Acceptor Properties of Tetrachloro(phenyl)phosphorane and of the Trichloro(phenyl)phosphonium ion

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The acceptor properties of $PPhCl_4$ and of the $[PPhCl_3]^+$ ion towards some Lewis bases have been investigated. Chloride ion adds to $PPhCl_4$ in the presence of a large cation to produce $[PPhCl_5]^-$, which exchanges rapidly with $PPhCl_4$ on the n.m.r. time scale. Unhindered pyridines L of sufficiently high basicity give molecular complexes $PPhCl_4{\cdot}L$, similar to those of PCl_5. Bidentate pyridines L′ yield ionic six-co-ordinate derivatives $[PPhCl_3L']Cl$; the cation has two isomeric forms which co-exist in solution. Pyridine reacts rapidly with $[PPhCl_3][SbCl_6]$ and $[PPhCl_3][PCl_6]$, apparently to give adducts of the molecular species, $PPhCl_4{\cdot}py$ and $MCl_5{\cdot}py$ (M = P or Sb). Bidentate pyridines L′ yield 1 : 1 complexes $[PPhCl_3L'][MCl_6]$, which are stable in solution if soluble and again show the presence of cationic isomers. Several new solid compounds have been isolated and further characterised by means of elemental analysis, i.r. spectroscopy, and in some instances ^{31}P n.m.r. and ^{35}Cl n.q.r. spectroscopy.

THE compound $PPhCl_4$ may be regarded as derived from the molecular form of phosphorus(V) chloride by substitution of an equatorial phenyl group into the trigonal bipyramid.[1,2] It is known to be molecular both in the solid state [1,2] and in solution, but may be readily converted into the pseudo-tetrahedral cation $[PPhCl_3]^+$ by reaction with a good chloride-ion acceptor such as antimony(V) or boron(III) chlorides.[2,3] No reactions of $PPhCl_4$ with Lewis bases have been reported, however. In previous papers we have described the acceptor properties of phosphorus(V) chloride towards the chloride ion [4] and pyridine bases,[5] and of the tetrachlorophosphonium ion $[PCl_4]^+$ towards pyridine bases.[6] We now report an extension of this work to both $PPhCl_4$ and the $[PPhCl_3]^+$ cation, to show the effect of the phenyl group on co-ordination reactions. Although the phenyl group is quite bulky, steric hindrance to complex formation is not expected to be important, since compounds such as PPh_5 are quite stable.[7] Complex formation in solution

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has been investigated by means of ^{31}P n.m.r. spectroscopy. Several new compounds have been isolated and further characterised by elemental analysis and i.r., ^{31}P n.m.r., and, in some cases, ^{35}Cl n.q.r. spectroscopy.

EXPERIMENTAL

All the 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 as described below or previously.[2,5,6] Tetra-alkylammonium chlorides were dried *in vacuo* for several hours at 373 K; the absence of moisture was shown by recording their i.r. spectra. The preparation of $PPhCl_4$, $[PPhCl_3][SbCl_6]$, and $[PPhCl_3][PCl_6]$ has been given in an earlier paper.[2]

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, using 8.4-mm outside-diameter sample tubes. Chemical shifts were measured relative to external P_4O_6, but have been converted into the phosphoric acid scale, with the upfield direction taken as positive. Infrared spectra of solids were recorded in the range 250—4 000 cm^{-1} as Nujol mulls on a Perkin-Elmer 457 instrument. Caesium iodide plates for the low-frequency region were protected by Polythene discs to prevent halogen exchange. Chlorine-35 n.q.r. frequencies at 77 K were measured as described previously.[6] Microanalyses for C, H, N, P, and Cl were carried out as in earlier papers;[2,5,6] the results for phosphorus and chlorine were usually found to be more reliable. Phosphorus analyses could not be performed for some complexes of 1,10-phenanthroline (phen) or 2,2′-bipyridyl (bipy) because of the formation of a red colour in the solution for spectrophotometry, after addition of the ammonium molybdate–ammonium vanadate reagent. This was probably due to incomplete decomposition of the ligand, which then complexes with metal ions from the reagent.

The preparation of new solid complexes is described below. Tetra-n-pentyl- and tetra-n-propyl-ammonium pentachloro(phenyl)phosphate were prepared by mixing the stoicheiometric quantities of $PPhCl_4$ and the appropriate tetra-alkylammonium chloride, both dissolved in the minimum quantity of CH_2Cl_2. The salt $[NPr^n_4][PPhCl_5]$ formed as a crystalline precipitate, but $[N(n\text{-}C_5H_{11})_4][PPhCl_5]$ remained in solution. The solution was cooled in ice–water and the solvent then removed slowly *in vacuo* until a small volume only remained, when a solid separated out. The yellowish white complexes were isolated, washed with pentane, and dried at the pump. The tetra-n-pentylammonium salt was also produced by heating a 1 : 1 mol ratio of the solid reagents, to produce a yellow oil at 368 K. On rapid cooling a solid was obtained having an identical i.r. spectrum (Discussion section) to that from the solution preparation. Elemental analyses for all the new compounds are given in Table 1.

The adducts of $PPhCl_4$ with pyridine (py) and 3-methyl- and 3,5-dimethyl-pyridine were prepared by slow addition of a slight excess of the base to a solution of $PPhCl_4$ in the minimum volume of nitrobenzene. A thick precipitate was produced in each case. The mixture was stirred for a few minutes to complete the reaction. The precipitate was then filtered off, washed with pentane, and dried *in vacuo* to yield a white or off-white solid. The pyridine adduct was similarly prepared in CH_2Cl_2 solution, and gave an identical i.r. spectrum to the product from nitrobenzene.

TABLE 1

Analytical data for $PPhCl_4$ and $[PPhCl_3]^+$ derivatives

		Analysis (%)									
		Found					Calc.				
Compound	Solvent	C	H	N	P	Cl	C	H	N	P	Cl
$[NPr^n_4][PPhCl_5]$	CH_2Cl_2	46.35	5.15	3.65	6.45	37.45	45.85	7.05	2.95	6.55	37.6
$[N(C_5H_{11})_4][PPhCl_5]$	CH_2Cl_2	53.75	5.85	2.25	5.50	31.5	53.5	8.45	2.40	5.30	30.35
$PPhCl_4\cdot py$	CH_2Cl_2	36.7	3.40	4.20	9.10	43.9	40.15	3.05	4.25	9.40	43.1
$PPhCl_4\cdot 3Me\text{-}py$	$PhNO_2$	43.65	3.55	4.20	9.05	41.35	42.0	3.55	4.10	9.05	41.35
$PPhCl_4\cdot 3,5Me_2\text{-}py$	$PhNO_2$	43.45	3.65	4.30	8.35	40.25	43.75	3.95	3.90	8.65	39.7
$[PPhCl_3(phen)]Cl$	$PhNO_2$	50.0	3.00	7.85	*	32.4	50.25	3.05	6.50	7.20	32.95
$[PPhCl_3(bipy)]Cl\cdot PhNO_2$	$PhNO_2$	48.85	3.25	7.65	5.50	26.8	49.95	3.45	7.95	5.85	26.8
$[PPhCl_3(bipy)]Cl$	CH_2Cl_2	46.4	5.65	6.70	6.65	39.5	47.3	3.25	6.90	7.65	34.9
	MeCN	47.15	3.30	9.20	7.75	33.8	47.3	3.25	6.90	7.65	34.9
	C_6H_6	49.7	4.05	7.00	6.90	32.5	47.3	3.25	6.90	7.65	34.9
	$EtNO_2$	47.9	3.05	7.10			47.3	3.25	6.90	7.65	34.9
$[PPhCl_3(phen)][SbCl_6]$	CH_2Cl_2	26.7	2.00	3.80	3.95	45.2	29.65	1.80	3.85	4.25	43.75
$[PPhCl_3(bipy)][SbCl_6]$	$EtNO_2$	25.6	2.00	4.35	4.20	45.25	27.25	1.85	3.95	4.40	45.25
$[PPhCl_3(bipy)][PCl_6]\cdot 0.25PhNO_2$	$PhNO_2$	29.95	2.30	4.75	9.60	49.8	32.6	2.25	4.90	9.60	49.45

* See text.

The complex $[PPhCl_3(phen)]Cl$ was obtained from a nitrobenzene solution of 1,10-phenanthroline and a slight excess of $PPhCl_4$ as a thick precipitate after several hours. The pale yellow product was isolated and dried as above. A phosphorus analysis could not be carried out because of the appearance of a red colour in the decomposed solution, as mentioned earlier. A similar preparation from equimolar quantities of $PPhCl_4$ and 2,2′-bipyridyl in nitrobenzene gave a rapid precipitation of the complex $[PPhCl_3(bipy)]Cl\cdot PhNO_2$ (Table 1). The presence of free nitrobenzene was confirmed by strong i.r. absorptions at 1 525, 1 345, 852, and 702 cm^{-1}.[8] The formation of the unsolvated species $[PPhCl_3(bipy)]Cl$ was attempted in various other solvents by following an identical preparative procedure; rapid precipitation was observed for all but benzene, where the solid which separated slowly was isolated after 3 d. Elemental analyses were not fully satisfactory (Table 1), however, except for the product from acetonitrile. The solid isolated from nitroethane appeared to contain free $EtNO_2$ since it showed i.r. bands at 1 547 and 876 cm^{-1}, although the C, H, and N analyses were

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[8] J. H. S. Green, W. Kynaston, and A. S. Lindsay, *Spectrochim. Acta*, 1961, **17**, 486.

close to the theoretical values for the unsolvated complex; no P and Cl analyses were performed on this sample.

The complex [$PPhCl_3$(phen)][$SbCl_6$] was prepared by mixing equimolar quantities of $PPhCl_4$ and phen, dissolved separately in the minimum volume of CH_2Cl_2, and adding dropwise the stoicheiometric amount of $SbCl_5$ mixed with a little CH_2Cl_2. The precipitate which formed was isolated as above in the form of a fawn powder. The complex [$PPhCl_3$(bipy)][$SbCl_6$] was obtained by slow addition of a solution of bipy in the minimum volume of nitroethane to a solution of [$PPhCl_3$][$SbCl_6$] in the same solvent. The white crystals which appeared after a short time were isolated, washed with CH_2Cl_2 and pentane, and dried *in vacuo*. The complex [$PPhCl_3$(bipy)][PCl_6]$\cdot$0.25$PhNO_2$ was produced by mixing solutions of [$PPhCl_3$]-[PCl_6] and bipy in nitrobenzene. A precipitate immediately formed and was separated as above. Although many of the i.r. absorptions of $PhNO_2$ are in the regions of absorption of the complex, bands [8] at 1 527, 1 348, and 852 cm^{-1} probably arise from the free $PhNO_2$ present.

RESULTS AND DISCUSSION

(*i*) *Acceptor Properties of* $PPhCl_4$ *towards the Chloride Ion.*—Solutions containing various mol ratios of [$N(n\text{-}C_5H_{11})_4$]Cl : $PPhCl_4$ in nitrobenzene were prepared; their ^{31}P n.m.r. spectra showed one peak only, which moved to higher field with increasing amount of chloride. The curve extrapolates to a limiting shift of *ca.* 203 p.p.m., which is clearly in the six-co-ordinate region for phosphorus chloro-compounds, and may be assigned to the pentachloro(phenyl)phosphate ion, $[PPhCl_5]^-$. The occurrence of a single peak shows that exchange between $PPhCl_4$ and $[PPhCl_5]^-$ is rapid on the n.m.r. time scale. The results indicate that $[PPhCl_5]^-$ is incompletely formed in nitrobenzene when the reagents are present in a 1 : 1 mol ratio, the shift then corresponding to *ca.* 75% association.

The reaction was investigated in other solvents, and the extent of association varied markedly with solvent polarity in the order $PhNO_2 > MeNO_2 > CH_2Cl_2 > CCl_4$. This sequence may be compared with the similar solvent dependence found for formation of $[SiCl_5]^-$.[9,10] Other chloride-ion donors with large cations such as [$N(n\text{-}C_3H_7)_4$]Cl and PPh_3Cl_2 [2] also showed evidence of association, since the $PPhCl_4$–$[PPhCl_5]^-$ peak moved upfield, but a direct quantitative comparison was not possible because of either hydrolysis difficulties or change of solvent. When $PPhCl_4$ and PPh_2Cl_3 were mixed in *sym*-tetrachloroethane, however, the peaks showed very little movement (−63.4, 47.4 p.p.m.) from those found for PPh_2Cl_3 (−67.4) and $PPhCl_4$ (39.3 p.p.m.) individually.[11] Association thus appeared not to occur, even though PPh_2Cl_3 is partially ionised to $[PPh_2Cl_2]^+$ and Cl^- in this solvent.[11] The lack of co-ordination is probably caused by strong hydrogen bonding between Cl^- and *sym*-tetrachloroethane, as found for the similar solvent chloroform in both the solid state and solution.[12–14]

The tetra-n-pentyl- and tetra-n-propyl-ammonium salts of $[PPhCl_5]^-$ were isolated as very moisture-sensitive solids (Experimental section). The ^{31}P n.m.r. spectrum of [$N(n\text{-}C_5H_{11})_4$][$PPhCl_5$] prepared from the melt showed a solid-state resonance at 223.3 ± 5.7 p.p.m., rather higher than the extrapolated solution shift, with a very sharp peak at 203.4 p.p.m. superimposed. The latter signal could arise from self-diffusion of the $[PPhCl_5]^-$ ion through the solid lattice, as observed in other systems.[15] The salt melts at <368 K, so the lattice is probably not very rigid at the spectrometer operating temperature (307.2 K). It is not clear why a broad signal and a sharp one should be produced simultaneously, however, unless there are two kinds of $[PPhCl_5]^-$ sites in the solid. Dissolution of some of the salt in a small quantity of unremoved solvent or $PPhCl_2O$ hydrolysis impurity to give a solution signal cannot be entirely discounted. The tetra-n-propylammonium salt showed a solid-state peak at 220 ± 5 p.p.m., with no liquid resonance superimposed. Some difference between solution and solid-state chemical shifts has been noted previously for other phosphorus compounds.[16]

The i.r. frequencies for these and other new solid compounds were recorded in the appropriate spectral ranges, and are available as Supplementary Publication No. SUP 22310 (8 pp.).* Marked differences from the spectrum of $PPhCl_4$ were found in all cases, particularly between 650 and 400 cm^{-1}.

The ^{35}Cl n.q.r. spectrum of [$N(C_5H_{11})_4$][$PPhCl_5$] at 77 K consisted of weak signals at 31.05, 30.97, 30.88, 30.56, and 30.475 MHz. Some differences in frequency between the chlorine *trans* to the phenyl group and the four mutually *trans* chlorines might have been expected, but these values all lie within the range of possible crystallographic splittings. The tetra-n-propylammonium salt gave a weak resonance at 30.995 MHz and two stronger, possibly double-intensity, lines at 29.625 and 29.585 MHz, more in keeping with the expected pattern. The weak signal presumably arises from the chlorine *trans* to phenyl in this instance, and it is possible that the highest-frequency line of the tetra-n-pentylammonium salt has the same assignment, in view of their similarity. The results suggest that the two salts are not isostructural, and that variations in P–Cl bond length occur within the pseudo-octahedral $[PPhCl_5]^-$ moiety. All the values differ considerably from those of $PPhCl_4$,[1,2] lying between the equatorial and axial resonance frequencies of this compound.

(*ii*) *Acceptor Properties towards Pyridine Bases.*—When solutions of $PPhCl_4$ in nitrobenzene or methylene

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1977, Index issue.

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[10] I. R. Beattie and K. M. Livingston, *J. Chem. Soc.* (*A*), 1969, 859.

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[12] R. M. Deiters, W. G. Evans, and D. H. McDaniel, *Inorg. Chem.*, 1968, **7**, 1615.

[13] R. D. Green and J. S. Martin, *J. Amer. Chem. Soc.*, 1968, **90**, 3659.

[14] P. Boule, *Compt. rend.*, 1970, **C270**, 1433.

[15] E. R. Andrew, ' Nuclear Magnetic Resonance,' Cambridge University Press, Cambridge, 1958.

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

chloride were treated with pyridine bases of lower basicity than pyridine itself[5,6] no apparent reaction occurred. Addition of pyridine to such solutions caused the immediate formation of a thick white precipitate, however. The isolated solid analysed as $PPhCl_4 \cdot py$ (Experimental section). Its ^{35}Cl n.q.r. spectrum at 77 K was completely different from that of $PPhCl_4$,[1,2] consisting of a single line at 27.26 MHz (signal-to-noise ratio 5 : 1). The observation of only one resonance indicates that pyridine is *trans* to the phenyl group in the pseudo-octahedral complex, since the alternative structure should give three ^{35}Cl n.q.r. signals in a 2 : 1 : 1 intensity ratio, for mutually *trans* chlorines, chlorine *trans* to phenyl, and chlorine *trans* to pyridine respectively. The ^{31}P n.m.r. spectrum of the solid showed a very broad line at 161.7 ± 2.7 p.p.m. again in the six-co-ordinate region for phosphorus chloro-compounds.

The adduct dissolved to a very limited extent in nitrobenzene, chloroform, or *sym*-tetrachloroethane, giving single peaks at 53.4, 47.3, and 44.5 p.p.m. respectively. The results suggest that ready dissociation takes place with equilibrium (1) lying well to the right-hand side.

$$PPhCl_4 \cdot py \rightleftharpoons PPhCl_4 + py \qquad (1)$$

This hypothesis was supported by adding pyridine in stages to a *sym*-tetrachloroethane solution of $PPhCl_4$; the single peak moved upfield and the complex was partially precipitated. The highest shift observed before solubility became too low for detection was 68.2 p.p.m., showing that excess of pyridine forces equilibrium (1) more to the left-hand side.

Solid complexes with the bases 3-methyl- and 3,5-dimethyl-pyridine, both of which are more basic than pyridine itself, were similarly synthesised (Experimental section). No complex formation was observed with 2-methyl- or 2,4,6-trimethyl-pyridine, probably because of steric hindrance.[5] The ^{35}Cl n.q.r. spectrum of the $3,5Me_2$-py complex at 77 K showed strong lines at 27.10 and 27.585 MHz. The average frequency is very close to the single line of the py complex, so the two signals probably arise from crystallographic splitting, with the phenyl group and base again occupying *trans* positions. No n.q.r. signals were detected from the 3Me-py adduct.

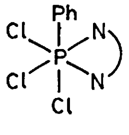
The solid-state ^{31}P n.m.r. shifts were 178.3 ± 7.7 p.p.m. for the 3Me-py and 182.6 ± 11.6 p.p.m. for the $3,5Me_2$-py adducts, slightly higher than found for the py analogue. All the three spectra showed, in addition, sharp lines corresponding to freely diffusing, almost uncomplexed, $PPhCl_4$, at 45.9 (py), 58.3 (3Me-py), and 48.0 p.p.m. ($3,5Me_2$-py), supporting the suggestion that these complexes dissociate readily.

Complex formation between $PPhCl_4$ and bidentate pyridines was also investigated. 1,10-Phenanthroline (phen) and $PPhCl_4$ were mixed in various proportions in nitrobenzene to give stable solutions. An approximately equimolar mixture showed two peaks in the six-co-ordinate region, at 135.4 and 150.5 p.p.m. Addition of more $PPhCl_4$ caused the appearance of a third peak, which moved downfield as the $PPhCl_4$: phen ratio increased (Table 2). This resonance is readily assigned to the $PPhCl_4$–$[PPhCl_5]^-$ equilibrium peak, described previously in this work. The two original signals remained constant in shift within experimental error, as shown. Addition of an equimolar amount of phen to $[PPhCl_3][SbCl_6]$ also caused the appearance of two peaks in similar positions. They clearly arise from $PPhCl_4$ or $[PPhCl_3]^+$–phen complexes, and in view of the rigid nature of this ligand unidentate co-ordination is extremely unlikely. There are two possible isomeric forms for $[PPhCl_3(phen)]^+$, as shown below. The two peaks may thus be assigned to these isomeric species. Isomerism in six-co-ordinate phosphorus chemistry has only been found previously with fluorine present,[17] and no ^{31}P n.m.r. data were given, so the isomer shift cannot be compared with the 15 p.p.m. observed here. Isomer shifts in octahedral complexes have been reported for other nuclei such as ^{59}Co and ^{195}Pt.[18,19] No attempt was made to assign the resonances to specific isomers; a particular configuration may sometimes be deduced from analysis of ^1H n.m.r. spectra of phen complexes,[20,21] but this would be extremely difficult with a mixture of isomers present in solution. The results show that neither isomer exchanges with $PPhCl_4$ (or $[PPhCl_5]^-$) on the n.m.r. time scale, since separate signals are observed. Some variation in their relative proportions occurs, as shown in Table 2, although the peak at *ca.* 135 p.p.m. is always the more intense.

TABLE 2

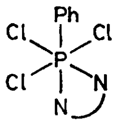
Phosphorus-31 n.m.r. data for $PPhCl_4$–phen mixtures in $PhNO_2$

Molar ratio $PPhCl_4$: phen	$\delta(^{31}P)$/p.p.m. A	B	C	Relative area A : B
0.98 : 1	135.4	150.5		100 : 43
1.78 : 1	136.4	150.9	128.5	100 : 39
2.64 : 1	136.8	151.5	105.8	100 : 25



(1)

phenyl *trans* to chlorine



(2)

phenyl *trans* to nitrogen

The complex $[PPhCl_3(phen)]Cl$ was isolated as a solid (Experimental section) but in insufficient quantity for solid-state n.m.r. or n.q.r. studies. It hydrolysed slowly in moist air, in contrast to $[PPhCl_3(phen)][SbCl_6]$ discussed below, showing the effect of the counter ion on stability.

When solutions of $PPhCl_4$ and 2,2′-bipyridyl (bipy) in various solvents were mixed precipitates were quickly

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[17] J. F. Nixon and J. R. Swain, *J. Chem. Soc. (A)*, 1970, 2075.

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[20] W. R. McWhinnie and J. D. Miller, *Adv. Inorg. Chem. Radiochem.*, 1969, **12**, 167.

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formed (Experimental section) and no solution n.m.r. data could be obtained. The solid from nitrobenzene analysed as $PPhCl_4{\cdot}bipy{\cdot}PhNO_2$, formulated as $[PPhCl_3(bipy)]Cl{\cdot}PhNO_2$, but analyses for the products from other solvents, although not fully satisfactory, were closer to the unsolvated complex. Solution investigation of the reaction in benzene was attempted since precipitation took place slowly in this solvent, but a signal for free $PPhCl_4$ only was found (47.5 p.p.m.), which decreased in intensity with time. The complex thus appears to be too insoluble for signals to be detected.

The solids gave very weak, broad, solid-state ^{31}P n.m.r. signals, and accurate chemical-shift data were very difficult to obtain. The product from CH_2Cl_2 gave a value of 158.5 ± 10.7 p.p.m., and the nitrobenzene solvate gave 157.3 ± 13.6 p.p.m., the good agreement being largely fortuitous. A reliable shift could not be determined for the product from benzene. The n.q.r. results for $[PPhCl_3(bipy)]Cl{\cdot}PhNO_2$ are discussed later, together with those for $[PPhCl_3(bipy)][SbCl_6]$ [section (*iii*)]. No ^{35}Cl n.q.r. signals were detected for the solid isolated from benzene.

(*iii*) *Acceptor Properties of the* $[PPhCl_3]^+$ *Cation.*—The acceptor properties of the $[PPhCl_3]^+$ cation, in the form of its $[SbCl_6]^-$ or $[PCl_6]^-$ salts, towards pyridine bases were studied to provide a comparison with $PPhCl_4$. Addition of 2 equivalents of pyridine to a nitrobenzene solution of $[PPhCl_3][SbCl_6]$ caused the formation of a white precipitate and the disappearance of the ^{31}P n.m.r. signal. The most probable reaction is the formation of an unstable ionic complex $[PPhCl_3(py)_2][SbCl_6]$, which then rearranges [equation (2)], analogously to the reaction of $[PCl_4][SbCl_6]$ with pyridine.[6] The phosphorus-

$$[PPhCl_3][SbCl_6] + 2\,py \longrightarrow [PPhCl_3(py)_2][SbCl_6] \longrightarrow PPhCl_4{\cdot}py + SbCl_5{\cdot}py \quad (2)$$

containing product $PPhCl_4{\cdot}py$ is too insoluble to give a solution spectrum. This conclusion is supported by the results for $[PPhCl_3][PCl_6]$; addition of 2 equivalents of pyridine to a solution of this complex in $PhNO_2$ produced a white precipitate and the appearance of a ^{31}P solution signal for $PCl_5{\cdot}py$, readily identified from its chemical shift.[5] The reaction is thus as in (3).

$$[PPhCl_3][PCl_6] + 2\,py \longrightarrow [PPhCl_3(py)_2][PCl_6] \longrightarrow PPhCl_4{\cdot}py + PCl_5{\cdot}py \quad (3)$$

A solution containing equimolar amounts of $[PPhCl_3][SbCl_6]$ and phen in $PhNO_2$ showed two ^{31}P n.m.r. peaks, at 135.1 and 149.7 p.p.m., as mentioned previously. These have been assigned to the two isomers of $[PPhCl_3(phen)]^+$. The solution remained stable for months, showing that no further reaction occurs in solution. The complex $[PPhCl_3(phen)][SbCl_6]$ was isolated as a solid (Experimental section) by addition of $SbCl_5$ to a solution of $[PPhCl_3(phen)]Cl$ in CH_2Cl_2. This method of preparation has the disadvantage that the product may be slightly contaminated by either $[PPhCl_3][SbCl_6]$ or $[SbCl_4(phen)][SbCl_6]$,[22] but an attempt to obtain the complex by mixing solutions of $[PPhCl_3][SbCl_6]$ and phen in $MeNO_2$ gave a yellow solid which contained no phosphorus. This was presumably an antimony(v) complex, and was not investigated further. The complex $[PPhCl_3(phen)][SbCl_6]$ gave a solid-state ^{31}P n.m.r. shift of 165.9 ± 6.2 p.p.m., which is quite close to the more upfield of the two cation resonances seen in solution. There is no direct evidence as to whether the solid contains one isomer only or a mixture, however. No ^{35}Cl n.q.r. signals were detectable.

Rather like $[PCl_4(phen)][SbCl_6]$,[6] the complex showed no tendency to hydrolyse. It remained unchanged on exposure to air overnight, as shown by its i.r. spectrum, and was not affected by addition of water. The stability to hydrolysis of complexes containing six-co-ordinate phosphorus(v) cations and $[SbCl_6]^-$ ions has been discussed previously.[6] On dissolution in nitrobenzene the complex gave a stable solution with ^{31}P n.m.r. peaks at 135.1 and 149.5 p.p.m., in the intensity ratio 10 : 3. These values are in excellent agreement with the previous solution data.

A solution containing equimolar quantities of $[PPhCl_3][PCl_6]$ and phen in $PhNO_2$ showed three ^{31}P n.m.r. signals, at 136.1, 151.1 (relative intensity 100 : 39), and 297.9 p.p.m. The first two peaks are again assigned to the isomers of $[PPhCl_3(phen)]^+$, while the signal at highest field is due to $[PCl_6]^-$.[4] The combined areas of the two cation peaks were approximately equal to that of the $[PCl_6]^-$ peak, and the complex $[PPhCl_3(phen)][PCl_6]$ appears to be stable in solution, unlike the bis(pyridine) derivative discussed earlier.

2,2′-Bipyridyl also formed 1 : 1 complexes with $[PPhCl_3]^+$ salts. A solution containing equimolar amounts of the base and $[PPhCl_3][SbCl_6]$ in $PhNO_2$ showed a ^{31}P resonance at 137.9 p.p.m. after spectrum accumulation. A second, very weak, signal appeared on some runs at 153.2 p.p.m. This system may thus contain one cation isomer predominantly in solution. The complex $[PPhCl_3(bipy)][SbCl_6]$ was prepared (Experimental section) and showed a broad solid-state ^{31}P resonance at 162.6 p.p.m., again closer to the shift of the higher-field isomer in solution. Mixing of $PhNO_2$ solutions of $[PPhCl_3][PCl_6]$ and bipy (1 : 1 mol ratio) caused the immediate formation of a white crystalline precipitate. Elemental analysis and i.r. spectroscopy indicated the presence of a small amount of nitrobenzene in the product, which is formulated as $[PPhCl_3(bipy)][PCl_6]{\cdot}0.25PhNO_2$ (Experimental section). This complex was prepared in insufficient quantity for either solid-state ^{31}P n.m.r. or ^{35}Cl n.q.r. spectroscopy. The i.r. spectra of both this complex and $[PPhCl_3(bipy)][SbCl_6]$ were very similar between 1 650 and 250 cm^{-1}, apart from bands due to $[SbCl_6]^-$, $[PCl_6]^-$, or $PhNO_2$. There are noticeable differences, however, from the spectra of the $PPhCl_4$–bipy reaction products from various solvents. In particular, the $[SbCl_6]^-$ and $[PCl_6]^-$ salts have a marked absence of absorptions between 510 and 475 cm^{-1}, while the $[PPhCl_3(bipy)]Cl$ samples show a

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

strong band between 495 and 490 cm^{-1}, together with a band of medium intensity between 488 and 483 cm^{-1}. These differences may arise from the presence of a predominant cation isomer, or a different isomer, for the $[MX_6]^-$ species relative to $[PPhCl_3(bipy)]Cl$.

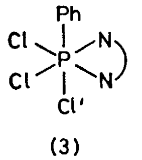
TABLE 3

Chlorine-35 n.q.r. frequencies for $[PPhCl_3(bipy)]^+$ salts at 77 K

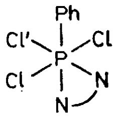
Complex	$\nu(^{35}Cl)$/MHz	Assignment
$[PPhCl_3(bipy)]Cl \cdot PhNO_2$	28.27	$[PPhCl_3(bipy)]^+$
	27.34	
	26.42	
$[PPhCl_3(bipy)][SbCl_6]$	29.82	$[PPhCl_3(bipy)]^+$
	27.96	
	27.49	
	25.09	$[SbCl_6]^-$
	24.66	
	24.53 *	
	24.20	
	23.99	
	23.80	

* Possible multiplet.

The ^{35}Cl n.q.r. frequencies for $[PPhCl_3(bipy)]Cl \cdot PhNO_2$ and $[PPhCl_3(bipy)][SbCl_6]$ at 77 K are given in Table 3, and support the above suggestion. Both spectra show three P–Cl signals, but for $[PPhCl_3(bipy)]Cl \cdot PhNO_2$ these occur between 26.4 and 28.3 (average 27.34) MHz, while the $[SbCl_6]^-$ salt shows two lines close together within this range, and one at higher frequency (average 28.42 MHz). These results, including the marked difference in average frequency, are compatible with the presence of different isomeric forms in each case. Both isomers (3) and (4) are expected to have two chlorines exhibiting similar frequencies and one having a rather different frequency (denoted Cl′). In transition-metal complexes of the type *cis*-$[MCl_4L_2]$ and $[MCl_3L_3]$ (L = py, PEt_3, or $AsEt_3$; M = Re, Os, Ir, or Pt), mutually *trans* chlorines are generally found at higher frequency than chlorines *trans* to the ligand L.[23,24] This is ascribed to the *trans* effect of L, which lowers the n.q.r. frequency of the *trans* chlorine, and to its *cis* effect which raises the frequency of a *cis* chlorine. If these effects apply in six-coordinate phosphorus complexes, isomer (4) should have two lines fairly close together at higher frequency and a more separated line at lower frequency. This pattern is not found for $[PPhCl_3(bipy)][SbCl_6]$, but could apply to $[PPhCl_3(bipy)]Cl \cdot PhNO_2$.



(3)



(4)

The alternative isomer (3) has two chlorines *trans* to pyridine nitrogens and one *trans* to the phenyl group, so the ^{35}Cl n.q.r. frequencies will depend on the relative magnitudes of the *trans* effects caused by these ligands. If this is greater for the nitrogen bases two signals should occur closer together at lower frequency, with a single, more separated, line at higher frequency. Some support for this type of splitting pattern in isomer (3) is provided by the ^{35}Cl n.q.r. results fror species such as $[PCl_4(phen)]^+$,[6] where the frequencies are quite similar for mutually *trans* chlorines and chlorines *trans* to nitrogen, and those for $[PPhCl_5]^-$ given in section (*i*), where the tetra-n-propylammonium salt in particular exhibits the highest frequency for chlorine *trans* to the phenyl group. The chlorine (Cl′) *trans* to phenyl in isomer (3) may thus resonate at an appreciably higher frequency than the other two chlorines, as observed for $[PPhCl_3(bipy)][SbCl_6]$. N.q.r. spectroscopy is not a technique which will readily detect the presence of small amounts of a different isomer, but we tentatively suggest that solid $[PPhCl_3(bipy)][SbCl_6]$ contains the cation predominantly in the form of isomer (3), while $[PPhCl_3(bipy)]Cl \cdot PhNO_2$ has the cation predominantly in the form of isomer (4). The variation in i.r. spectra between samples of $[PPhCl_3(bipy)]Cl$ produced from different solvents could well be due to variation in the proportions of isomers present.

The results show that both $PPhCl_4$ and $[PPhCl_3]^+$ are capable of exhibiting acceptor properties towards Lewis bases. They are much poorer in this respect than PCl_5 [5] or $[PCl_4]^+$,[6] since pyridines of fairly high basicity must be used. The compound $PPhCl_4$ forms $[PPhCl_5]^-$ with excess of chloride ion in a solvent of suitable polarity, molecular 1 : 1 adducts with unhindered pyridines of sufficiently high basicity, and ionic 1 : 1 complexes $[PPhCl_3L']Cl$ with bidentate pyridines L′. The cations are capable of existing in two isomeric forms, both of which have been detected in solution. The salts of $[PPhCl_3]^+$ do not form stable complexes with pyridine, probably because of rearrangement, but give stable derivatives with bidentate pyridines, which can be very resistant to hydrolysis with a suitable counter ion such as $[SbCl_6]^-$. Isomeric forms of the cationic complexes co-exist in solution, but n.q.r. data at 77 K suggest that solid complexes of $[PPhCl_3(bipy)]^+$ may exist predominantly in one form, which varies with the counter ion.

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[24] C. W. Fryer, *Chem. Comm.*, 1970, 902.