogen to form molecular adducts, except for 2-cyanopyridine which may be attached *via* the cyano-group. Complex formation may be inhibited by both steric effects (large ring substituents in the 2 position) and electronic effects (decreasing base strength), but the former appear to predominate. Some methylpyridines are chlorinated by $PCl_5$, leading to formation of $PCl_3$. Bidentate pyridines co-ordinate to form the ionic species $[PCl_4L]Cl$, $[PCl_4L]$-$[PCl_6]$, or mixtures thereof, but the solution-stable species under our conditions is the 2 : 1 adduct $[PCl_4L]$-$[PCl_6]$.

The results may be compared with those for a similar series of unidentate pyridines and the acceptor molecules

$BF_3$ and $AlBr_3$.[42] Although $AlBr_3$ is usually a much stronger acceptor than $BF_3$, which is comparable with $PCl_5$ in its Lewis-acid properties towards pyridine,[8] the smaller molecule $BF_3$ formed complexes even with 2-substituted (F, Cl, Br, or CN) pyridines. Only a small amount of $AlBr_3$ was co-ordinated under the same conditions, in the order 2CN- $<$ 2Cl- $<$ 2F- $<$ 2Br-. The importance of steric hindrance to complex formation is thus emphasised. 2-Methyl- and 3-methyl-pyridine showed no reaction other than addition, in contrast to their behaviour towards $PCl_5$, while complex formation with non-hindered ligands (py, 4CN-, 3Cl-, and 3Br-py) was essentially complete.

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[42] H. H. Perkampus and U. Krüger, *Ber. Bunsengesellschaft Phys. Chem.*, 1967, **71**, 439.