# Acceptor Properties of Some Methyl- and Ethyl-chlorophosphoranes and their Derivatives with Lewis Acids

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The acceptor properties of the alkylchlorophosphoranes $PR_nCl_{5-n}$ (R = Me, $n$ = 1 or 2; R = Et, $n$ = 1—3), and of their derivatives with suitable Lewis acids ($SbCl_5$ or $PCl_5$), towards the Lewis bases $Cl^-$, pyridine, 2,2'-bipyridine, and 1,10-phenanthroline have been investigated, using mainly [31]P n.m.r. spectroscopy. Complex formation was found to occur with $PMeCl_4$, $PEtCl_4$, and their derivatives, but the di- and tri-alkylchlorophosphoranes showed no evidence of acceptor abilities. Several new compounds have been isolated, and further characterised by elemental analysis and (in some cases) i.r. spectroscopy.

The alkylchlorophosphoranes $PR_nCl_{5-n}$ (R = Me or Et; $n$ = 1—3) may readily be prepared, and have been shown by a variety of physical methods, including vibrational,[1,2] [31]P n.m.r.,[3] and [35]Cl n.q.r.[3,4] spectroscopy, to have ionic structures $PR_nCl_{4-n}{}^+Cl^-$ in the solid state. These conclusions were confirmed by the preparation of 1 : 1 adducts with strong Lewis acids such as $SbCl_5$, $BCl_3$, or $AlCl_3$, which contain the corresponding alkylchlorophosphonium ions and therefore give very similar solid-state [31]P n.m.r. shifts.[3] The acceptor properties of these compounds towards Lewis bases such as the chloride ion, pyridine, and the bidentate pyridines 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) have not been investigated in detail, however. A preliminary study by Reeve[5] indicated that $PMeCl_4$ would form a six-co-ordinate complex with the chloride ion in a suitable solvent, but insufficient starting material was available for this work to be extended further. Russian workers found u.v. evidence for formation of $PEtCl_5{}^-$ in the reactions of $PEtCl_4$ with $NMe_4Cl$ or $PEt_3Cl_2$, but concluded that $PEtCl_4$ existed predominantly in the molecular form in these solutions.[6]

In earlier papers the acceptor properties of phosphorus(v) chloride,[7] the $PCl_4{}^+$ ion,[8] $PPhCl_4$ and the $PPhCl_3{}^+$ ion,[9] and some $o$-phenylenedioxy-derivatives of phosphorus(v) chloride[10] towards suitable Lewis bases have been described. This work has now been extended to the series of methyl- and ethyl-chlorophosphoranes $PR_nCl_{5-n}$ (R = Me, $n$ = 1 or 2; R = Et, $n$ = 1—3) and their derivatives. Several new compounds have been isolated and characterised by elemental analysis, vibrational and [31]P n.m.r. spectroscopy.

## Experimental

All manipulations including n.m.r. sample preparation were carried out either under an inert atmosphere of dry nitrogen or in vacuo. Chemicals of the best available commercial grade were used, in general without further purification except for tetra-alkylammonium chlorides which were dried as described previously.[11] Chlorocarbon solvents were stored over 4A molecular sieve under nitrogen, while hydrocarbon solvents were dried over sodium wire and then stored in the same way. The compounds $PMeCl_4$, $PMe_2Cl_3$, $PEt_2Cl_3$, and $PEt_3Cl_2$ were prepared by chlorination of $PMeCl_2$, $Me_2P(S)P(S)Me_2$, $Et_2P(S)P(S)Et_2$, and $PEt_3$ respectively.[3] Hexachloroantimonate derivatives of the alkylchlorophosphoranes were obtained by treatment of a solution (or slurry in the case of $PMe_2Cl_3$) of the parent compound with an approximately equimolar quantity of antimony(v) chloride, also dissolved in a suitable inert solvent.[3] The mixtures were stirred to ensure complete reaction, the solid products were separated, washed with $CH_2Cl_2$ and low-boiling light petroleum (b.p. 30—40 °C), and if necessary

dried in vacuo. Elemental analyses for new phosphorus compounds are given in Table 1.

$N(n-C_5H_{11})_4{}^+PMeCl_5{}^-$.—Equimolar quantities of $PMeCl_4$ and $N(n-C_5H_{11})_4Cl$ were dissolved separately in the minimum amount of $CH_2Cl_2$. The chloride solution was added to the $PMeCl_4$ solution, with stirring. When no crystals formed on cooling, the solvent was removed in vacuo to yield a white sticky solid.

$NEt_4{}^+PMeCl_5{}^-$.—A similar method was employed to that described above. After complete addition of the chloride solution, the mixture was stirred for 10 min. The solvent was then removed in vacuo, leaving a fine white solid in the flask.

$PMeCl_3(py){}^+Cl^-\cdot py$.—An excess of pyridine (py) was added to a solution of $PMeCl_4$ in $CH_2Cl_2$, with stirring, resulting in the immediate formation of a yellow precipitate. The excess of py and solvent were removed in vacuo, leaving a pale brown solid. Analysis (Table 1) indicated the presence of 2 mol of pyridine per mol of the complex, but n.m.r. evidence (Results and Discussion section) suggested that the compound should be formulated as above, with one pyridine only attached to phosphorus.

$PMeCl_3(bipy){}^+Cl^-$.—Equimolar quantities of $PMeCl_4$ and 2,2'-bipyridine (bipy) were dissolved separately in the minimum amount of $CH_2Cl_2$; the bipy solution was added to the $PMeCl_4$ solution, with stirring. The white precipitate which immediately formed was separated, washed with $CH_2Cl_2$ and low-boiling light petroleum, and dried to yield a white solid.

$PMeCl_3(phen){}^+Cl^-$.—This compound was similarly prepared from $PMeCl_4$ and 1,10-phenanthroline (phen) in $PhNO_2$ as solvent. It was obtained as a white solid after washing with light petroleum.

$PMeCl_3(bipy){}^+SbCl_6{}^-$.—This complex was prepared from equimolar quantities of $PMeCl_3{}^+SbCl_6{}^-$ and bipy in $CH_2Cl_2$. A brown solution was formed, which after a few minutes deposited a light brown precipitate. The solid was separated and washed with low-boiling light petroleum.

$PMeCl_3(phen){}^+SbCl_6{}^-$.—(i) In $PhNO_2$. Equimolar quantities of $PMeCl_3{}^+SbCl_6{}^-$ and phen were dissolved separately in the minimum amount of $PhNO_2$. The phen solution was added slowly, with stirring, forming a yellow solution which after a few minutes yielded a thick yellow precipitate. The yellow solid was separated and washed with

**Table 1.** Elemental analyses for phosphorus compounds

| Compound | Found (%) | | | | | | Calculated (%) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | C | H | N | P | Cl | Sb | C | H | N | P | Cl | Sb |
| PMeCl₃⁺SbCl₆⁻ | 2.4 | 0.70 | | 6.3 | 65.4 | 25.0 | 2.5 | 0.60 | | 6.4 | 65.5 | 25.0 |
| N(C₅H₁₁)₄⁺PMeCl₅⁻ | 46.7 | 9.4 | 2.7 | 6.1 | 34.0 | | 48.3 | 9.1 | 2.7 | 5.9 | 34.0 | |
| NEt₄⁺PMeCl₅⁻ | 30.5 | 6.9 | 3.9 | 8.3 | 49.7 | | 30.6 | 6.6 | 4.0 | 8.8 | 50.1 | |
| PMeCl₃(py)⁺Cl⁻·py | 36.8 | 4.2 | 7.6 | 9.3 | 42.3 | | 38.2 | 3.8 | 8.1 | 9.0 | 41.0 | |
| PMeCl₃(bipy)⁺Cl⁻ | 39.4 | 3.4 | 9.1 | 9.3 | 42.6 | | 38.4 | 3.2 | 8.1 | 9.0 | 41.2 | |
| PMeCl₃(phen)⁺Cl⁻ | 42.5 | 2.9 | 8.5 | 9.0 | 39.4 | | 42.4 | 3.0 | 7.6 | 8.4 | 38.5 | |
| PMeCl₃(bipy)⁺SbCl₆⁻ | 19.5 | 1.7 | 4.7 | 3.9 | 48.7 | 19.7 | 20.5 | 1.7 | 4.4 | 4.8 | 49.6 | 18.9 |
| PMeCl₃(phen)⁺SbCl₆⁻·PhNO₂ | 29.1 | 2.1 | 5.7 | 3.3 | 38.1 | 19.2 | 28.9 | 2.0 | 5.3 | 3.9 | 40.4 | 15.4 |
| PMeCl₃(phen)⁺SbCl₆⁻ | 22.0 | 2.0 | 4.2 | 3.5 | 47.7 | 18.0 | 23.4 | 1.7 | 4.2 | 4.6 | 47.8 | 18.3 |
| PMe₂Cl₂⁺PCl₆⁻ | 6.1 | 1.6 | | 16.3 | 74.6 | | 6.4 | 1.6 | | 16.5 | 75.5 | |
| PEtCl₄ | 12.0 | 2.5 | | 15.3 | 70.4 | | 11.9 | 2.5 | | 15.3 | 70.3 | |
| PEtCl₃⁺SbCl₆⁻ | 4.3 | 0.65 | | 6.1 | 61.5 | 24.0 | 4.8 | 1.0 | | 6.2 | 63.7 | 24.3 |
| N(C₅H₁₁)₄⁺PEtCl₅⁻ | 50.2 | 10.5 | 3.5 | 5.4 | 32.5 | | 49.3 | 9.2 | 2.6 | 5.8 | 33.1 | |
| PEtCl₄·py | 31.0 | 3.8 | 6.6 | 10.8 | 49.4 | | 29.9 | 3.6 | 5.0 | 11.0 | 50.5 | |
| PEtCl₃(bipy)⁺Cl⁻ | 39.7 | 3.6 | 7.1 | 8.3 | 38.4 | | 40.3 | 3.7 | 7.8 | 8.7 | 39.6 | |
| PEtCl₃(phen)⁺Cl⁻ | 45.3 | 3.8 | 9.1 | 8.4 | 36.8 | | 44.0 | 3.4 | 7.3 | 8.1 | 37.1 | |
| PEtCl₃(bipy)⁺SbCl₆⁻ | 21.0 | 2.3 | 5.3 | 4.6 | 47.3 | 18.6 | 21.9 | 2.0 | 4.3 | 4.7 | 48.6 | 18.5 |
| PEtCl₃(phen)⁺SbCl₆⁻ | 23.7 | 2.1 | 3.2 | * | 45.8 | 17.2 | 24.7 | 1.9 | 4.1 | 4.5 | 46.8 | 17.9 |
| PEt₂Cl₂⁺SbCl₆⁻ | 9.5 | 2.4 | | 6.4 | 58.0 | 25.2 | 9.7 | 2.0 | | 6.3 | 57.4 | 24.6 |
| PEt₃Cl⁺SbCl₆⁻ | 14.7 | 3.9 | | 6.6 | 51.4 | 25.1 | 14.8 | 3.1 | | 6.3 | 50.8 | 24.9 |

* Red colour obtained, making determination of P impossible; see ref. 9.

low-boiling light petroleum. Analysis (Table 1) revealed that it contained 1 mol of $PhNO_2$ per mol of the complex, as confirmed by the i.r. spectrum.[12,13] It is therefore formulated as PMeCl₃(phen)⁺SbCl₆⁻·PhNO₂.

(*ii*) *In* $MeNO_2$. A solution containing stoicheiometric amounts of PMeCl₄ and phen in $MeNO_2$ was prepared, and SbCl₅ was added dropwise. A light brown solid was precipitated, and isolated as above.

PMe₂Cl₂⁺PCl₆⁻.—Pentachlorophosphorane (0.88 g, 4.2 mmol) was dissolved in $CH_2Cl_2$ and added to a slurry of PMe₂Cl₃ (0.71 g, 4.2 mmol) in the same solvent. An off-white precipitate was formed. The mixture was left to stir for 10 min, and the product then isolated as above.

PEtCl₄.—A simple method was adopted for the preparation of this compound from the complex PEtCl₃⁺AlCl₄⁻, obtained by the method of Parshall.[14] The complex was dissolved in $CCl_4$ and an equimolar quantity of dry NEt₄Cl was added, with stirring. The NEt₄⁺AlCl₄⁻ which precipitated was filtered off, and the solvent removed *in vacuo* from the filtrate to give the desired phosphorane as an off-white solid. Other batches were prepared by chlorination of PEtCl₂.

N(n-C₅H₁₁)₄⁺PEtCl₅⁻.—An equimolar quantity of N(n-C₅H₁₁)₄Cl dissolved in a small amount of $CH_2Cl_2$ was added to a concentrated solution of PEtCl₄ in the same solvent, with stirring. The solvent was removed *in vacuo*, giving the compound as a yellow sticky solid. An attempt to prepare NEt₄⁺PEtCl₅⁻ by similar means resulted only in the formation of a mixture of the starting materials, as shown conclusively by its solid-state ³¹P n.m.r. spectrum. It is thus possible that the tetraethylammonium cation is not large enough to stabilise the anion in this instance.

PEtCl₃(py)⁺Cl⁻.—An equimolar amount of pyridine was added dropwise to a solution of PEtCl₄ in $CH_2Cl_2$, with constant stirring. The white precipitate which immediately formed was isolated and washed with low-boiling light petroleum.

PEtCl₃(bipy)⁺Cl⁻.—A solution of bipy in the minimum amount of $CH_2Cl_2$ was added to an equimolar quantity of PEtCl₄ dissolved in the same solvent, with stirring. The solution was cooled in a refrigerator, leading to the formation of a white precipitate. The solid was isolated as above.

PEtCl₃(phen)⁺Cl⁻.—This compound was prepared in a similar way to the bipy complex. The white precipitate which formed after a few minutes was isolated as above.

PEtCl₃(bipy)⁺SbCl₆⁻.—The salt PEtCl₃⁺SbCl₆⁻ (1.90 g, 4 mmol) was dissolved in $CH_2Cl_2$ and an equimolar amount of bipy was added, with stirring. A white precipitate soon formed, and was isolated as above after stirring for 10 min to complete the reaction.

PEtCl₃(phen)⁺SbCl₆⁻.—This complex was prepared in a similar manner to the bipy complex, except that precipitation was immediate and stirring was continued for 20 min.

³¹P N.m.r. spectra were recorded at 307.2 K on a Fourier-transform spectrometer as described previously.[15] Chemical shifts were measured relative to 85% $H_3PO_4$, with the down-field direction taken as positive. Microanalyses (C, H, N, P, and Cl) were obtained as described in earlier papers,[3,7] and Sb was determined by atomic absorption spectroscopy. Infrared spectra were recorded on a Perkin-Elmer 457 instrument using Nujol mulls on CsI plates, protected by Polythene discs where necessary. ³⁵Cl N.q.r. spectra were also recorded as described previously.[3,8]

## Results and Discussion

*Acceptor Properties of* PMeCl₄.—This compound is known to have the ionic structure PMeCl₃⁺Cl⁻ in the solid state.[1-3] This was confirmed by recording its ³⁵Cl n.q.r. spectrum; two signals in a 1 : 2 intensity ratio were observed, at 30.80 and 31.225 (77), 30.675 and 31.15 (195), and 30.575 and 31.03 MHz (293 K). The results at 77 K are in good agreement with previous data.[3] A ³¹P shift of 120.0 p.p.m. in the solid state also agreed well with values for PMeCl₄ and its adducts with

**Table 2.** I.r. bands (cm$^{-1}$) for PMeCl$_4$ and PMeCl$_5^-$ salts (650—250 cm$^{-1}$)

| PMeCl$_4$ | 606s, 546s, 498w, 480s, 440s, 394w, 330w, 284s, 270s |
|---|---|
| N(n-C$_5$H$_{11}$)$_4^+$PMeCl$_5^-$ | 602s br, 544s, 494s, 470w, 449m, 384s br, 356m, 348w, 332w, 319vw, 292vw, 284w |
| NEt$_4^+$PMeCl$_5^-$ | 602s br, 543m, 522w, 512w, 470m, 443(sh), 415m, 376s br, 331w, 297m, 282w |

Lewis acids.[3] The compound has been shown by vibrational spectroscopy to have a molecular form with $C_{2v}$ symmetry in non-ionising solvents.[1] Phosphorus-31 solution shifts of −43.6 (CCl$_4$), −41.0 (C$_6$H$_6$), −38.7 (CH$_2$Cl$_2$),[5] −35.5 (PhNO$_2$), and −21.1 p.p.m. (EtNO$_2$) were recorded, which suggest that the compound is predominantly molecular in all these solvents, although limited ionisation is possible in EtNO$_2$, with rapid exchange between PMeCl$_3^+$ and PMeCl$_4$.

Solutions containing various molar ratios of N(n-C$_5$H$_{11}$)$_4$Cl to PMeCl$_4$ were prepared in PhNO$_2$. A single $^{31}$P resonance was observed in each case, which moved upfield with increasing chloride concentration. The highest shift attained (for 3.1 : 1 and 4.5 : 1 ratios of Cl$^-$ to PMeCl$_4$) was −204.7 p.p.m., but extrapolation gave a limiting value of −205.0 p.p.m., ascribed to the pentachloromethylphosphate ion, PMeCl$_5^-$. The results indicate that this ion is incompletely formed in PhNO$_2$ with a 1 : 1 ratio of reagents present (ca. 80% association was calculated), and that it is in a dynamic equilibrium with PMeCl$_4$, equation (1). The compound N(n-C$_5$H$_{11}$)$_4^+$PMeCl$_5^-$ was

$$\text{PMeCl}_4 + \text{N(n-C}_5\text{H}_{11})_4\text{Cl} \rightleftharpoons \text{N(n-C}_5\text{H}_{11})_4{}^+\text{PMeCl}_5{}^- \quad (1)$$
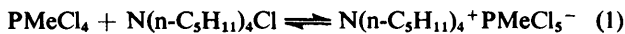
isolated as a sticky white solid. In the solid state it gave a sharp $^{31}$P resonance at −208.0 p.p.m., the sharpness probably being due to its viscous nature. The salt NEt$_4^+$PMeCl$_5^-$ was similarly obtained as a white solid; it gave a broad resonance at −206.5 ± 1.5 p.p.m. in the solid state. Both shifts are thus in good agreement with the solution value. The i.r. spectra of the salts differed considerably from that of PMeCl$_4$ in the lower-frequency (650—250 cm$^{-1}$) region, the most notable feature being a new strong broad band centred at 384 cm$^{-1}$ for the N(n-C$_5$H$_{11}$)$_4^+$ and 376 cm$^{-1}$ for the NEt$_4^+$ salts respectively (Table 2).

When pyridine was added to a solution of PMeCl$_4$ in CH$_2$Cl$_2$ a white precipitate was formed and the $^{31}$P n.m.r. spectrum showed a broad peak at 48.3 p.p.m. The compound PMeCl$_4$ reacted exothermically with neat pyridine and a pale yellow solid was precipitated, the mixture again giving a broad solution peak at 48.5 p.p.m. The chemical shifts are intermediate between those of PMeCl$_3^+$ and molecular PMeCl$_4$, and are therefore tentatively assigned to the five-co-ordinate adduct PMeCl$_3$(py)$^+$. A pale brown solid was isolated from CH$_2$Cl$_2$ solution, analysis of which indicated the presence of 2 mol of pyridine per mol of PMeCl$_4$. In the solid state its spectrum consisted of a broad peak at 29.0 p.p.m., however, again compatible with a five- rather than a six-co-ordinate adduct, so one of the py molecules may be present as a solvate. It is therefore formulated as PMeCl$_3$(py)$^+$Cl$^-$·py. The difference between the solution and solid-state shift values is not surprising in view of the results for other phosphorus compounds.[16]

When a solution of either 2,2′-bipyridine (bipy) or 1,10-phenanthroline (phen) was added to a solution of PMeCl$_4$ in CH$_2$Cl$_2$ or PhNO$_2$ an immediate precipitate was formed and no solution n.m.r. data could be obtained. Elemental analysis indicated the formation of a 1 : 1 complex, formulated as PMeCl$_3$L$^+$Cl$^-$, in each instance, where L is bipy or phen.

The solid bipy complex gave a broad $^{31}$P resonance with maxima at −145.1 and −148.4 p.p.m., but no signals were detected from the phen complex.

An attempt was made to compare the relative acceptor abilities of PMeCl$_4$ and PPhCl$_4$[9] by mixing them together in both CH$_2$Cl$_2$ and PhNO$_2$, but the $^{31}$P solution spectra showed clearly that no reaction had taken place, since signals from the starting materials only were observed.

*Acceptor Properties of* PMeCl$_3^+$SbCl$_6^-$.—This compound was prepared as described; in the solid state it gave a shift of 120.9 p.p.m. and shifts of 120.9 p.p.m. in PhNO$_2$ and 120.4 p.p.m. in CH$_2$Cl$_2$ solution. When an excess of pyridine was added to a solution of the compound in nitrobenzene a white precipitate was immediately formed, and the $^{31}$P n.m.r. spectrum of the solution showed a broad peak at 48.3 p.p.m., assigned as above to PMeCl$_3$(py)$^+$. By analogy with the reaction of PMe$_2$Cl$_2^+$PCl$_6^-$ with py described subsequently, the reaction (2) probably takes place.

$$\text{PMeCl}_3{}^+\text{SbCl}_6{}^- + 2\text{py} \longrightarrow$$
$$\text{PMeCl}_3(\text{py})^+\text{Cl}^- + \text{SbCl}_5\text{·py} \quad (2)$$
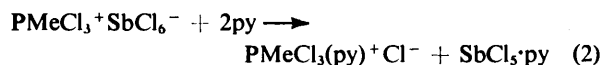
The solution $^{31}$P n.m.r. spectrum after addition of a small amount of bipy to PMeCl$_3^+$SbCl$_6^-$ in PhNO$_2$ showed three peaks at 119.3 (starting material), −145.1, and −150.0 p.p.m. When more bipy was added the lower-field signal disappeared, leaving the two high-field signals. Initially the resonance at −150.0 p.p.m. was more intense, but after 2 h the signals were of equal intensity. No further change was detected when the spectrum was recorded 2 h later. These signals are assigned to the two possible isomers of the PMeCl$_3$(bipy)$^+$ cation, (I) and (II).



(I)            (II)
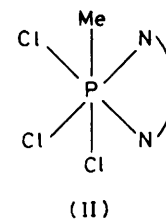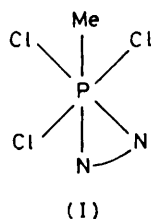
Unfortunately in this instance the method of pairwise interactions [11,15,17-20] cannot be used to assign specific configurations to each isomer, since there are too many unknown terms such as the N−N 'internal' term for the bidentate ligand. Similar isomeric cations were found in the reaction of PPhCl$_4$ or PPhCl$_3^+$SbCl$_6^-$ with bidentate pyridines.[9] The solid-state spectrum for PMeCl$_3$(bipy)$^+$Cl$^-$ described above thus presumably contains contributions from both isomers, accounting for the double maximum. The present solution results suggest that initially one of the isomers is formed in a higher concentration, but that rearrangement then takes place and both isomers are of comparable thermodynamic stability. The complex was isolated from CH$_2$Cl$_2$ solution and in the solid state gave a broad peak centred at −145.1 p.p.m.

When phen was added to a solution of PMeCl$_3^+$SbCl$_6^-$ in PhNO$_2$ or EtNO$_2$ two equally intense peaks at −143.5 and −148.4 p.p.m., ascribed to the two isomers of PMeCl$_3$-(phen)$^+$, and comparable with the bipy complexes, were observed, but the configurations of the individual isomers could not be assigned. The EtNO$_2$ solution spectrum also contained a minor peak at 45.3 p.p.m., ascribed to the hydrolysis product MePOCl$_2$.[21] The complex was isolated from MeNO$_2$, EtNO$_2$, and PhNO$_2$ solutions; only the com-
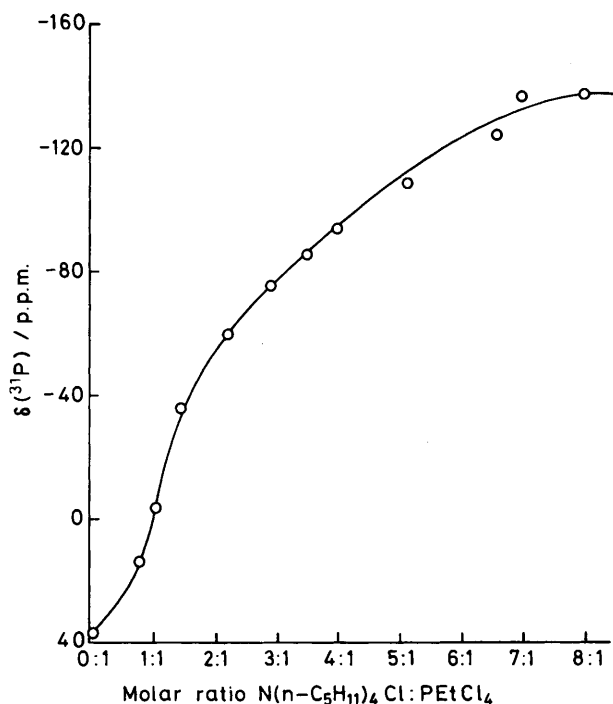
**Figure.** $\delta(^{31}P)$ (p.p.m.) for various molar ratios of $N(n-C_5H_{11})_4Cl$ to PEtCl₄ in PhNO₂

pound from EtNO₂ gave a solid-state spectrum, consisting of broad overlapping peaks with maxima at $-145.1$ and $-150.0$ p.p.m., and a sharp spike due to MePOCl₂ at 45.3 p.p.m. This product was not analysed because of the presence of the impurity. The yellow solid isolated from PhNO₂ analysed as having 1 mol of PhNO₂ present; this was confirmed by the sharp absorptions at 1 350 and 840 cm⁻¹ and a weak band at 400 cm⁻¹ in its i.r. spectrum.[12,13] Similar phosphorus complexes containing PhNO₂ of solvation have been obtained previously.[8-10]

*Acceptor Properties of* PMe₂Cl₃ *and* PMe₂Cl₂⁺SbCl₆⁻.— The compound PMe₂Cl₃ is also ionic in the solid state.[2,3] This was confirmed by the observation of single ³⁵Cl n.q.r. signals at 29.80 (77), 29.63 (195), and 29.30 MHz (293 K). The value at 77 K is in excellent agreement with previous results.[3] The solid-state ³¹P n.m.r. spectrum consisted of a broad resonance at $127.5 \pm 3$ p.p.m., again agreeing well with literature data.[3] The acceptor properties could not be investigated successfully, however, since the compound was found to be insoluble in all common organic solvents. Solution n.m.r. data have been obtained, but only in 25 oleum as solvent.[22] Attempts to force the compound into solution were made by adding a solution of either a tetra-alkylammonium chloride or 1,10-phenanthroline to the solid compound, but without success. An intimate equimolar mixture of PMe₂Cl₃ and $N(n-C_5H_{11})_4Cl$ was melted in a sealed tube and the ³¹P n.m.r. spectrum of the cooled mixture was recorded. There were no signals attributable to six-co-ordinate anions, although peaks were apparent at 206.4(m), 195.2(m), 88.7(s), and 51.5(s) p.p.m. Three of these peaks were tentatively assigned to PCl₄⁻ (206.4),[23] PMeCl₂ (195.2),[21] and PMe₃Cl⁺ (88.7),[3,22] suggesting that scrambling of the methyl groups as well as redox reactions, possibly with formation of Cl₃⁻, may have occurred. The resonance at 51.5 p.p.m. was difficult to assign, however. There was no evidence of acceptor properties shown by PMe₂Cl₃ in any of these reactions.

The compound PMe₂Cl₃ reacted with PCl₅ to yield

**Table 3.** I.r. bands (cm⁻¹) for PEtCl₄ and $N(n-C_5H_{11})_4{}^+PEtCl_5^-$ (650—250 cm⁻¹)

| | |
|---|---|
| PEtCl₄ | 642s, 616s, 590m, 438s br, 380m, 357w, 342w, 286mw, 259m |
| $N(n-C_5H_{11})_4{}^+PEtCl_5^-$ | 648s, 620s, 592s, 576w, 512s, 490m, 460w, 448s, 390s, 352w, 320m, 260w |

PMe₂Cl₂⁺PCl₆⁻, confirming that PCl₅ is a much better acceptor. The product gave ³¹P n.m.r. signals at 124.2 (PMe₂-Cl₂⁺) and $-298.0$ p.p.m. (PCl₆⁻) in PhNO₂ solution. The salt PMe₂Cl₂⁺SbCl₆⁻ was also prepared, and gave a signal at 124.2 p.p.m. in PhNO₂ solution. Dissolution of these compounds in neat pyridine resulted in a white precipitate and the disappearance of the resonance for PMe₂Cl₂⁺, but in the case of PMe₂Cl₂⁺PCl₆⁻ a signal was observed at $-230.6$ p.p.m., readily assigned to PCl₅·py.[7,24] The precipitate is almost certainly PMe₂Cl₃, and the reaction (3) appears to occur. No

$$PMe_2Cl_2{}^+PCl_6^- + py \longrightarrow PMe_2Cl_3 + PCl_5 \cdot py \quad (3)$$

solution ³¹P signals were obtained from the mixture of py with PMe₂Cl₂⁺SbCl₆⁻, strongly suggesting that the reaction is as in equation (4). Addition of either bipy or phen to a solution

$$PMe_2Cl_2{}^+SbCl_6^- + py \longrightarrow PMe_2Cl_3 + SbCl_5 \cdot py \quad (4)$$
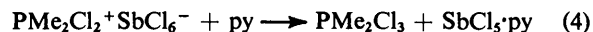
of PMe₂Cl₂⁺SbCl₆⁻ in either CH₂Cl₂ or PhNO₂ did not reveal any new peak, or alteration in the position of the PMe₂Cl₂⁺ signal. It was therefore concluded that neither PMe₂Cl₃ nor its derivatives show acceptor properties towards the chloride ion or pyridine bases.

*Acceptor Properties of* PEtCl₄ *and* PEtCl₃⁺SbCl₆⁻.—The compound PEtCl₄, too, is ionic, as shown by its solid-state ³¹P n.m.r. shift of $127.5 \pm 2$ p.p.m., and its ³⁵Cl n.q.r. spectrum which consisted of three signals in a 1 : 1 : 1 intensity ratio, at 31.025, 31.200, and 31.375 (77), 30.800, 31.025, and 31.175 (195), and 30.575, 30.725, and 30.950 MHz (293 K). The values at 77 K are very similar to those reported previously,[4] as well as to the frequencies for PEtCl₃⁺AlCl₄⁻.[3] The compound PEtCl₄ was found to be very soluble in organic solvents, and solution shifts of 35.5 (PhNO₂), 21.1 (MeNO₂; lit.,[25] 26.7), 12.9 (MeCN; lit.,[25] 24.4), $-27.5$ (CS₂), $-24.2$ (C₆H₆; lit.,[25] $-25.7$), and $-24.2$ p.p.m. (CH₂Cl₂) were recorded. The shift is thus very solvent dependent and the compound appears to ionise to some extent in the more polar solvents, with rapid exchange between PEtCl₃⁺ and molecular PEtCl₄. The shift is also likely to be concentration dependent, possibly accounting for differences from previous results[25] in some instances. The values for the last three solvents are very similar, suggesting that a single molecular species may be present in less polar solvents.

Addition of $N(n-C_5H_{11})_4Cl$ to a solution of PEtCl₄ in PhNO₂ caused the single peak to move upfield. The highest shift attained was $-137.1$ p.p.m., although extrapolation gave a limiting value of $-138.0$ p.p.m. (Figure). Clearly association is less extensive at a comparable concentration in this system than for PMeCl₄-Cl⁻, but percentage associations are difficult to calculate because of uncertainty about the shift value of molecular PEtCl₄ in PhNO₂. The equilibrium (5) evidently

$$PEtCl_4 + Cl^- \rightleftharpoons PEtCl_5^- \quad (5)$$

exists, however, and the value of $-138.0$ p.p.m. is ascribed to the shift of the PEtCl₅⁻ ion. The tetra-n-pentylammonium compound was isolated as a sticky solid; its i.r. spectrum (Table 3) differed from that of PEtCl₄, as expected. Its solid-

state $^{31}P$ n.m.r. spectrum showed a single quite sharp peak at $-63.8$ p.p.m., indicating that it is partially dissociated at the spectrometer operating temperature of 307.2 K. Attempts to prepare the tetraethylammonium analogue were unsuccessful (Experimental section), and the $NEt_4^+$ cation may possibly not be large enough to stabilise the anion. These results are entirely compatible with u.v. evidence for partial formation only of $PEtCl_5^-$ when $PEtCl_4$ is treated with either $NMe_4Cl$ or $PEt_3Cl_2$.[6] Similar stability has been found for the $PBr_3$-$NR_4Br$ systems, where $NPr^n_4^+PBr_4^-$, but not $NEt_4^+PBr_4^-$, may be isolated in crystalline form from solution.[26,27]

When pyridine was added to $PEtCl_4$ in $CH_2Cl_2$ a white precipitate was immediately formed and no $^{31}P$ solution spectrum could be obtained. A similar reaction was observed between $PEtCl_4$ and neat pyridine. The compound was isolated from $CH_2Cl_2$ solution and analysed as a 1 : 1 adduct. It was insoluble in both $PhNO_2$ and neat pyridine, and no solution spectra could be recorded. In view of the structure of the starting material, the adduct probably has the structure $PEtCl_3(py)^+Cl^-$, with a five-co-ordinate cation as for $PMeCl_3(py)^+$, but direct evidence is lacking. The compound also failed to give a signal in the solid state, but this is not too surprising for a five-co-ordinate species.[16]

When a less than equimolar amount of bipy was added to $PEtCl_4$ in $CH_2Cl_2$ solution, signals at $-24.2(m)$ $(PEtCl_4)$, $-127.5(s)$, and $-135.5(s)$ p.p.m. were observed, as well as a weak peak at 53.3 p.p.m. ascribed to the hydrolysis product $EtPOCl_2$.[21] The two high-field peaks are assigned to the two possible isomers of the cation $PEtCl_3(bipy)^+$. Further addition of bipy resulted in the formation of a thick white precipitate, the solution spectrum now showing only the signal from the hydrolysis product. A similar reaction occurred in $PhNO_2$ with the isomeric peaks being found at $-127.5$ and $-137.1$ p.p.m., the former being the more intense. The compound was isolated from $CH_2Cl_2$ solution, and analysed as the expected 1 : 1 adduct. Separate configurations could not be assigned to the isomers, as in the case of the $PMeCl_3L^+$ complexes. No solid-state spectrum could be obtained. A similar reaction took place with 1,10-phenanthroline. A less than equimolar amount added to $PEtCl_4$ in $CH_2Cl_2$ caused the appearance of $^{31}P$ signals at $-24.2$ (starting material), $-127.5$, and $-130.6$ p.p.m. The two equally intense high-field signals were assigned to the two isomers of $PEtCl_3(phen)^+$. Addition of more phen caused a white precipitate to form and the solution signals disappeared. In $PhNO_2$ a white precipitate was formed immediately. The complex isolated from $CH_2Cl_2$ solution analysed as a 1 : 1 adduct; in the solid state it gave a broad $^{31}P$ signal at $-138.2 \pm 5$ p.p.m., in quite good agreement with the solution shifts.

Similar complexes were obtained from $PEtCl_3^+SbCl_6^-$. When bipy was added to $PEtCl_3^+SbCl_6^-$ in $CH_2Cl_2$ two $^{31}P$ signals were seen at $-130.0$ and $-132.2$ p.p.m., the latter being the more intense. Since the relative intensities of the isomer peaks were reversed in the $PEtCl_4$-bipy system, it appears that the two isomers are of comparable thermodynamic stability, the proportions depending on the starting material. The phen complex precipitated immediately and no solution data could be obtained. It gave a broad signal at $-130.1 \pm 6$ p.p.m. in the solid state, but no signals were detectable from the bipy complex. The isolated solids analysed as 1 : 1 adducts and are formulated as $PEtCl_3L^+SbCl_6^-$, where L = bipy or phen.

*Acceptor Properties of* $PEt_2Cl_3$, $PEt_3Cl_2$, *and Derivatives.*— The compound $PEt_2Cl_3$ is reported to be ionic, both in the solid[2-4] and in solution in polar solvents,[3,4,25] although it is probably molecular in $C_6H_6$ solution.[4,25] In the solid state it gave a broad $^{31}P$ resonance at $141.8 \pm 2$ p.p.m., in good agreement

with previous data.[3] In $CH_2Cl_2$ and $PhNO_2$ it gave single peaks at 127.3 and 125.8 p.p.m. respectively, showing that it exists predominantly in the ionic form in these solvents, and that any association to molecular $PEt_2Cl_3$ must be slight. Shifts of 137.3 and 137.9 p.p.m. have been reported for solutions in MeCN and $MeNO_2$ respectively, and of 18.5 p.p.m. in $C_6H_6$.[4,25] Addition of a source of chloride ion [either $NEt_4Cl$ or $N(n-C_5H_{11})_4Cl$] to $PEt_2Cl_3$ in either $CH_2Cl_2$ or $PhNO_2$ caused no change in the peak position, indicating that no complex formation takes place under the experimental conditions. Similarly, addition of py, bipy, or phen to a solution of $PEt_2Cl_3$ in either solvent did not result in precipitation or in the appearance of new solution peaks or shifts in the signal position. The compound $PEt_2Cl_3$ thus appears to possess no acceptor properties towards these Lewis bases in solution. The salt $PEt_2Cl_2^+SbCl_6^-$ [$\delta(^{31}P)$ 137.1 p.p.m. in $CH_2Cl_2$ or $PhNO_2$] likewise showed no acceptor properties towards py, bipy, or phen.

The compound $PEt_3Cl_2$ is also ionic in the solid state,[3,4] and in MeCN or $MeNO_2$ as solvents, although it is insoluble in benzene.[4,25] It gave a shift of $106.4 \pm 1$ p.p.m. in the solid state, in good agreement with a previous value.[3] No change in its $^{31}P$ n.m.r. spectrum in either $CH_2Cl_2$ or $PhNO_2$ solution was found, however, on addition of $Cl^-$, py, bipy, or phen, and similar results for the pyridine bases were obtained from the adduct $PEt_3Cl^+SbCl_6^-$ [$\delta(^{31}P)$ (solid) 111.3 p.p.m.]. Hence the $PEt_3Cl^+$ cation also shows no acceptor properties under the experimental conditions. This result is not surprising in view of the data for $PEt_2Cl_2^+$, since acceptor ability is expected to decrease along the series $PCl_4^+ > PRCl_3^+ > PR_2Cl_2^+ > PR_3Cl^+ > PR_4^+$, and the phosphonium salts $PR_4^+Cl^-$ are expected to be chloride-ion donors.

We therefore conclude that $PMeCl_4$, $PEtCl_4$, and the derivatives of these compounds with $SbCl_5$ show acceptor properties towards suitable Lewis bases. The compounds $PMeCl_4$ and $PEtCl_4$ form adducts with the chloride ion, which can be isolated with appropriate large cations. The complexes containing $PMeCl_5^-$ appear to be more stable than those of $PEtCl_5^-$, although direct comparison is difficult since $PEtCl_4$ seems from the chemical shifts to be more extensively ionised in $PhNO_2$ than is $PMeCl_4$. The parent compounds form adducts with pyridine, formulated as $PMeCl_3(py)^+Cl^-$·py and $PEtCl_3(py)^+Cl^-$ respectively, but $PMeCl_3^+SbCl_6^-$ reacts with py, probably giving $PMeCl_3(py)^+Cl^-$ and $SbCl_5$·py. The corresponding reaction with $PEtCl_3^+SbCl_6^-$ was not investigated. All these phosphorus compounds form 1 : 1 adducts with the bidentate pyridines bipy and phen, the solution spectra of which (where obtainable) show the presence of both possible isomers, which in general appear to be of comparable stability. No acceptor properties were found for $PMe_2Cl_3$, $PEt_2Cl_3$, $PEt_3Cl_2$, or their $SbCl_5$ derivatives. The monomethyl and -ethyl compounds are much poorer acceptors than $PCl_5$[7] or the $PCl_4^+$ ion,[8] as expected from the inductive effect of the alkyl group, and in this respect are similar to $PPhCl_4$ and the $PPhCl_3^+$ ion.[9] A direct comparison of the relative acceptor abilities of $PMeCl_4$ and $PPhCl_4$ was not possible, since the two compounds did not react with each other. The inductive effect is expected to be greater for the methyl group, which could make $PMeCl_4$ a poorer acceptor, but the larger phenyl group could sterically hinder the approach of bulky ligands in particular. The two effects could thus compensate to some extent, and the compounds may well possess similar acceptor abilities.

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