

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

By Keith B. Dillon, Roger N. Reeve, and Thomas C. Waddington,\* Chemistry Department, University of Durham, South Road, Durham DH1 3LE

The acceptor properties of  $\text{PCl}_3(\text{cat})$  and  $\text{PCl}(\text{cat})_2$  ( $\text{cat} = \text{O}_2\text{C}_6\text{H}_4$ ) towards some Lewis bases have been investigated in solution by means of  $^{31}\text{P}$  n.m.r. spectroscopy. The compound  $\text{PCl}_3(\text{cat})$  is a better acceptor than  $\text{PCl}(\text{cat})_2$ , which is comparable with  $\text{PPhCl}_4$  studied previously. The cations  $[\text{PCl}_2(\text{cat})]^+$  and  $[\text{P}(\text{cat})_2]^+$  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  $^{31}\text{P}$  n.m.r. and/or  $^{35}\text{Cl}$  n.q.r. spectroscopy.

THE *o*-phenylenedioxy-derivatives of phosphorus(v) chloride,  $\text{PCl}_3(\text{O}_2\text{C}_6\text{H}_4)$  or  $\text{PCl}_3(\text{cat})$ , and  $\text{PCl}(\text{O}_2\text{C}_6\text{H}_4)_2$  or  $\text{PCl}(\text{cat})_2$ , were both first prepared by Anschütz and his co-workers in the 1920's,<sup>1,2</sup> but their Lewis-acid and Lewis-base behaviour has been little investigated. In previous papers we have described the acceptor properties of  $\text{PCl}_5$  towards the chloride ion<sup>3</sup> and pyridine bases,<sup>4</sup> of the tetrachlorophosphonium ion,<sup>5</sup> and of the phenyl-substituted derivatives  $\text{PPhCl}_4$  and  $[\text{PPhCl}_3]^+$ .<sup>6</sup> 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  $[\text{PCl}_2(\text{cat})]^+$  and  $[\text{P}(\text{cat})_2]^+$  have been prepared by reaction of antimony(v) chloride with  $\text{PCl}_3(\text{cat})$  and  $\text{PCl}(\text{cat})_2$  respectively. The presence of the bidentate aromatic groups was expected to impose certain geometrical constraints, particularly for four-co-ordinate species such as  $[\text{P}(\text{cat})_2]^+$ , as indeed was the case. No acceptor properties have been reported for  $\text{PCl}_3(\text{cat})$ , but in a very recent paper Schmidpeter *et al.*<sup>7</sup> have described the formation of both neutral 1:1 and cationic 1:2 complexes of  $\text{PCl}(\text{cat})_2$  and pyridine or 4-methylpyridine, formulated as  $\text{PCl}(\text{cat})_2\cdot\text{py}$  and  $[\text{P}(\text{py})_2(\text{cat})_2]\text{Cl}$  respectively. A 1:1 ionic complex of  $\text{PCl}(\text{cat})_2$  and 2,2'-bipyridyl, with the structure  $[\text{P}(\text{bipy})(\text{cat})_2]\text{Cl}$ , was also prepared.<sup>7</sup> 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  $^{31}\text{P}$  n.m.r. spectroscopy of some acceptor properties of  $\text{PCl}_3(\text{cat})$ ,  $[\text{PCl}_2(\text{cat})]^+$ ,  $\text{PCl}(\text{cat})_2$ , and  $[\text{P}(\text{cat})_2]^+$ . 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.<sup>4</sup> A commercial sample of  $\text{PCl}_3(\text{cat})$  and a sample prepared from  $\text{PCl}(\text{cat})$  as described in a previous publication<sup>8</sup> were used in the course of this work; the products gave identical  $^{31}\text{P}$  chemical shifts of 26.3 p.p.m. in  $\text{CH}_2\text{Cl}_2$  and 27.2 p.p.m. in  $\text{PhNO}_2$ , in good agreement with other determinations in various solvents.<sup>9-11</sup> The compound  $\text{PCl}(\text{cat})_2$  was prepared by the optimum method of Ramirez *et al.*<sup>11</sup> Its  $^{31}\text{P}$  n.m.r. spectrum showed signals at 10.0 p.p.m. in  $\text{CH}_2\text{Cl}_2$  and 10.5 p.p.m. in  $\text{PhNO}_2$ , as expected,<sup>10-12</sup> but weak resonances at 31.1 ( $\text{CH}_2\text{Cl}_2$ ) and 31.4 p.p.m. ( $\text{PhNO}_2$ ) were also found after spectrum accumulation. These were ascribed to the hydrolysis product  $\text{P}(\text{OH})(\text{cat})_2$  and compare with a shift of 31.8 p.p.m. for the authentic material in benzene solution.<sup>13</sup> 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.<sup>3-6</sup> Chemical shifts were measured with respect to external  $\text{P}_4\text{O}_6$ , but are quoted relative to 85%  $\text{H}_3\text{PO}_4$ , with the upfield direction taken as positive. Elemental analysis, i.r. spectra, and  $^{35}\text{Cl}$  n.q.r. spectra were also obtained as described previously.<sup>3-6</sup> 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 stoichiometric quantities of  $\text{PCl}_3(\text{cat})$  and the appropriate tetra-alkyl ammonium chloride, dissolved in the minimum quantity of the solvent shown in Table I. 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

<sup>1</sup> L. Anschütz, H. Boedecker, W. Broecker, and F. Wenizer, *Annalen*, 1927, **454**, 71.

<sup>2</sup> L. Anschütz, *Berichte*, 1926, **B59**, 2848.

<sup>3</sup> K. B. Dillon, R. J. Lynch, R. N. Reeve, and T. C. Waddington, *J. Inorg. Nuclear Chem.*, 1974, **36**, 815.

<sup>4</sup> K. B. Dillon, R. N. Reeve, and T. C. Waddington, *J.C.S. Dalton*, 1977, 1410.

<sup>5</sup> K. B. Dillon, R. N. Reeve, and T. C. Waddington, *J.C.S. Dalton*, 1977, 2382.

<sup>6</sup> K. B. Dillon, R. N. Reeve, and T. C. Waddington, *J.C.S. Dalton*, 1978, 1318.

<sup>7</sup> A. Schmidpeter, T. von Criegern, and K. Blanck, *Z. Naturforsch.*, 1976, **B31**, 1058.

<sup>8</sup> K. B. Dillon, R. N. Reeve, and T. C. Waddington, *J. Inorg. Nuclear Chem.*, 1976, **38**, 1439.

<sup>9</sup> R. A. Y. Jones and A. R. Katritzky, *Angew. Chem.*, 1962, **74**, 60.

<sup>10</sup> E. Fluck, H. Gross, H. Binder, and J. Gloede, *Z. Naturforsch.*, 1966, **B21**, 1125.

<sup>11</sup> F. Ramirez, A. J. Bigler, and C. P. Smith, *Tetrahedron*, 1968, **24**, 5041.

<sup>12</sup> H. Binder, *Z. anorg. Chem.*, 1971, **384**, 193.

<sup>13</sup> K. B. Dillon and M. P. Nisbet, unpublished work.

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  $[\text{PPhCl}_3][\text{PCl}_4(\text{cat})]$  was similarly prepared from  $\text{PPhCl}_4$  and  $\text{PCl}_3(\text{cat})$  (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  $\text{PCl}_3(\text{cat})$  (1 : 2) were dissolved together in the minimum quantity of  $\text{CH}_2\text{Cl}_2$ . 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.

both in solution and in the solid, and could be handled without difficulty.

An attempt was made to prepare  $[\text{PCl}_2(\text{cat})][\text{BCl}_4]$  by reaction of excess of  $\text{BCl}_3$  with  $\text{PCl}_3(\text{cat})$  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  $\text{PCl}_3(\text{cat})$ .

**2,2'-Bipyridyldichloro(o-phenylenedioxy)phosphonium Hexachloroantimonate(v)-Nitrobenzene (4/3).**—This complex was obtained by adding a solution of the stoichiometric quantity of bipy in  $\text{PhNO}_2$  to solid  $[\text{PCl}_2(\text{cat})][\text{SbCl}_6]$ . A very exothermic reaction occurred and there was an immediate yellow colouration. A little more  $\text{PhNO}_2$  was added and the mixture stirred for a few minutes. Originally the

TABLE 1  
Analytical data for some o-phenylenedioxy-derivatives of phosphorus(v) chloride

Complex	Solvent	Analysis (%)									
		Found					Calc.				
		C	H	N	P	Cl	C	H	N	P	Cl
$[\text{N}(\text{C}_5\text{H}_{11})_4][\text{PCl}_4(\text{cat})]$	$\text{CCl}_4$	53.6	7.85	3.25	5.75	24.8	53.9	8.35	2.40	5.35	24.45
$[\text{N}(\text{C}_5\text{H}_9)_4][\text{PCl}_4(\text{cat})]$	$\text{CH}_2\text{Cl}_2$	47.1	6.80	3.05	6.55	29.75	46.25	6.90	3.00	6.65	30.35
$[\text{PPhCl}_3][\text{PCl}_4(\text{cat})]$	$\text{CH}_2\text{Cl}_2$	27.95	1.85		11.65	51.5	29.1	1.85		12.5	50.1
$[\text{PCl}_2(\text{bipy})(\text{cat})][\text{PCl}_4(\text{cat})]$	$\text{CH}_2\text{Cl}_2$	41.0	3.35	4.35	9.10	33.85	40.85	2.50	4.35	9.55	32.9
$[\text{PCl}_2(\text{bipy})(\text{cat})][\text{PCl}_4(\text{cat})]\cdot\text{PhNO}_2$	$\text{PhNO}_2$	43.9	4.00	5.35	8.30	29.3	43.65	2.75	5.45	8.05	27.6
$[\text{PCl}_2(\text{phen})(\text{cat})][\text{PCl}_4(\text{cat})]$	$\text{CH}_2\text{Cl}_2$	42.3	2.20	4.25	9.05	31.8	42.95	2.40	4.15	9.25	31.7
$[\text{PCl}_2(\text{cat})][\text{SbCl}_6]$	$\text{CH}_2\text{Cl}_2$	*	*		6.50	52.35	13.25	0.75		5.70	52.1
$[\text{PCl}_2(\text{bipy})(\text{cat})][\text{SbCl}_6]\cdot 0.75\text{PhNO}_2$	$\text{PhNO}_2$	30.05	2.40	4.60	4.10	34.6	31.05	2.00	4.85	3.90	35.75
$[\text{N}(\text{C}_5\text{H}_{11})_4][\text{PCl}_2(\text{cat})_2]$	None	61.65	8.05	2.35	5.00	11.7	62.35	8.50	2.25	5.00	11.5
$[\text{P}(\text{cat})_2][\text{SbCl}_6]$	$\text{CH}_2\text{Cl}_2$	*	*		5.30	36.8	24.8	1.40		5.35	36.55
$[\text{P}(\text{phen})(\text{cat})_2][\text{SbCl}_6]$	$\text{PhNO}_2$	37.4	2.30	4.05	3.50	27.5	37.85	2.10	3.70	4.05	27.9

\* See text.

$[\text{PCl}_2(\text{bipy})(\text{cat})][\text{PCl}_4(\text{cat})]\cdot\text{PhNO}_2$ .—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  $\text{PCl}_3(\text{cat})$  and 1,10-phenanthroline (2 : 1) were dissolved separately in  $\text{CH}_2\text{Cl}_2$ . 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 stoichiometric quantity of antimony(v) chloride to a solution of  $\text{PCl}_3(\text{cat})$  in  $\text{CH}_2\text{Cl}_2$ , 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  $[\text{P}(\text{cat})_2][\text{SbCl}_6]$ , since they would involve the use of metal capsules. All the reactions involving  $[\text{PCl}_2(\text{cat})][\text{SbCl}_6]$  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  $[\text{PCl}_2(\text{cat})][\text{SbCl}_6]$  had time to decompose. The reasons for this behaviour are discussed later; the adducts formed by co-ordination were much more stable

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  $\text{PCl}(\text{cat})_2$  and  $[\text{N}(\text{n-C}_5\text{H}_{11})_4]\text{Cl}$  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  $\text{CH}_2\text{Cl}_2$  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  $\text{PCl}(\text{cat})_2$  and  $\text{SbCl}_5$  in the minimum quantity of  $\text{CH}_2\text{Cl}_2$ , 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  $[\text{PCl}_2(\text{cat})][\text{SbCl}_6]$ , 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  $\text{PhNO}_2$ ,

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,<sup>9-11</sup> are in agreement with a five-coordinate 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,<sup>14</sup> 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,<sup>15,16</sup> and shows weak acceptor properties towards chloride ion and pyridine bases.<sup>6</sup>

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

TABLE 2

Phosphorus-31 n.m.r. data for  $[N(n-C_5H_{11})_4]Cl-PCl_3(cat)$  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.<sup>6</sup> 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  $[N(n-C_5H_{11})_4][PCl_4(cat)]$ . The solid complex was subsequently isolated and showed a narrow  $^{31}P$  solid-state resonance at  $162 \pm 2$  p.p.m., in good agreement with the solution data. The shift is intermediate between those of  $[PPhCl_5]^-$  (ref. 6) and  $[P(cat)_3]^-$ ,<sup>17</sup> 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.<sup>6,18</sup>) 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

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

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,<sup>3,4,6</sup> and is ascribed to a reduction in the P-Cl bond strength. Between 1600 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.

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  $-101.6$  ( $[PPhCl_3]^+$ )<sup>16,19</sup> and  $163 \pm 5.5$  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,<sup>16</sup> 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

<sup>14</sup> R. M. Hart and M. A. Whitehead, *J. Chem. Soc. (A)*, 1971, 1738.

<sup>15</sup> V. I. Svergun, V. G. Rozinov, E. F. Grechkin, V. G. Timokhin, Yu. K. Maksyumin, and G. K. Semin, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1970, 1918.

<sup>16</sup> K. B. Dillon, R. J. Lynch, R. N. Reeve, and T. C. Waddington, *J.C.S. Dalton*, 1976, 1243.

<sup>17</sup> D. Hellwinkel and H.-J. Wilfinger, *Chem. Ber.*, 1970, 103, 1056.

<sup>18</sup> E. R. Andrew, 'Nuclear Magnetic Resonance,' Cambridge University Press, Cambridge, 1958.

<sup>19</sup> A. Schmidpeter and H. Brecht, *Angew. Chem.*, 1967, 79, 535.



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  $\text{PCl}_3(\text{cat})$  was increased (Table 4), while the two peaks

TABLE 4

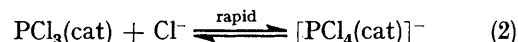
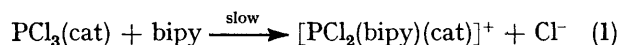
Phosphorus-31 n.m.r. shifts (p.p.m.) for  $\text{PCl}_3(\text{cat})$ -py mixtures in  $\text{PhNO}_2$

Ratio py : $\text{PCl}_3(\text{cat})$	$\delta(^{31}\text{P})/\text{p.p.m.}$			Relative intensity 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

at higher field did not vary greatly. The pseudo-octahedral molecular complex  $\text{PCl}_3(\text{cat})\cdot\text{py}$  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  $^{31}\text{P}$  n.m.r. spectroscopy in favourable circumstances, as shown previously for  $[\text{PPhCl}_3(\text{phen})]^+$ .<sup>6</sup> 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  $\text{PCl}_3(\text{cat})$  complexes than for their  $\text{PPhCl}_4$  analogues. The signal at lowest field appears to be more favoured by higher relative concentrations of pyridine, and is assigned to the cationic species  $[\text{PCl}_2(\text{py})_2(\text{cat})]^+$ , formed by displacement of chlorine by pyridine from the neutral adduct. This is supported by the  $^{31}\text{P}$  shift for  $[\text{PCl}_2(\text{py})_2(\text{cat})]^-[\text{SbCl}_6]$ , 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.

An equimolar mixture of 2,2'-bipyridyl and  $\text{PCl}_3(\text{cat})$  in  $\text{PhNO}_2$  showed two strong  $^{31}\text{P}$  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  $\text{CH}_2\text{Cl}_2$  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  $\text{PCl}_3(\text{cat})$  : bipy mixture in  $\text{CH}_2\text{Cl}_2$  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  $[\text{PCl}_2(\text{bipy})(\text{cat})]^+$  and the variable

peak to the  $\text{PCl}_3(\text{cat})$ - $[\text{PCl}_4(\text{cat})]^-$  equilibrium described previously. The reaction is readily explained by equations (1) and (2). Since  $\text{PCl}_3(\text{cat})$  and  $[\text{PCl}_4(\text{cat})]^-$



exchange rapidly on the n.m.r. time scale the upfield peak moves to higher field as the proportion of  $[\text{PCl}_4(\text{cat})]^-$  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  $\text{PCl}_3(\text{cat}) + [\text{PCl}_4(\text{cat})]^-$ . The limiting value for the intensities in a 2 : 1  $\text{PCl}_3(\text{cat})$  : bipy mixture will be 1 : 1, corresponding to complete formation of  $[\text{PCl}_2(\text{bipy})(\text{cat})][\text{PCl}_4(\text{cat})]$ , 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  $\text{CH}_2\text{Cl}_2$ .

There are two possible geometrical isomers for the cationic complex, with *cis* and *trans* chlorines respectively, but only one cation resonance was observed in  $\text{CH}_2\text{Cl}_2$  solution. During one experiment in  $\text{PhNO}_2$ , 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  $[\text{PCl}_2(\text{bipy})(\text{cat})][\text{PCl}_4(\text{cat})]$  was isolated from  $\text{CH}_2\text{Cl}_2$  solution, whereas  $\text{PhNO}_2$  solutions yielded the nitrobenzene solvate.

The i.r. spectra of the products were very similar, containing absorptions assignable to both  $[\text{PCl}_2(\text{bipy})(\text{cat})]^+$  and  $[\text{PCl}_4(\text{cat})]^-$ , except for additional bands at 1531s, 1348s, and 398w  $\text{cm}^{-1}$  from the solvate, due to  $\text{PhNO}_2$ .<sup>20</sup> The absorptions between 650 and 300  $\text{cm}^{-1}$  are listed in Table 5. The solid-state  $^{31}\text{P}$  n.m.r. spec-

TABLE 5

Infrared bands ( $\text{cm}^{-1}$ ) for bipy complexes of  $\text{PCl}_3(\text{cat})$  between 650 and 300  $\text{cm}^{-1}$

Complex	
$[\text{PCl}_2(\text{bipy})(\text{cat})][\text{PCl}_4(\text{cat})]$	624m, 542 (sh), 536 (sh), 526s, 517s, 504s, 474s, 458m, 450m, 424s, 383m, 363m, 302w
$[\text{PCl}_2(\text{bipy})(\text{cat})][\text{PCl}_4(\text{cat})]\cdot\text{PhNO}_2$	647w, 626s, 602w, 547s, 537 (sh), 524s,br, 503m, 474s, 465s, 460s, 448m, 423s, 398w,* 383m, 360 (sh), 352 (sh), 303w

\*  $\text{PhNO}_2$ .

trum of  $[\text{PCl}_2(\text{bipy})(\text{cat})][\text{PCl}_4(\text{cat})]\cdot\text{PhNO}_2$  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 line-widths. The value compares well with the average solution shift for the two species of 138 p.p.m.

An equimolar mixture of  $\text{PCl}_3(\text{cat})$  and 1,10-phenan-

<sup>20</sup> J. H. S. Green, W. Kynaston, and A. S. Lindsay, *Spectrochim. Acta*, 1961, **17**, 486.

throline in  $\text{PhNO}_2$  showed only one peak initially, due to the cation  $[\delta(^{31}\text{P})\ 118.8\ \text{p.p.m.}]$ , but the 2 : 1 complex  $[\text{PCl}_2(\text{phen})(\text{cat})][\text{PCl}_4(\text{cat})]$  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  $\{[\text{PCl}_2(\text{phen})(\text{cat})]^+\}$ , 129.9, 157.2  $\{[\text{PCl}_4(\text{cat})]^-$ , 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  $[\text{PCl}_4(\text{phen})]^+$ ,<sup>4,5</sup> produced either from  $\text{PCl}_5$  impurity in commercial  $\text{PCl}_3(\text{cat})$  or by disproportionation of  $[\text{PCl}_2(\text{phen})(\text{cat})]^+$ .

The solid complex  $[\text{PCl}_2(\text{phen})(\text{cat})][\text{PCl}_4(\text{cat})]$  was isolated from  $\text{CH}_2\text{Cl}_2$  solution. Its i.r. spectrum between 650 and 250  $\text{cm}^{-1}$  contained absorptions at 634m, 621s, 613w, 596w, 570(sh), 568m, 547s, 513s, 492s, 478s, 468m, 456m, 447s, 438s, 426s, 376m, 358w, 343w, and 298w  $\text{cm}^{-1}$ . With this complex the frequencies for  $[\text{PCl}_4(\text{cat})]^-$  appear to be slightly displaced from the values found for other salts. The solid-state  $^{31}\text{P}$  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  $^{35}\text{Cl}$  n.q.r. studies.

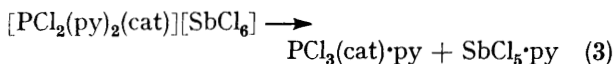
In view of the good acceptor characteristics of  $\text{PCl}_3(\text{cat})$  and its ready solubility in a range of organic solvents,<sup>11</sup> some other liquid potential donors were tried, to see whether any change in chemical shift would be produced. In order to distinguish solvent effects from 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  $\text{PCl}_3(\text{cat})$  itself in a variety of non-co-ordinating solvents lies between 25 and 28 p.p.m.,<sup>9-11</sup> 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,<sup>21</sup> and also suggested by the preferential co-ordination of  $\text{PMe}_3$  rather than  $\text{NMe}_3$  by  $\text{PF}_5$ .<sup>22</sup> Although  $\text{PV}$  was not included in Ahrlund's table of class b acceptors,<sup>21</sup> no experimental evidence in favour of its exclusion was presented.

(ii)  $[\text{PCl}_2(\text{cat})][\text{SbCl}_6]$  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  $[\text{PCl}_4]^+$ , and the even greater sensitivity to moisture or other nucleophiles of  $[\text{P}(\text{cat})_2]^+$ . The salt showed a single sharp  $^{31}\text{P}$  n.m.r. resonance in the solid state at  $-71.7\ \text{p.p.m.}$ , fully in agreement with a four-co-ordinate structure. It dissolved in  $\text{PhNO}_2$  to yield a signal at  $-77.1\ \text{p.p.m.}$ , but the solution was unstable, presumably because of slow reaction with the solvent. Trichlorophosphine oxide formed a more stable solution  $\{ \delta(^{31}\text{P}) -77.8\ \text{p.p.m. for } [\text{PCl}_2(\text{cat})]^+ \}$ , but this turned purple over a period of days. After 2 weeks, equally intense signals were found at  $-77.0$  and  $-66.3\ \text{p.p.m.}$ , the identity of the latter being unknown.

The solid at 77 K showed  $^{35}\text{Cl}$  n.q.r. lines at 31.725 and 30.047 MHz due to  $[\text{PCl}_2(\text{cat})]^+$ , and at 25.36, 24.425, 24.20, and 24.07 MHz due to  $[\text{SbCl}_6]^-$ . The separation of the cation signals is larger than expected for crystallographic effects in phosphorus(v) chloro-compounds of possible  $\text{C}_{2v}$  symmetry.<sup>16</sup> The highest frequency line attributable to  $[\text{SbCl}_6]^-$  is also higher than usually found,<sup>16</sup> 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  $\text{cm}^{-1}$  were found at 636s, 593w, 566m, 423s, 417w, 397w, *ca.* 360sh, and *ca.* 330s,br  $\text{cm}^{-1}$ . The strong broad band at *ca.* 330  $\text{cm}^{-1}$  is attributable to  $[\text{SbCl}_6]^-$ , while the strong absorption at 636  $\text{cm}^{-1}$  is assigned to a P-Cl stretch from the cation, and lies at higher frequency than the P-Cl bands of  $\text{PCl}_3(\text{cat})$ , as expected.

A  $\text{PhNO}_2$  solution containing  $[\text{PCl}_2(\text{cat})][\text{SbCl}_6]$  and pyridine in a 1 : 2 mol ratio gave a single  $^{31}\text{P}$  n.m.r. peak at 124.8 p.p.m., assigned to  $[\text{PCl}_2(\text{py})_2(\text{cat})]^+$ . 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)



similar to the rapid disproportionation observed with  $[\text{PCl}_4(\text{py})_2]^+$  species.<sup>5</sup>

The isolation of a nitrobenzene solvate on addition of  $[\text{PCl}_2(\text{cat})][\text{SbCl}_6]$  to a  $\text{PhNO}_2$  solution of bipy has been described. The second sample had i.r. absorptions at 1531(sh) and 1347s  $\text{cm}^{-1}$  due to  $\text{PhNO}_2$ .<sup>20</sup> Between 650 and 250  $\text{cm}^{-1}$  bands were apparent at 627m, 543m, 532w, 509s, 457m, 452m, 420s, 383m, and 342s,br  $\text{cm}^{-1}$ , the last of these due to  $[\text{SbCl}_6]^-$ . Many of the lines are in similar positions to absorptions in the spectrum of

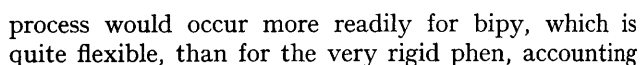
<sup>21</sup> S. Ahrlund, *Structure and Bonding*, 1966, **1**, 207.

<sup>22</sup> C. W. Schultz and R. W. Rudolph, *J. Amer. Chem. Soc.*, 1971, **93**, 1898.



The acceptor properties of  $\text{PCl}(\text{cat})_2$  towards pyridine and 4-methylpyridine in chloroform as solvent have been described recently by Schmidpeter *et al.*<sup>7</sup> They found two  $^{31}\text{P}$  n.m.r. signals for mol ratios of  $\text{py} : \text{PCl}(\text{cat})_2 \geq 0.5 : 1$ . The first peak moved upfield and decreased in intensity with increasing py concentration, and was ascribed to  $\text{PCl}(\text{cat})_2 \cdot \text{py}$  in rapid equilibrium with

The data are consistent with slow displacement of  $\text{Cl}^-$  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  $\text{PCl}(\text{cat})_2$  by the potentially bidentate pyridine  $\text{L}'$ , followed by slow release of chloride [reaction (4)]. This



<sup>25</sup> R. N. Reeve, Ph.D. Thesis, Durham University, 1975.

satisfactorily for the difference in reaction rates. The complexes of bidentate pyridines with  $[\text{P}(\text{cat})_2]^+$  prepared directly from  $[\text{P}(\text{cat})_2][\text{SbCl}_6]$ , where no chloride displacement is necessary, were formed immediately [section (iv)].

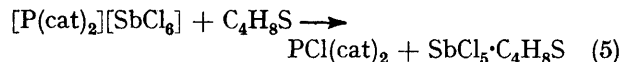
(iv)  $[\text{P}(\text{cat})_2][\text{SbCl}_6]$  and its Acceptor Properties.—The preparation and ready decomposition of this salt have been described in previous sections. The salt gave a narrow  $^{31}\text{P}$  solid-state signal at  $-44.0$  p.p.m., in agreement with a four-co-ordinate structure. 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  $\text{H}_3\text{PO}_4$  and  $\text{P}(\text{OH})(\text{cat})_2$  hydrolysis products. Like  $[\text{PCl}_2(\text{cat})][\text{SbCl}_6]$ , the solid turned yellow on addition of Nujol. It showed i.r. bands between  $660$  and  $300\text{ cm}^{-1}$  at  $657\text{s}$ ,  $597\text{w}$ ,  $528\text{w}$ ,  $468\text{s}$ ,  $416\text{s}$  and *ca.*  $335\text{s}$ ,  $\text{br cm}^{-1}$ , the last one assigned to  $[\text{SbCl}_6]^-$ . The spectrum differs considerably from that of  $\text{PCl}(\text{cat})_2$ .

A 1 : 2 mixture of  $[\text{P}(\text{cat})_2][\text{SbCl}_6]$  and pyridine in  $\text{PhNO}_2$  yielded a single  $^{31}\text{P}$  n.m.r. signal at  $101.7$  p.p.m., readily assigned to the  $[\text{P}(\text{py})_2(\text{cat})_2]^+$  ion.<sup>7</sup> 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  $\text{PCl}(\text{cat})_2\cdot\text{py}$ , but the extent of any disproportionation is expected to be small in view of the results for  $\text{PCl}(\text{cat})_2\text{-py}$  mixtures.

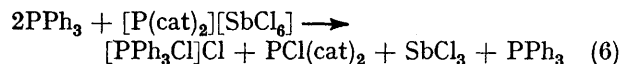
Equimolar mixtures of  $[\text{P}(\text{cat})_2][\text{SbCl}_6]$  with bipy and phen in  $\text{PhNO}_2$  gave single peaks at  $93.4$  and  $89.9$  p.p.m. respectively, corresponding to the cationic complexes  $[\text{PL}'(\text{cat})_2]^+$ . {A shift of  $94.7$  p.p.m. has been reported for  $[\text{P}(\text{bipy})(\text{cat})_2][\text{SbCl}_6]$  in dimethylformamide.<sup>7</sup>} Unlike the reactions with  $\text{PCl}(\text{cat})_2$ , 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  $[\text{P}(\text{phen})(\text{cat})_2][\text{SbCl}_6]$  was isolated as a solid. It gave a broad

$^{31}\text{P}$  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.<sup>26</sup> The solid, originally orange, turned green over some weeks, but without changing its i.r. spectrum, which contained absorptions between  $650$  and  $250\text{ cm}^{-1}$  at  $645\text{w}$ ,  $638\text{w}$ ,  $612\text{w}$ ,  $576\text{w}$ ,  $545\text{s}$ ,  $514\text{w}$ ,  $499\text{w}$ ,  $476\text{w}$ ,  $456\text{w}$ ,  $446\text{w}$ ,  $429\text{w}$ ,  $400\text{w}$ , and  $339\text{s cm}^{-1}$  ( $[\text{SbCl}_6]^-$ ).

Attempts to co-ordinate other ligands to  $[\text{P}(\text{cat})_2]^+$  led to complex reactions. Addition of tetrahydrothiophene in  $\text{PhNO}_2$  produced a peak at  $10.7$  p.p.m., assigned to  $\text{PCl}(\text{cat})_2$ , and a black deposit from  $\text{SbCl}_5\cdot\text{C}_4\text{H}_8\text{S}$  or decomposition products thereof [reaction (5)]. A 2 : 1



mixture of triphenylphosphine and  $[\text{P}(\text{cat})_2][\text{SbCl}_6]$  in  $\text{PhNO}_2$  gave signals of approximately equal intensity at  $-64.8$  ( $\text{PPh}_3\text{Cl}^+$ ),<sup>3, 16, 19, 27-29</sup>  $6.2$  ( $\text{PPh}_3$ ),<sup>30</sup> and  $10.8$  p.p.m.  $[\text{PCl}(\text{cat})_2]$ , suggesting that  $[\text{SbCl}_6]^-$  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  $[\text{P}(\text{cat})_2]^+$  reacts to increase its co-ordination number, but cationic complexes do not appear to be formed.

The overall results confirm that cat derivatives of phosphorus(v) chloride, particularly  $\text{PCl}_3(\text{cat})$ , 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.

We thank Dr. R. J. Lynch for recording the  $^{35}\text{Cl}$  n.q.r. spectra and for helpful discussions, R. Coult for some microanalyses, and the S.R.C. for the award of a maintenance grant (to R. N. R.).

[7/2243 Received, 21st December, 1977]

<sup>26</sup> K. B. Dillon and T. C. Waddington, *Spectrochim. Acta*, 1971, **A27**, 1381.

<sup>27</sup> G. A. Wiley and W. R. Stine, *Tetrahedron Letters*, 1967, 2321.

<sup>28</sup> H. P. Latscha, *Z. Naturforsch.*, 1968, **B23**, 139.

<sup>29</sup> D. B. Denney, D. Z. Denney, and B. C. Chang, *J. Amer. Chem. Soc.*, 1968, **90**, 6332.

<sup>30</sup> V. Mark, C. H. Dungan, M. M. Crutchfield, and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 227.