Acceptor Properties of some *o*-Phenylenedioxy-derivatives of Phosphorus(V) Chloride

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The acceptor properties of PCl_3(cat) and PCl(cat)$_2$ (cat = $O_2C_6H_4$) towards some Lewis bases have been investigated in solution by means of ^{31}P n.m.r. spectroscopy. The compound PCl_3(cat) is a better acceptor than PCl(cat)$_2$, which is comparable with $PPhCl_4$ studied previously. The cations $[PCl_2(cat)]^+$ and $[P(cat)_2]^+$ have been prepared for the first time; these species are extremely reactive, probably because of their strained geometries, and readily increase their co-ordination number. Several new solid complexes have been isolated, and further characterised by elemental analysis, i.r., and in some cases ^{31}P n.m.r. and/or ^{35}Cl n.q.r. spectroscopy.

THE *o*-phenylenedioxy-derivatives of phosphorus(V) chloride, $PCl_3(O_2C_6H_4)$ or PCl_3(cat), and $PCl(O_2C_6H_4)_2$ or PCl(cat)$_2$, were both first prepared by Anschütz and his co-workers in the 1920's,[1,2] but their Lewis-acid and Lewis-base behaviour has been little investigated. In previous papers we have described the acceptor properties of PCl_5 towards the chloride ion[3] and pyridine bases,[4] of the tetrachlorophosphonium ion,[5] and of the phenyl-substituted derivatives $PPhCl_4$ and $[PPhCl_3]^+$.[6] It was therefore of interest to extend this work to *o*-phenylenedioxy-compounds, and observe the effect of the substituents on the acceptor properties of the phosphorus(V) species. In addition, the new cationic species $[PCl_2(cat)]^+$ and $[P(cat)_2]^+$ have been prepared by reaction of antimony(V) chloride with PCl_3(cat) and PCl(cat)$_2$ respectively. The presence of the bidentate aromatic groups was expected to impose certain geometrical constraints, particularly for four-co-ordinate species such as $[P(cat)_2]^+$, as indeed was the case. No acceptor properties have been reported for PCl_3(cat), but in a very recent paper Schmidpeter *et al.*[7] have described the formation of both neutral 1 : 1 and cationic 1 : 2 complexes of PCl(cat)$_2$ and pyridine or 4-methylpyridine, formulated as PCl(cat)$_2$·py and $[P(py)_2(cat)_2]$Cl respectively. A 1 : 1 ionic complex of PCl(cat)$_2$ and 2,2′-bipyridyl, with the structure [P(bipy)(cat)$_2$]Cl, was also prepared.[7] Our results and conclusions, where they overlap, are in very good agreement with theirs. We report the results of an investigation by means of solution ^{31}P n.m.r. spectroscopy of some acceptor properties of PCl_3(cat), $[PCl_2(cat)]^+$, PCl(cat)$_2$, and $[P(cat)_2]^+$. Several new solid compounds have been isolated and characterised.

EXPERIMENTAL

All the manipulations, including the preparation of n.m.r. samples, were carried out either *in vacuo* or under an inert atmosphere of dry nitrogen. Particular difficulty was experienced in handling certain compounds, as described subsequently, since they decomposed quickly even in an inert-atmosphere box or on contact with a metal spatula. Glass spatulas were therefore necessary when transfer of these compounds was required. Chemicals of the best available commercial grade were used, generally without further purification, except as described below or previously.[4] A commercial sample of PCl_3(cat) and a sample prepared from PCl(cat) as described in a previous publication[8] were used in the course of this work; the products gave identical ^{31}P chemical shifts of 26.3 p.p.m. in CH_2Cl_2 and 27.2 p.p.m. in $PhNO_2$, in good agreement with other determinations in various solvents.[9-11] The compound PCl(cat)$_2$ was prepared by the optimum method of Ramirez *et al.*[11] Its ^{31}P n.m.r. spectrum showed signals at 10.0 p.p.m. in CH_2Cl_2 and 10.5 p.p.m. in $PhNO_2$, as expected,[10-12] but weak resonances at 31.1 (CH_2Cl_2) and 31.4 p.p.m. ($PhNO_2$) were also found after spectrum accumulation. These were ascribed to the hydrolysis product P(OH)(cat)$_2$ and compare with a shift of 31.8 p.p.m. for the authentic material in benzene solution.[13] Recrystallisation from dry benzene–hexane effected a considerable reduction in the concentration of this impurity.

Phosphorus-31 n.m.r. spectra were recorded as described previously.[3-6] Chemical shifts were measured with respect to external P_4O_6, but are quoted relative to 85% H_3PO_4, with the upfield direction taken as positive. Elemental analysis, i.r. spectra, and ^{35}Cl n.q.r. spectra were also obtained as described previously.[3-6] Phosphorus and chlorine analyses were in general considered to be more reliable than data from the automatic C, H, and N analyser, which sometimes produced unusual C : H or C : N ratios. The preparation of new solid complexes is described below.

Tetrakis(n-pentyl)- and Tetrakis(n-propyl)-ammonium Tetrachloro(o-phenylenedioxy)phosphate.—These salts were prepared by mixing stoicheiometric quantities of PCl_3(cat) and the appropriate tetra-alkyl ammonium chloride, dissolved in the minimum quantity of the solvent shown in Table 1. The tetrakis(n-pentyl)ammonium complex formed as a yellow viscous layer above a clear liquid. The upper layer was separated and the solvent removed *in vacuo* to yield a pale yellow solid. The tetrakis(n-propyl)ammonium analogue was formed in a very exothermic reaction, and separated as a bright yellow solid when the

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mixture had cooled sufficiently. The product was isolated after 90 min, washed with pentane, and dried *in vacuo*. (The pentane caused the solid to cake together.) Elemental analyses for these and other new compounds are given in Table 1.

The complex $[PPhCl_3][PCl_4(cat)]$ was similarly prepared from $PPhCl_4$ and $PCl_3(cat)$ (1 : 1), appearing as an immediate bright yellow crystalline precipitate which was isolated and dried as above.

2,2′-Bipyridyldichloro(o-*phenylenedioxy*)*phosphonium Tetrachloro*(o-*phenylenedioxy*)*phosphate*.—2,2′-Bipyridyl and $PCl_3(cat)$ (1 : 2) were dissolved together in the minimum quantity of CH_2Cl_2. The solution was kept at 307.2 K (the n.m.r. spectrometer operating temperature) for several hours, by which time a solid bright orange mass had formed. This was separated and purified as above.

TABLE 1

Analytical data for some *o*-phenylenedioxy-derivatives of phosphorus(v) chloride

		Analysis (%)									
		Found					Calc.				
Complex	Solvent	C	H	N	P	Cl	C	H	N	P	Cl
$[N(C_5H_{11})_4][PCl_4(cat)]$	CCl_4	53.6	7.85	3.25	5.75	24.8	53.9	8.35	2.40	5.35	24.45
$[N(C_3H_7)_4][PCl_4(cat)]$	CH_2Cl_2	47.1	6.80	3.05	6.55	29.75	46.25	6.90	3.00	6.65	30.35
$[PPhCl_3][PCl_4(cat)]$	CH_2Cl_2	27.95	1.85		11.65	51.5	29.1	1.85		12.5	50.1
$[PCl_2(bipy)(cat)][PCl_4(cat)]$	CH_2Cl_2	41.0	3.35	4.35	9.10	33.85	40.85	2.50	4.35	9.55	32.9
$[PCl_2(bipy)(cat)][PCl_4(cat)]\cdot PhNO_2$	$PhNO_2$	43.9	4.00	5.35	8.30	29.3	43.65	2.75	5.45	8.05	27.6
$[PCl_2(phen)(cat)][PCl_4(cat)]$	CH_2Cl_2	42.3	2.20	4.25	9.05	31.8	42.95	2.40	4.15	9.25	31.7
$[PCl_2(cat)][SbCl_6]$	CH_2Cl_2	*	*		6.50	52.35	13.25	0.75		5.70	52.1
$[PCl_2(bipy)(cat)][SbCl_6]\cdot 0.75PhNO_2$	$PhNO_2$	30.05	2.40	4.60	4.10	34.6	31.05	2.00	4.85	3.90	35.75
$[N(C_5H_{11})_4][PCl_2(cat)_2]$	None	61.65	8.05	2.35	5.00	11.7	62.35	8.50	2.25	5.00	11.5
$[P(cat)_2][SbCl_6]$	CH_2Cl_2	*	*		5.30	36.8	24.8	1.40		5.35	36.55
$[P(phen)(cat)_2][SbCl_6]$	$PhNO_2$	37.4	2.30	4.05	3.50	27.5	37.85	2.10	3.70	4.05	27.9

* See text.

$[PCl_2(bipy)(cat)][PCl_4(cat)]\cdot PhNO_2$.—The previous reaction was repeated in nitrobenzene, giving a clear yellow solution, which formed a solid mass after overnight stirring and then leaving for another day at room temperature. The solid appeared, after drying, as a bright yellow powder with a reddish tinge; the tinge disappeared each time the complex was mixed with solvent, but reappeared on drying.

Dichloro(1,10-*phenanthroline*)(o-*phenylenedioxy*)*phosphonium Tetrachloro*(o-*phenylenedioxy*)*phosphate*.—The compounds $PCl_3(cat)$ and 1,10-phenanthroline (2 : 1) were dissolved separately in CH_2Cl_2. The solutions were mixed and stirred overnight, yielding an orange precipitate which appeared as a fine powder after drying.

Dichloro(o-*phenylenedioxy*)*phosphonium Hexachloroantimonate*(v).—The salt was prepared by addition of the stoicheiometric quantity of antimony(v) chloride to a solution of $PCl_3(cat)$ in CH_2Cl_2, and isolated as a white solid. It was extremely unstable, reacting within seconds when exposed to the atmosphere in a glove-box, and within days in a stoppered container inside the box. It was also decomposed by contact with metal spatulas. Carbon, hydrogen, and nitrogen microanalyses were not attempted for this complex or for $[P(cat)_2][SbCl_6]$, since they would involve the use of metal capsules. All the reactions involving $[PCl_2(cat)][SbCl_6]$ were carried out as quickly as possible. Ligands were mixed with nitrobenzene and the solid dissolved in the mixture, so that co-ordination would take place before $[PCl_2(cat)][SbCl_6]$ had time to decompose. The reasons for this behaviour are discussed later; the adducts formed by co-ordination were much more stable both in solution and in the solid, and could be handed without difficulty.

An attempt was made to prepare $[PCl_2(cat)][BCl_4]$ by reaction of excess of BCl_3 with $PCl_3(cat)$ in methylene chloride solution, but the white solid obtained after evaporation of the solvent appeared to be starting material, since it was soluble in pentane. It also did not mull in Nujol. Boron trichloride is presumably not a strong enough Lewis acid to abstract a chlorine from $PCl_3(cat)$.

2,2′-Bipyridyldichloro(o-*phenylenedioxy*)*phosphonium Hexachloroantimonate*(v)-*Nitrobenzene* (4/3).—This complex was obtained by adding a solution of the stoicheiometric quantity of bipy in $PhNO_2$ to solid $[PCl_2(cat)][SbCl_6]$. A very exothermic reaction occurred and there was an immediate yellow colouration. A little more $PhNO_2$ was added and the mixture stirred for a few minutes. Originally the yellow solid was isolated and dried at this stage, but in a later preparation the solution was kept for several hours at 307.2 K, and then at room temperature for several days, before the solid was separated. The products gave identical i.r. spectra, but, on storing under nitrogen, green spots appeared in the first sample, and the mass slowly turned yellow-green. This colour change did not take place in the second sample.

Tetrakis(*n-pentyl*)*ammonium Dichlorobis*(o-*phenylenedioxy*)*phosphate*.—Equimolar quantities of $PCl(cat)_2$ and $[N(n-C_5H_{11})_4]Cl$ were intimately mixed, and the mixture rapidly heated to 413 K, giving a yellow-brown viscous melt. The liquid was allowed to cool rapidly with continuous swirling and yielded a yellowish waxy solid. Preparation was also attempted by evaporating a CH_2Cl_2 solution of the components *in vacuo* between 243 and 253 K, but i.r. spectroscopy showed that the solid obtained was contaminated with starting material.

Bis(o-*phenylenedioxy*)*phosphonium Hexachloroantimonate*(v).—This salt was prepared from equimolar quantities of $PCl(cat)_2$ and $SbCl_5$ in the minimum quantity of CH_2Cl_2, and was isolated as quickly as possible in the form of an off-white, almost fawn, powder. It was extremely sensitive to moisture, was decomposed by contact with metal spatulas, and appeared to be even less stable than $[PCl_2(cat)][SbCl_6]$, being attacked more readily in stoppered containers. It also reacted with galatin capsules, so that phosphorus and chlorine microanalyses had to be carried out using glass capsules. Its co-ordination properties were again studied by mixing the potential ligand with $PhNO_2$, and then dissolving solid $[P(cat)_2][SbCl_6]$ in the mixture. The adducts were far more stable, both in solution and in the solid, than the parent complex.

1,10-Phenanthrolinebis(o-phenylenedioxy)phosphonium Hexachloroantimonate(v).—1,10-Phenanthroline was dissolved in the minimum quantity of $PhNO_2$, and the mixture added to an equimolar amount of solid $[P(cat)_2][SbCl_6]$. The solid dissolved on stirring, but an orange precipitate was quickly formed. This was isolated and dried to give an orange powder.

RESULTS AND DISCUSSION

(*i*) *Acceptor Properties of* $PCl_3(cat)$.—The ^{31}P n.m.r. chemical shifts for $PCl_3(cat)$ in solution, both in this work and elsewhere,[9-11] are in agreement with a five-co-ordinate molecular structure. The ^{35}Cl n.q.r. spectrum of the solid at 77 K has signals of equal intensity at 27.841, 31.233, and 31.761 MHz,[14] showing that the cat group occupies one axial and one equatorial position in a trigonal bipyramid. The compound is thus similar to $PPhCl_4$, which has a molecular structure in both phases with an equatorial phenyl group,[15,16] and shows weak acceptor properties towards chloride ion and pyridine bases.[6]

The ^{31}P chemical shifts for mixtures of $[N(n\text{-}C_5H_{11})_4]Cl$ and $PCl_3(cat)$ in various solvents are shown in Table 2.

TABLE 2

Phosphorus-31 n.m.r. data for $[N(n\text{-}C_5H_{11})_4]Cl$–$PCl_3(cat)$ mixtures

Mol ratio Cl^- : $PCl_3(cat)$	Solvent	$\delta(^{31}P)$/p.p.m.
1 : 1	$PhNO_2$	150.7
Excess of Cl^-	$PhNO_2$	157.3
1 : 1	CH_2Cl_2	157.3
1 : 1	CCl_4	159.1

A single peak only was observed in each case. The value for the 1 : 1 solution in nitrobenzene indicates at least partial association of Cl^- with $PCl_3(cat)$ to give $[PCl_3(cat)]^-$. The maximum upfield shift caused by addition of more chloride was 157.3 p.p.m., so that the 1 : 1 solution corresponds to *ca.* 95% association. The result for a 1 : 1 mol ratio of the reagents in CH_2Cl_2 shows that association is virtually complete in this solvent. The compound $PCl_3(cat)$ is thus a better chloride-ion acceptor than $PPhCl_4$ under similar conditions.[6] In CCl_4, solutions of the reagents in a 1 : 1 mol ratio produced a yellow viscous layer above a clear solution; the shift found for the upper layer is ascribed to completely associated $[N(n\text{-}C_5H_{11})_4][PCl_4(cat)]$. The solid complex was subsequently isolated and showed a narrow ^{31}P solid-state resonance at 162 ± 2 p.p.m., in good agreement with the solution data. The shift is intermediate between those of $[PPhCl_5]^-$ (ref. 6) and $[P(cat)_3]^-$,[17] as expected for the proposed structure. (In addition a superimposed sharp liquid line was observed at 158.7 p.p.m., possibly due to diffusion of the anion through the solid lattice.[6,18]) The tetrakis(n-propyl)ammonium salt was also prepared but did not stabilise in the spectrometer and no solid-state shift could be obtained.

The i.r. spectra of the two salts between 650 and 250 cm^{-1} are given in Table 3, with that of $PCl_3(cat)$ for comparison. Both complexes show a lowering of frequency of lines attributable to P–Cl stretches compared with $PCl_3(cat)$, and their spectra appear to be considerably simplified. A lowering of i.r. frequency on formation of six-co-ordinate neutral or anionic species from five-co-ordinate phosphorus chloro-compounds is generally observed,[3,4,6] and is ascribed to a reduction in the P–Cl bond strength. Between 1 600 and 800 cm^{-1} the spectra of the salts were obscured by a very broad band from the cation. Neither of the complexes yielded a ^{35}Cl n.q.r. spectrum at 77 K.

TABLE 3

Infrared bands (cm^{-1}) for $[PCl_4(cat)]^-$ salts and $PCl_3(cat)$ between 650 and 250 cm^{-1}

Compound	
$[N(C_5H_{11})_4][PCl_4(cat)]$	620s, 596m, 586m, 552w, 522s, 473s, 448s, 425s, 361s, 342w, 298w
$[NPr_4][PCl_4(cat)]$	622s, 598w, 586w, 552w, 522s, 468s, 447s, 424s, 352s, 300w, 286w
$PCl_3(cat)$	644m, 622w, 588s, 537s, 500w, 458s, 430w, 403w, 376w, 317w, 264m

When solutions of $PPhCl_4$ and $PCl_3(cat)$ in CH_2Cl_2 were mixed a yellow solid was obtained which analysed as a 1 : 1 adduct (Experimental section). The solid-state ^{31}P n.m.r. spectrum consisted of signals at −101.6 ($[PPhCl_3]^+$)[16,19] and 163 ± 5.5 p.p.m. $\{[PCl_4(cat)]^-\}$, showing that the complex has an ionic structure. These results confirm the much better acceptor properties of $PCl_3(cat)$ compared with $PPhCl_4$. The i.r. spectrum between 650 and 340 cm^{-1} showed absorptions at 647s ($[PPhCl_3]^+$), 618s $\{[PCl_4(cat)]^-\}$, 608m ($[PPhCl_3]^+$), 590m $\{[PCl_4(cat)]^-\}$, 568m, 543s ($[PPhCl_3)]^+$), 517s 496w, 472s $\{[PCl_4(cat)]^-\}$, 458w ($[PPhCl_3]^+$), 443s 439s, 400m, 362s, and 340w cm^{-1} $\{[PCl_4(cat)]^-\}$, in complete agreement with the suggested structure when compared with other values for $[PPhCl_3]^+$ and $[PCl_4(cat)]^-$ (Table 3). The ^{35}Cl n.q.r. spectrum at 77 K contained a broad multiplet of resonances at 31.01, 31.16, and 31.28 MHz (signal-to-noise ratios 5.5 : 1, 10 : 1, and 9 : 1 respectively). The signals could all arise from the cation,[16] but it seems more probable that the anion and cation resonances occur at similar frequencies and possibly overlap, since no other signals were detected.

The acceptor properties of $PCl_3(cat)$ towards pyridine bases were also investigated. An equimolar mixture of pyridine and $PCl_3(cat)$ in $PhNO_2$ showed three peaks, all

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in the six-co-ordinate region (Table 4), with relative intensities as indicated. The relative intensity of the smallest peak increased somewhat as the ratio of pyridine to $PCl_3(cat)$ was increased (Table 4), while the two peaks at higher field did not vary greatly. The pseudo-octahedral molecular complex $PCl_3(cat)\cdot py$ has two possible isomeric forms, with pyridine *trans* either to chlorine or to an oxygen from the cat group. The presence of geometrical isomers can be detected by ^{31}P n.m.r. spectroscopy in favourable circumstances, as shown previously for $[PPhCl_3(phen)]^+$.[6] The two peaks at higher field are therefore assigned to these isomers. Although the shift difference is smaller in this instance, the whole range of chemical shifts is smaller for $PCl_3(cat)$ complexes than for their $PPhCl_4$ analogues. The signal at lowest field appears to be more favoured by higher relative concentrations of pyridine, and is assigned to the cationic species $[PCl_2(py)_2(cat)]^+$, formed by displacement of chlorine by pyridine from the neutral adduct. This is supported by the ^{31}P shift for $[PCl_2(py)_2(cat)][SbCl_6]$, reported in the following section. Only one peak due to cationic species was observed in both cases, even though several isomers are possible. This indicates either a preferred configuration or rapid exchange between isomers in solution.

TABLE 4

Phosphorus-31 n.m.r. shifts (p.p.m.) for $PCl_3(cat)$–py mixtures in $PhNO_2$

Ratio	$\delta(^{31}P)$/p.p.m.			Relative intensity
py : $PCl_3(cat)$	*a*	*b*	*c*	a : (*b* + *c*)
1 : 1	125.9	129.9	136.7	4.7 : 100
2 : 1	125.9	130.1	136.9	5.5 : 100
5 : 1	125.2	129.7	137.1	7.1 : 100

An equimolar mixture of 2,2′-bipyridyl and $PCl_3(cat)$ in $PhNO_2$ showed two strong ^{31}P n.m.r. signals in the six-co-ordinate region, one at *ca.* 119 p.p.m. which remained constant in shift and an initially stronger one at higher field, which moved further upfield with time reaching a value of 154.7 p.p.m. after several hours. During this time the signals became of approximately equal intensity. A yellow solid was deposited as the reaction proceeded. The results in CH_2Cl_2 solution were very similar; a 1 : 1 mixture showed an initially smaller peak at 118.7 p.p.m. (average) which remained constant in shift but increased in relative intensity, eventually becoming stronger than the upfield peak which moved progressively from 133.9 to 150.8 p.p.m. A 2 : 1 $PCl_3(cat)$: bipy mixture in CH_2Cl_2 also showed a constant signal at 118.8 p.p.m. (average) and a variable one, at 124.3 p.p.m., 30 min after mixing but at 145.4 p.p.m. after 5 h. The intensity ratio of the lower- to the higher-field signal at this stage was just less than 1 : 1. The peak at *ca.* 119 p.p.m. is attributed to the cationic complex $[PCl_2(bipy)(cat)]$,$^+$ and the variable peak to the $PCl_3(cat)$–$[PCl_4(cat)]^-$ equilibrium described previously. The reaction is readily explained by equations (1) and (2). Since $PCl_3(cat)$ and $[PCl_4(cat)]^-$

$$PCl_3(cat) + bipy \xrightarrow{slow} [PCl_2(bipy)(cat)]^+ + Cl^- \quad (1)$$

$$PCl_3(cat) + Cl^- \overset{rapid}{\rightleftharpoons} [PCl_4(cat)]^- \quad (2)$$

exchange rapidly on the n.m.r. time scale the upfield peak moves to higher field as the proportion of $[PCl_4(cat)]^-$ in the equilibrium mixture increases. The slowness of reaction (1) explains the variation in relative intensity, since the cation concentration will initially be lower than that of unchanged $PCl_3(cat)$ + $[PCl_4(cat)]^-$. The limiting value for the intensities in a 2 : 1 $PCl_3(cat)$: bipy mixture will be 1 : 1, corresponding to complete formation of $[PCl_2(bipy)(cat)][PCl_4(cat)]$, but in the 1 : 1 mixtures the intensities are less amenable to discussion because of precipitation of the 2 : 1 complex, which was isolated from a 2 : 1 mixture in CH_2Cl_2.

There are two possible geometrical isomers for the cationic complex, with *cis* and *trans* chlorines respectively, but only one cation resonance was observed in CH_2Cl_2 solution. During one experiment in $PhNO_2$, however, a small but definite peak was found at 133.0 p.p.m., which could arise from the second isomer. This signal could not be confirmed because of the instability of concentrated solutions prepared *in situ*, caused by slow precipitation of the 2 : 1 complex. The solid complex $[PCl_2(bipy)(cat)][PCl_4(cat)]$ was isolated from CH_2Cl_2 solution, whereas $PhNO_2$ solutions yielded the nitrobenzene solvate.

The i.r. spectra of the products were very similar, containing absorptions assignable to both $[PCl_2(bipy)(cat)]^+$ and $[PCl_4(cat)]^-$, except for additional bands at 1 531s, 1 348s, and 398w cm^{-1} from the solvate, due to $PhNO_2$.[20] The absorptions between 650 and 300 cm^{-1} are listed in Table 5. The solid-state ^{31}P n.m.r. spectrum of $[PCl_2(bipy)(cat)][PCl_4(cat)]\cdot PhNO_2$ showed a single broad absorption centred at 145 p.p.m., and no resolution into the expected two components was apparent; this effect is due to the small shift difference between the constituent ions compared with their linewidths. The value compares well with the average solution shift for the two species of 138 p.p.m.

TABLE 5

Infrared bands (cm^{-1}) for bipy complexes of $PCl_3(cat)$ between 650 and 300 cm^{-1}

Complex	
$[PCl_2(bipy)(cat)][PCl_4(cat)]$	624m, 542 (sh), 536 (sh), 526s, 517s, 504s, 474s, 458m, 450m, 424s, 383m, 363m, 302w
$[PCl_2(bipy)(cat)][PCl_4(cat)]\cdot PhNO_2$	647w, 626s, 602w, 547s, 537 (sh), 524s,br, 503m, 474s, 465s, 460s, 448m, 423s, 398w,* 383m, 360 (sh), 352 (sh), 303w

* $PhNO_2$.

An equimolar mixture of $PCl_3(cat)$ and 1,10-phenan-

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

throline in $PhNO_2$ showed only one peak initially, due to the cation [$\delta(^{31}P)$ 118.8 p.p.m.], but the 2 : 1 complex $[PCl_2(phen)(cat)][PCl_4(cat)]$ was completely formed after <2 h, the shift for the anion then being 156.6 p.p.m. (The latter may not have been detectable originally because of broadening by the reaction.) Spectrum accumulation was carried out after several hours, to detect any minor peaks. Resonances were found at 118.7 {$[PCl_2(phen)(cat)]^+$}, 129.9, 157.2 {$[PCl_4(cat)]^-$, most intense peak}, and 194.4 p.p.m. The peak at 129.9 p.p.m. was only slightly above the noise level, but could arise from the second cation isomer. The fourth peak must be cationic to equalise the cation : anion areas, and is assigned to $[PCl_4(phen)]^+$,[4,5] produced either from PCl_5 impurity in commercial $PCl_3(cat)$ or by disproportionation of $[PCl_2(phen)(cat)]^+$.

The solid complex $[PCl_2(phen)(cat)][PCl_4(cat)]$ was isolated from CH_2Cl_2 solution. Its i.r. spectrum between 650 and 250 cm^{-1} contained absorptions at 634m, 621s, 613w, 596w, 570(sh), 568m, 547s, 513s, 492s, 478s, 468m, 456m, 447s, 438s, 426s, 376m, 358w, 343w, and 298w cm^{-1}. With this complex the frequencies for $[PCl_4(cat)]^-$ appear to be slightly displaced from the values found for other salts. The solid-state ^{31}P n.m.r. spectrum showed a single broad line centred at 146.6 p.p.m., with perhaps very slight resolution into the expected two constituent peaks. Neither this complex nor the bipy complexes were prepared in sufficient quantity for ^{35}Cl n.q.r. studies.

In view of the good acceptor characteristics of PCl_3-(cat) and its ready solubility in a range of organic solvents,[11] some other liquid potential donors were tried, to see whether any change in chemical shift would be produced. In order to distinguish solvent effects from co-ordination the solutions were prepared as concentrated as possible, their spectra recorded, then they were diluted with the same potential donor solvent and their spectra re-recorded. Diethyl ether and tetrahydrofuran gave no detectable co-ordination shift under these conditions, but tetrahydrothiophene caused a small upfield shift, from 30.2 p.p.m. in concentrated solution to 33.1 p.p.m. in the same solution diluted eight-fold. The chemical shift for $PCl_3(cat)$ itself in a variety of non-co-ordinating solvents lies between 25 and 28 p.p.m.,[9-11] so that weak complex formation may occur with tetrahydrothiophene. The co-ordination of sulphur in preference to oxygen is indicative of class b behaviour, as deduced for arsenic and antimony(v) species,[21] and also suggested by the preferential co-ordination of PMe_3 rather than NMe_3 by PF_5.[22] Although P^V was not included in Ahrland's table of class b acceptors,[21] no experimental evidence in favour of its exclusion was presented.

(*ii*) $[PCl_2(cat)][SbCl_6]$ *and its Acceptor Properties.*—The preparation of this salt and its very reactive nature have already been described. Its vulnerability to nucleophilic attack presumably arises partly from the positive charge and co-ordinative unsaturation, and partly from the steric strain arising from the cat group. The strain may be readily relieved by the change in geometry involved in going to a higher co-ordination number. This hypothesis is supported by the comparative stability of $[PCl_4]^+$, and the even greater sensitivity to moisture or other nucleophiles of $[P(cat)_2]^+$. The salt showed a single sharp ^{31}P n.m.r. resonance in the solid state at −71.7 p.p.m., fully in agreement with a four-co-ordinate structure. It dissolved in $PhNO_2$ to yield a signal at −77.1 p.p.m., but the solution was unstable, presumably because of slow reaction with the solvent. Trichlorophosphine oxide formed a more stable solution {$\delta(^{31}P)$ −77.8 p.p.m. for $[PCl_2(cat)]^+$}, but this turned purple over a period of days. After 2 weeks, equally intense signals were found at −77.0 and −66.3 p.p.m., the identity of the latter being unknown.

The solid at 77 K showed ^{35}Cl n.q.r. lines at 31.725 and 30.047 MHz due to $[PCl_2(cat)]^+$, and at 25.36, 24.425, 24.20, and 24.07 MHz due to $[SbCl_6]^-$. The separation of the cation signals is larger than expected for crystallographic effects in phosphorus(v) chlorocompounds of possible C_{2v} symmetry.[16] The highest frequency line attributable to $[SbCl_6]^-$ is also higher than usually found,[16] so the possibility of a cation–anion interaction *via* a chlorine, thus lowering the symmetry, cannot be discounted. The solid turned bright yellow on addition of Nujol, possibly due to reaction; i.r. absorptions between 650 and 300 cm^{-1} were found at 636s, 593w, 566m, 423s, 417w, 397w, *ca.* 360sh, and *ca.* 330s,br cm^{-1}. The strong broad band at *ca.* 330 cm^{-1} is attributable to $[SbCl_6]^-$, while the strong absorption at 636 cm^{-1} is assigned to a P–Cl stretch from the cation, and lies at higher frequency than the P–Cl bands of $PCl_3(cat)$, as expected.

A $PhNO_2$ solution containing $[PCl_2(cat)][SbCl_6]$ and pyridine in a 1 : 2 mol ratio gave a single ^{31}P n.m.r. peak at 124.8 p.p.m., assigned to $[PCl_2(py)_2(cat)]^+$. The solution was quite stable, unlike that in the absence of pyridine. Although various isomers are possible, the single resonance indicates either a rapid solution exchange or a preferred configuration. After 2 months the main peak was at 125.4 p.p.m., constant within experimental error, but a new small peak was detected at 134.8 p.p.m. This may arise from a slow reaction (3)

$$[PCl_2(py)_2(cat)][SbCl_6] \longrightarrow PCl_3(cat){\cdot}py + SbCl_5{\cdot}py \qquad (3)$$

similar to the rapid disproportionation observed with $[PCl_4(py)_2]^+$ species.[5]

The isolation of a nitrobenzene solvate on addition of $[PCl_2(cat)][SbCl_6]$ to a $PhNO_2$ solution of bipy has been described. The second sample had i.r. absorptions at 1 531(sh) and 1 347s cm^{-1} due to $PhNO_2$.[20] Between 650 and 250 cm^{-1} bands were apparent at 627m, 543m, 532w, 509s, 457m, 452m, 420s, 383m, and 342s,br cm^{-1}, the last of these due to $[SbCl_6]^-$. Many of the lines are in similar positions to absorptions in the spectrum of

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[21] S. Ahrland, *Structure and Bonding*, 1966, **1**, 207.

[22] C. W. Schultz and R. W. Rudolph, *J. Amer. Chem. Soc.*, 1971, **93**, 1898.

$[PCl_2(bipy)(cat)][PCl_4(cat)]$, suggesting that the same cation isomer may be present in both salts. The complex showed remarkable resistance to hydrolysis; the solid gradually became paler on exposure to air, and did not dissolve in water although there was again a slight colour change. In contrast, $[PCl_2(bipy)(cat)][PCl_4(cat)]{\cdot}PhNO_2$ hydrolysed slowly in moist air, showing the importance of the counter ion to stability. Other very stable hexachloroantimonates of six-co-ordinate phosphorus(v) cations have been found previously.[4-6] The solid was obtained in insufficient quantity for either ^{31}P n.m.r. or ^{35}Cl n.q.r. studies.

(*iii*) *Acceptor Properties of* $PCl(cat)_2$.—Like $PCl_3(cat)$, $PCl(cat)_2$ has been considered to have a five-co-ordinate molecular structure.[7] This has been confirmed very recently by a single-crystal *X*-ray structure determination,[23] which has shown that the geometry is considerably displaced from a trigonal bipyramid towards a rectangular pyramid, with the chlorine occupying the axial rather than a basal position. The ^{35}Cl n.q.r. spectrum of the solid at 77 K consists of a single line at 27.25 MHz. Interestingly, this value is similar to that of the axial chlorine in $PCl_3(cat)$,[14] although the P–Cl bond length [23] of 2.031 Å is closer to that of the equatorial than the axial chlorines in molecular (phosphorus(v) chloride.[24]

Addition of $[N(n\text{-}C_5H_{11})_4]Cl$ to a solution of $PCl(cat)_2$ in $PhNO_2$ caused an upfield movement of the single ^{31}P resonance, from 52.9 p.p.m. for a mol ratio of $Cl^- : PCl(cat)_2$ of 1.03 : 1 to 66.1 p.p.m. for a mol ratio of 3.24 : 1. From the data a limiting shift of 66.3 p.p.m. for $[PCl_2(cat)_2]^-$ was extrapolated, with a probable error of <1 p.p.m. A 1 : 1 mixture appears to be *ca.* 74% associated, very similar to the degree of association of $[PPhCl_5]^-$ under comparable conditions.[6] The compound $PCl(cat)_2$ is thus a poorer acceptor than $PCl_3(cat)$, at least towards Cl^-. The chemical shift is low for a six-co-ordinate species, but may be compared with literature data for other six-co-ordinate phosphorus(v) compounds having two cat groups.[7,17] The compound was obtained as a solid by fusing the components at 413 K and then cooling rapidly. It gave a fairly broad ^{31}P resonance at 69.5 ± 2.5 p.p.m., in good agreement with the solution data. Unfortunately no ^{35}Cl n.q.r. signals were observable, which could have given valuable information on the stereochemistry of $[PCl_2(cat)_2]^-$ in the solid state. The i.r. spectrum between 650 and 350 cm^{-1} showed absorptions at 639s, 636s, 617w, 546(sh), 539s, 494s, 470s, and 426s cm^{-1}, considerably simplified with respect to the spectrum of $PCl(cat)_2$ in this region.

The acceptor properties of $PCl(cat)_2$ towards pyridine and 4-methylpyridine in chloroform as solvent have been described recently by Schmidpeter *et al.*[7] They found two ^{31}P n.m.r. signals for mol ratios of $py : PCl(cat)_2 \geqslant 0.5 : 1$. The first peak moved upfield and decreased in intensity with increasing py concentration, and was ascribed to $PCl(cat)_2{\cdot}py$ in rapid equilibrium with $PCl(cat)_2$. A shift of 84.5 p.p.m. for $PCl(cat)_2{\cdot}py$ was deduced. The second peak remained constant in shift at 100.0 p.p.m., but increased in intensity with the py concentration, and was attributed to the cationic species $[P(py)_2(cat)_2]^+$.[7] Our results in CH_2Cl_2 solution are very similar,[25] except that the molecular species remained in a higher concentration for a given excess of pyridine. At a mol ratio of $py : PCl(cat)_2$ of 3.1 : 1, for example, the ^{31}P signals were at 85.4 and 101.3 p.p.m., in an intensity ratio of *ca.* 4 : 7. The presence of one signal only for both the neutral and cationic species suggests either that one isomer is formed preferentially or that there is rapid exchange between the isomers. A *cis* configuration has been deduced for $[P(py)_2(cat)_2]^+$ in solution from ^1H n.m.r. studies.[7] This system provides the first clear example of pyridine being a strong enough ligand to displace a chloride ion from P^V when present in sufficiently high concentration, although this process may happen to a limited extent with $PCl_3(cat)$, as discussed earlier. Phosphorus(v) chloride forms only the 1 : 1 molecular adduct even when dissolved in neat pyridine, and no displacement of chloride occurs.[4]

The formation of the very stable complex $[P(bipy)(cat)_2]Cl{\cdot}0.5CHCl_3$, and of a number of other salts of this cation, has also been described by Schmidpeter *et al.*[7] The reaction is much slower than with pyridine, however. Phosphorus-31 n.m.r. shifts of 93.5 p.p.m. in $CHCl_3$ and 96.0 p.p.m. in water were obtained for the parent complex.[7] The reaction between $PCl(cat)_2$ and bipy in $PhNO_2$ appears to be more complicated.[25] Initially an equimolar mixture of the reagents in this solvent gave a single peak at 16.7 p.p.m., only slightly displaced from the position of $PCl(cat)_2$. After 4 d two signals were present at 52.0 and 95.4 p.p.m., in the intensity ratio *ca.* 43 : 100. The more intense signal is assigned to $P(bipy)(cat)_2]^+$, and the lower-field peak to the $PCl(cat)_2$–$[PCl_2(cat)_2]^-$ exchanging system established between unchanged $PCl(cat)_2$ and the chloride liberated on formation of the cation. The solution thus appears to contain a mixture of the 1 : 1 and 2 : 1 complexes, rather than the 1 : 1 species only. 1,10-Phenanthroline seemed to react much more slowly still; after 6 h a single peak was found at 14.9 p.p.m., and 6 d later the only change was a small upfield movement to 17.7 p.p.m.

The data are consistent with slow displacement of Cl^- by a bidentate pyridine. The small upfield shifts observed initially in both systems may indicate that reaction proceeds *via* very weak unidentate co-ordination to $PCl(cat)_2$ by the potentially bidentate pyridine L′, followed by slow release of chloride [reaction (4)]. This

$$\mathrm{PCl(cat)_2 + L'} \rightleftharpoons \underset{(\mathrm{L'}\ \text{unidentate})}{\mathrm{PCl(cat)_2{\cdot}L'}} \xrightarrow{\text{slow}} \underset{(\mathrm{L'}\ \text{bidentate})}{\mathrm{[PL'(cat)_2]^+}} + \mathrm{Cl^-} \qquad (4)$$

process would occur more readily for bipy, which is quite flexible, than for the very rigid phen, accounting

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[23] R. K. Brown and R. R. Holmes, *Inorg. Chem.*, 1977, **16**, 2294.

[24] W. J. Adams and L. S. Bartell, *J. Mol. Structure*, 1971, **8**, 23.

[25] R. N. Reeve, Ph.D. Thesis, Durham University, 1975.

satisfactorily for the difference in reaction rates. The complexes of bidentate pyridines with $[P(cat)_2]^+$ prepared directly from $[P(cat)_2][SbCl_6]$, where no chloride displacement is necessary, were formed immediately [section (iv)].

(*iv*) $[P(cat)_2][SbCl_6]$ *and its Acceptor Properties*.—The preparation and ready decomposition of this salt have been described in previous sections. The salt gave a narrow ^{31}P solid-state signal at −44.0 p.p.m., in agreement with a four-co-ordinate structure. A freshly prepared nitrobenzene solution gave a resonance at −42.4 p.p.m., in good agreement with the solid shift, although a small unassigned peak at 19.6 p.p.m. was also found. The solution rapidly turned black, and after 3 d showed signals at 0.3 and 37.2 p.p.m., possibly due to H_3PO_4 and $P(OH)(cat)_2$ hydrolysis products. Like $[PCl_2(cat)][SbCl_6]$, the solid turned yellow on addition of Nujol. It showed i.r. bands between 660 and 300 cm^{-1} at 657s, 597w, 528w, 468s, 416s and *ca.* 335s,br cm^{-1}, the last one assigned to $[SbCl_6]^-$. The spectrum differs considerably from that of $PCl(cat)_2$.

A 1 : 2 mixture of $[P(cat)_2][SbCl_6]$ and pyridine in $PhNO_2$ yielded a single ^{31}P n.m.r. signal at 101.7 p.p.m., readily assigned to the $[P(py)_2(cat)_2]^+$ ion.[7] The solution seemed quite stable, and gave a very similar result after 5 d although a brown tinge was apparent. A long spectrum accumulation revealed a very small peak at 83 p.p.m., presumably due to $PCl(cat)_2 \cdot py$, but the extent of any disproportionation is expected to be small in view of the results for $PCl(cat)_2$–py mixtures.

Equimolar mixtures of $[P(cat)_2][SbCl_6]$ with bipy and phen in $PhNO_2$ gave single peaks at 93.4 and 89.9 p.p.m. respectively, corresponding to the cationic complexes $[PL'(cat)_2]^+$. {A shift of 94.7 p.p.m. has been reported for $[P(bipy)(cat)_2][SbCl_6]$ in dimethylformamide.[7]} Unlike the reactions with $PCl(cat)_2$, there was thus no hindrance to formation of the phen complex. The solutions were also comparatively stable; they changed somewhat in colour and produced greenish precipitates over a period of weeks, but the only solution signals found were those for the cationic species, now at 96.0 (bipy) and 92.5 p.p.m. (phen). The complex $[P(phen)(cat)_2][SbCl_6]$ was isolated as a solid. It gave a broad ^{31}P solid-state resonance at 72 p.p.m., rather lower than the solution shift. Differences between solid-state and solution values have been observed in other systems.[26] The solid, originally orange, turned green over some weeks, but without changing its i.r. spectrum, which contained absorptions between 650 and 250 cm^{-1} at 645w, 638w, 612w, 576w, 545s, 514w, 499w, 476w, 456w, 446w, 429w, 400w, and 339s cm^{-1} ($[SbCl_6]^-$).

Attempts to co-ordinate other ligands to $[P(cat)_2]^+$ led to complex reactions. Addition of tetrahydrothiophene in $PhNO_2$ produced a peak at 10.7 p.p.m., assigned to $PCl(cat)_2$, and a black deposit from $SbCl_5 \cdot C_4H_8S$ or decomposition products thereof [reaction (5)]. A 2 : 1 mixture of triphenylphosphine and $[P(cat)_2][SbCl_6]$ in $PhNO_2$ gave signals of approximately equal intensity at −64.8 $(PPh_3Cl]^+)$,[3,16,19,27-29] 6.2 (PPh_3),[30] and 10.8 p.p.m. $[PCl(cat)_2]$, suggesting that $[SbCl_6]^-$ is reduced according to equation (6). This was supported by repeating the reaction with equimolar quantities of the reagents, when only two equally intense signals at −64.8 and 10.9 p.p.m. were present. In both instances $[P(cat)_2]^+$ reacts to increase its co-ordination number, but cationic complexes do not appear to be formed.

$$[P(cat)_2][SbCl_6] + C_4H_8S \longrightarrow PCl(cat)_2 + SbCl_5 \cdot C_4H_8S \quad (5)$$

$$2PPh_3 + [P(cat)_2][SbCl_6] \longrightarrow [PPh_3Cl]Cl + PCl(cat)_2 + SbCl_3 + PPh_3 \quad (6)$$

The overall results confirm that cat derivatives of phosphorus(V) chloride, particularly $PCl_3(cat)$, possess good acceptor properties towards suitable Lewis bases. Four-co-ordinate phosphorus(V) cations containing cat groups are extremely reactive because of their strained geometry, and increase their co-ordination numbers readily, although not always with the formation of ionic complexes.

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