The Acceptor Properties of some Pentafluorophenylphosphorus(v) Species

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The acceptor properties of $P(C_6F_5)_nCl_{5-n}$ ($1 \leqslant n \leqslant 3$), $[P(C_6F_5)_nCl_{4-n}]^+$ ($1 \leqslant n \leqslant 3$), and $[P(C_6F_5)Br_3]^+$ towards Lewis bases, such as the chloride ion and uni- and bi-dentate pyridines, have been investigated. Several new complexes have been isolated, and characterised by elemental analysis and (in some cases) ^{31}P n.m.r. and/or i.r. spectroscopy.

In previous publications from this group the acceptor properties of various organophosphorus(v) species towards Lewis bases, such as the chloride ion and uni- and bi-dentate pyridines, have been described.[1-4] In general the introduction of organo-groups diminishes the acceptor ability compared with that of PCl_5[5] or $[PCl_4]^+$,[6] and no Lewis-acid properties were found for PR_2Cl_3 or $[PR_2Cl_2]^+$, where R = Me,[3] Et,[3] or Ph,[7] although $PRCl_4$ and $[PRCl_3]^+$ did show such properties.[1,3] No investigations have been reported, however, of the acceptor properties of organophosphorus(v) chloro- or bromo-derivatives with very electronegative organic substituents. The presence of such substituents might be expected to reinforce to some extent the Lewis-acid ability of the phosphorus atom, since a reduction in the electron density around phosphorus should make it more positive and a better acceptor. We have therefore carried out a systematic study of the acceptor properties of the pentafluorophenylphosphorus(v) species $P(C_6F_5)_nCl_{5-n}$ ($1 \leqslant n \leqslant 3$), $[P(C_6F_5)_nCl_{4-n}]^+$ ($1 \leqslant n \leqslant 3$), and $[P(C_6F_5)Br_3]^+$ towards Lewis bases, such as chloride ions [for $P(C_6F_5)_nCl_{5-n}$] and uni- and bi-dentate pyridines. Several new complexes have been isolated, and characterised by elemental analysis and (in some cases) ^{31}P n.m.r. and/or i.r. spectroscopy.

Experimental

All manipulations including n.m.r. sample preparation were carried out either under an inert atmosphere of dry nitrogen or *in vacuo*. Chemicals of the best available commercial grade were used, in general without further purification except for tetraalkylammonium chlorides which were dried as described previously,[8] and chlorine which was dried by passing it through a column of phosphorus pentoxide. Solvents were degassed on the vacuum line to remove any oxygen present, and stored over molecular sieves. The preparations of $P(C_6F_5)Cl_2$,[9] $P(C_6F_5)Br_2$,[9] and $P(C_6F_5)_2Cl$[10] have been described in earlier papers; $P(C_6F_5)_3$ was similarly prepared from a 3:1 reaction between $Mg(C_6F_5)Br$ and PBr_3, and was isolated as a white solid above 378 K at 0.5 mmHg (*ca.* 67 Pa). It was necessary to heat the condenser with a hair-dryer to transfer the solid to the receiving flask. The compound was purified by extracting it with low-boiling light petroleum to remove any $P(C_6F_5)_2Br$, leaving the desired phosphine [$\delta(^{31}P)$ −75.5 p.p.m. (CH_2Cl_2); lit.,[11] −75.5 p.p.m. (C_6H_6)]. The phosphoranes $P(C_6F_5)_nCl_{5-n}$ ($1 \leqslant n \leqslant 3$) were obtained by chlorination of the appropriate phosphine with dry Cl_2 gas, and $P(C_6F_5)Br_4$, which had not been reported previously, was prepared by adding a slight excess of Br_2 dropwise to a solution of $P(C_6F_5)Br_2$ in CH_2Cl_2, with constant stirring. The suspension was allowed to stir for 30 min, and the solid product was isolated, washed with CH_2Cl_2, and dried *in vacuo*, to yield a fine orange solid. Elemental analyses for this and other new compounds are given in Table 1.

The hexachloroantimonates $[P(C_6F_5)_nCl_{4-n}]^+SbCl_6^-$ were prepared by 1:1 reactions between the phosphoranes $P(C_6F_5)_nCl_{5-n}$ and $SbCl_5$ in CH_2Cl_2. The mixtures were allowed to stir for 10—15 min to complete the reaction, and the solid products were filtered off, washed with CH_2Cl_2, and dried if necessary *in vacuo*. Tetrachloroborates were similarly prepared; a two-necked flask containing a solution of the phosphorane in CH_2Cl_2 was connected to a Schlenk tube containing BCl_3 under reduced pressure, and gaseous BCl_3 was allowed to flow into the solution, with constant stirring, until a white solid formed. The solvent and excess of BCl_3 were removed *in vacuo*, and the product was washed with low-boiling (303—313 K) light petroleum. Tetrachloroiodates were obtained as yellow solids from 1:1 reactions of the phosphorane with ICl_3 in CH_2Cl_2. The products were isolated in a similar manner. The salt $[P(C_6F_5)Br_3][BBr_4]$ was synthesised by adding BBr_3 dropwise to an equimolar quantity of $P(C_6F_5)Br_4$ dispersed as a slurry in CH_2Cl_2. The mixture was allowed to stir for 20 min and the solvent was then removed *in vacuo*. The product was washed with light petroleum.

$[NPr^n_4][P(C_6F_5)Cl_5]$.—This compound was prepared by a 1:1 reaction between $P(C_6F_5)Cl_4$ and dry NPr^n_4Cl. The phosphorane was dissolved in a small quantity of dry CH_2Cl_2, and a solution of the chloride in the same solvent was added, with constant stirring. This was continued for 10 min and the solvent was then evaporated. The salt was dried *in vacuo*. It could not be washed with low-boiling light petroleum since this caused dissociation back to the original components. Attempts to prepare the analogous tetraethylammonium salt in a pure state were unsuccessful, the product consisting of a mixture of NEt_4Cl and $[NEt_4][P(C_6F_5)Cl_5]$.

$[P(C_6F_5)Cl_3(phen)][SbCl_6]$.—A solution of 1,10-phenanthroline(phen) in CH_2Cl_2 was added to a slurry of an equimolar amount of $[P(C_6F_5)Cl_3][SbCl_6]$ in the same solvent, with constant stirring. The solid dissolved as the ligand was added, and after a few minutes of stirring a precipitate formed. The solid was filtered off and washed with light petroleum.

$[P(C_6F_5)Cl_3(phen)][BCl_4]$.—This compound was prepared in a similar manner to the hexachloroantimonate. It was isolated by evaporation of the solvent *in vacuo*.

$[P(C_6F_5)Cl_3(bipy)][SbCl_6]$.—Equimolar amounts of $P(C_6F_5)Cl_4$ and 2,2′-bipyridine(bipy) were dissolved separately in CH_2Cl_2, and the solutions were mixed. An equimolar quantity of $SbCl_5$ was added dropwise to this mixture, which was allowed to stir for some minutes. The precipitate which formed was isolated and purified as above.

$[P(C_6F_5)Cl_3(bipy)][BCl_4]$.—The first stage was as in the

Table 1. Elemental analyses of new compounds

	Found (%)						Calc. (%)					
Compound	C	H	N	P	Cl or Br	I, Sb, or B	C	H	N	P	Cl or Br	I, Sb, or B
$[P(C_6F_5)Cl_3][SbCl_6]$	12.4	—	—	4.5	49.0	20.2	11.3	—	—	4.8	49.9	19.1
$[P(C_6F_5)Cl_3][BCl_4]$	16.7	—	—	6.3	54.2	2.1	15.8	—	—	6.8	54.3	2.4
$[P(C_6F_5)Cl_3][ICl_4]$	13.9	—	—	4.9	43.4	22.6	12.6	—	—	5.4	43.3	22.1
$[P(C_6F_5)_2Cl_2][SbCl_6]$	18.7	—	—	4.2	35.6	15.4	18.7	—	—	4.0	36.8	15.8
$[P(C_6F_5)_2Cl_2][BCl_4]$	25.5	—	—	5.6	36.3	1.9	24.5	—	—	5.3	36.1	1.8
$[P(C_6F_5)_2Cl_2][ICl_4]$	20.3	—	—	4.1	29.7	18.8	20.5	—	—	4.4	30.2	18.0
$[P(C_6F_5)_3Cl][SbCl_6]$	24.4	—	—	3.0	26.4	12.7	24.0	—	—	3.4	27.5	13.5
$[P(C_6F_5)_3Cl][BCl_4]$	31.1	—	—	3.2	24.1	2.1	30.0	—	—	4.3	24.6	1.5
$[P(C_6F_5)_3Cl][ICl_4]$	26.4	—	—	3.6	22.8	15.3	25.9	—	—	3.7	21.2	15.2
$P(C_6F_5)Br_4$	13.4	—	—	5.9	61.7	—	13.9	—	—	6.0	61.7	—
$[P(C_6F_5)Br_3][BBr_4]$	10.2	—	—	4.3	69.5	1.7	9.4	—	—	4.0	72.8	1.4
$[NPr_4][P(C_6F_5)Cl_5]$	39.6	5.9	1.7	5.2	32.1	—	38.5	5.0	2.5	5.5	31.6	—
$P(C_6F_5)Cl_4{\cdot}py$ *	32.0	1.4	3.3	4.9	28.1	—	31.5	1.2	3.3	7.4	33.8	—
$[P(C_6F_5)Cl_3(phen)][SbCl_6]$	26.7	0.9	2.0	3.2	34.4	15.1	26.4	1.0	3.4	3.8	39.0	14.9
$[P(C_6F_5)Cl_3(phen)][BCl_4]$	33.1	1.5	4.4	4.4	38.6	1.6	33.9	1.3	4.4	4.9	38.9	1.7
$[P(C_6F_5)Cl_3(bipy)][SbCl_6]$	22.4	0.9	1.1	4.5	40.0	15.7	24.2	1.0	3.5	3.9	40.1	15.3
$[P(C_6F_5)Cl_3(bipy)][BCl_4]$	31.7	1.4	2.5	5.5	38.1	1.9	31.3	1.3	4.6	5.1	40.5	1.8
$[P(C_6F_5)_2Cl_2(phen)][SbCl_6]$	30.3	1.0	2.4	2.7	28.4	12.5	30.3	0.9	3.0	3.3	29.8	12.8
$[P(C_6F_5)_2Cl_2(bipy)][SbCl_6]$	32.1	1.1	3.0	2.8	27.4	12.9	28.5	0.9	3.0	3.3	30.6	13.1
$[P(C_6F_5)_2Cl_2(phen)][BCl_4]$	38.7	1.4	2.9	4.1	27.3	1.9	37.5	1.1	3.6	4.0	27.7	1.4
$[P(C_6F_5)_2Cl_2(bipy)][BCl_4]$	31.3	1.2	2.3	2.4	28.4	2.4	35.5	1.1	3.8	4.2	28.6	1.5
$[P(C_6F_5)_3Cl(phen)][SbCl_6]$	30.7	0.4	1.0	3.0	21.7	10.8	33.3	0.8	2.6	2.9	22.9	11.3
$[P(C_6F_5)Br_3(bipy)]Br$	30.4	1.2	3.5	4.2	46.9	—	28.5	1.2	4.2	4.6	47.4	—
$[P(C_6F_5)Br_3(phen)][BBr_4]$ *	26.0	1.7	2.6	2.9	48.2	1.2	22.8	0.9	3.0	3.3	59.0	1.1
$[P(C_6F_5)Br_3(bipy)][BBr_4]$ *	23.8	1.6	2.8	2.8	53.5	1.4	20.8	0.9	3.0	3.4	60.5	1.2

* See text.

synthesis of the hexachloroantimonate. The gaseous BCl_3 was allowed to flow into the mixture with constant stirring until reaction was complete. The mixture was filtered to remove any $[P(C_6F_5)Cl_3][BCl_4]$, and the filtrate was evaporated to dryness *in vacuo* to give the desired product.

$[P(C_6F_5)_2Cl_2(phen)][SbCl_6]$ *and* $[P(C_6F_5)_2Cl_2(phen)][BCl_4]$.—These compounds were obtained from 1:1 reactions between a slurry of $[P(C_6F_5)_2Cl_2][SbCl_6]$ or $[P(C_6F_5)_2Cl_2][BCl_4]$ in CH_2Cl_2 and a solution of 1,10-phenanthroline in the same solvent, which was added dropwise, with constant stirring. The mixture was allowed to stir for 30 min before the solvent was removed *in vacuo.*

$[P(C_6F_5)_2Cl_2(bipy)][SbCl_6]$ *and* $[P(C_6F_5)_2Cl_2(bipy)][BCl_4]$.—These complexes were similarly prepared from 1:1 reactions between the $[P(C_6F_5)_2Cl_2]^+$ salt and 2,2′-bipyridine. The reaction mixture was allowed to stir for 1 h before the solvent was removed *in vacuo*, to yield yellow ($SbCl_6^-$) and orange (BCl_4^-) solids respectively.

$[P(C_6F_5)_3Cl(phen)][SbCl_6]$.—The salt $[P(C_6F_5)_3Cl][SbCl_6]$ was suspended in CH_2Cl_2, and a solution of an equimolar quantity of 1,10-phenanthroline in CH_2Cl_2 was added, with constant stirring, which was continued for 20 min. The solvent was evaporated *in vacuo* to yield the solid compound.

$[P(C_6F_5)Br_3(bipy)]Br$.—The compound $P(C_6F_5)Br_4$ was suspended in a small amount of CH_2Cl_2, and an equimolar quantity of 2,2′-bipyridine was added, with stirring, which was continued for 30 min. The mixture was filtered to remove any unreacted $P(C_6F_5)Br_4$ and the filtrate was evaporated *in vacuo* to give a yellow solid.

$[P(C_6F_5)Br_3(phen)][BBr_4]$ *and* $[P(C_6F_5)Br_3(bipy)][BBr_4]$.—An equimolar quantity of 1,10-phenanthroline or 2,2′-bipyridine was added to a slurry of $[P(C_6F_5)Br_3][BBr_4]$ in CH_2Cl_2. The mixture was allowed to stir for 30 min and then evaporated to dryness to yield a fine yellow solid in each case. Analyses of both products were high in carbon and low in bromine, indicating that pure compounds had not been obtained (Table 1). This is discussed further in the Results and Discussion section.

Analyses were carried out as in previous publications;[3,5] boron was determined by atomic absorption spectroscopy, following combustion in an oxygen flask with dilute H_2O_2 solution. I.r., ^{31}P and ^{11}B n.m.r. spectra were recorded as described previously;[4,10] chemical shifts for ^{31}P are expressed relative to external 85% H_3PO_4, and for ^{11}B relative to external $B(OMe)_3$, with the downfield (higher-frequency) direction taken as positive. ^{35}Cl n.q.r. spectra were also obtained as described in previous work.[12]

Results and Discussion

(*a*) *Acceptor Properties of* $P(C_6F_5)Cl_4$.—The compound $P(C_6F_5)Cl_4$ gave a ^{31}P n.m.r. resonance at -70.9 p.p.m. in CH_2Cl_2, in excellent agreement with the literature value.[13] Its structure has been confirmed as trigonal bipyramidal, with the organo-group axial, by ^{35}Cl n.q.r. spectroscopy.[13,14] When NR_4Cl ($R = Et$ or Pr^n) was added to a solution of the phosphorane in CH_2Cl_2, the ^{31}P n.m.r. signal moved upfield, reaching a limiting shift of -240.0 p.p.m. in the presence of a large excess of chloride ions. This behaviour is similar to that of $PPhCl_4$,[1] $PMeCl_4$,[3] and $PEtCl_4$,[3] and is ascribed to formation of the $[P(C_6F_5)Cl_5]^-$ ion.[15] The salt was isolated from a 1:1 reaction of the phosphorane with NPr^n_4Cl; it gave a resonance at -183.4 p.p.m. when redissolved in $PhNO_2$, showing that it is partially dissociated in this solvent. Its i.r. spectrum (Nujol mull) showed the expected strong broad band for the anion, with a maximum at 420 cm^{-1}. A pure compound could not be isolated from the NEt_4Cl–$P(C_6F_5)Cl_4$ reaction, elemental analysis showing that the product was a mixture of NEt_4Cl and the desired compound.

Calculations based on the chemical shifts of $PRCl_4$ and $PRCl_5^-$, and the shifts observed experimentally for different $PRCl_4$:Cl^- molar ratios, showed that the degree of association for a particular molar ratio of NEt_4Cl to $P(C_6F_5)Cl_4$ in CH_2Cl_2 was higher than for the same ratio of NEt_4Cl to $PPhCl_4$. This suggests that the presence of the electronegative pentafluorophenyl group increases the Lewis-acid character of the phosphorane.

An attempt was made to compare the relative acceptor abilities of $P(C_6F_5)Cl_4$, $PPhCl_4$, $PMeCl_4$, and PCl_5, by mixing a solution of $P(C_6F_5)Cl_4$ with an equimolar quantity of a solution of one of the other phosphoranes in CH_2Cl_2 or $PhNO_2$ in an n.m.r. tube, and recording the ^{31}P n.m.r. spectra of the mixtures. Rather surprisingly, no reaction appeared to take place in any of the systems, and signals were observed only from the starting materials in each case. This applied even to PCl_5, which was expected to be a better chloride-ion acceptor since it forms PCl_6^- salts with $PPhCl_4$ and $PMeCl_4$. The compound $P(C_6F_5)Cl_4$ shows a marked reluctance to break a P–Cl bond and form a cation, as shown by its failure to react with bidentate pyridines, described below. This is possible with strong Lewis acids such as $SbCl_5$, BCl_3, or ICl_3, but it appears that PCl_5 is not a strong enough Lewis acid to convert the five-co-ordinate phosphorane into a four-co-ordinate quasi-phosphonium ion.

When excess of pyridine (py) was added to a solution of $P(C_6F_5)Cl_4$ in CH_2Cl_2 a white precipitate was immediately produced, and no solution signals could be obtained. A solid was isolated from a 1:1 reaction, but proved to be rather unstable. When redissolved in excess of CH_2Cl_2 it showed only one ^{31}P signal at −75.8 p.p.m., ascribed to the phosphorane, or to a rapidly exchanging system containing only a very small proportion of the six-co-ordinate adduct. The analyses showed that a pure product had not been obtained, being low in P and Cl (Table 1). When $P(C_6F_5)Cl_4$ was treated with excess of py in $PhNO_2$ two new resonances were detected at −192.8 and −201.0 p.p.m. These were assigned to the two possible isomers of $P(C_6F_5)Cl_4$·py, with the organo-group *cis* or *trans* to py. The alternative possibility of the formation of two of the three possible isomers of $[P(C_6F_5)Cl_3(py)_2]^+$ seems most unlikely in view of the results with bidentate pyridines, the shift observed for one isomer of this ion in the reaction of $[P(C_6F_5)Cl_3][SbCl_6]$ with py, and the difficulty in breaking a P–Cl bond of the phosphorane, as discussed above.

On the assumption that pairwise interaction terms[16] can be transferred from other six-co-ordinate phosphorus(V) species such as PCl_6^-,[17] PCl_5·py,[5] and $[P(C_6F_5)Cl_5]^-$,[15] an estimate can be made of the expected shift for *trans*-$P(C_6F_5)Cl_4$·py of −169.8 p.p.m. While numerical agreement is poor, perhaps not surprisingly in view of the sizes of the organic substituents, which may distort the geometry away from regular octahedral, this suggests that the lower-field resonance at −192.8 p.p.m. probably arises from the *trans* isomer, in keeping with the observation that *cis* isomers of six-co-ordinate phosphorus species usually resonate at higher field than do their *trans* analogues.[8,15,17–21] The adduct decomposed when redissolved in $PhNO_2$, and no signals could be obtained in the six-co-ordinate region. It seems clear overall that a 1:1 adduct with pyridine is formed, and is stabilised to some extent by insolubility in non-polar solvents such as CH_2Cl_2, and by the presence of excess of py in $PhNO_2$, allowing solution signals for both possible isomers to be obtained. The complex is not stable, however, to redissolution in either CH_2Cl_2 or $PhNO_2$.

No six-co-ordinate species were detected when phen or bipy was added to a solution of $P(C_6F_5)Cl_4$ in either CH_2Cl_2 or $PhNO_2$, and no change was observed in the position of the phosphorane resonance at −70.8 p.p.m. Hence these ligands do not form six-co-ordinate complexes $[P(C_6F_5)Cl_3L]^+Cl^-$, which would involve the breaking of a P–Cl bond, although complexes containing these cations can be prepared by starting from $[P(C_6F_5)Cl_3]^+$ salts, as discussed in the following section. This contrasts with the behaviour of $PPhCl_4$ towards bidentate pyridines, where the formation of ionic six-co-ordinate cationic complexes was observed.[1]

(*b*) *Acceptor Properties of the* $[P(C_6F_5)Cl_3]^+$ *ion.*—The formation of salts containing the $[P(C_6F_5)Cl_3]^+$ ion by the strong Lewis acids $SbCl_5$, BCl_3, and ICl_3 has been described (Experimental section). The $SbCl_6^-$ and BCl_4^- salts both gave ^{31}P n.m.r. signals at 82.2 p.p.m. in $PhNO_2$ or $MeNO_2$ solution, and in the solid state. The ICl_4^- salt resonated at 77.5 p.p.m. in $PhNO_2$, but in CH_2Cl_2 the resonance occurred at 38.4 p.p.m., suggesting partial dissociation to $P(C_6F_5)Cl_4$ and ICl_3, with rapid exchange between the four- and five-co-ordinate phosphorus species. The compounds gave the expected i.r. band for the $SbCl_6^-$ ion at 335 cm^{-1},[22,23] a broad band with maximum at 645 cm^{-1} for the BCl_4^- ion,[12,24] and a band at 260 cm^{-1} for the ICl_4^- ion[25] respectively. The ^{35}Cl n.q.r. signals at 77 K for the cation in $[P(C_6F_5)Cl_3][SbCl_6]$ were observed at 31.475(1), 31.600(2), 31.825(1), and 32.150(2) MHz (relative intensities in parentheses), suggesting the presence of at least two cations in the unit cell. No signals were detected at 195 K or room temperature, or for the $SbCl_6^-$ anion at any temperature. The tetrachloroborate gave three equally intense ^{35}Cl n.q.r. signals at 77 K for the cation, at 31.146, 32.175, and 32.448 MHz. Interestingly, only two signals were seen at 195 K, at 30.400(1) and 32.500(2) MHz, suggesting a possible phase transition between these temperatures. Four equally intense signals were also detected from the BCl_4^- ion at both temperatures, with frequencies of 20.236, 21.010, 21.300, and 21.675 MHz (77 K), and 19.988, 20.775, 20.950, and 21.230 MHz (195 K). All four resonances show a normal temperature dependence, so the structure of the anion probably remains unaffected by the phase transition. No n.q.r. signals were detected from the tetrachloroiodate at any temperature, and its acceptor properties were not investigated.

When a small amount of 2,2′-bipyridine (bipy) was added to a solution of $[P(C_6F_5)Cl_3]SbCl_6$ two new ^{31}P n.m.r. peaks at −177.3 and −188.6 p.p.m. were observed, ascribed to the two possible isomers of the $[P(C_6F_5)Cl_3(bipy)]^+$ cation, with the C_6F_5 group either *cis* or *trans* to one of the co-ordinating nitrogens. Although direct evidence is lacking, it is again possible that the *trans* isomer is the one with the lower-field (higher-frequency) resonance, by comparison with the results for other six-co-ordinate phosphorus systems.[8,15,17–21] These signals disappeared with the addition of more bipyridine to the solution, which caused precipitation. A solid compound was obtained from a 1:1:1 reaction between $P(C_6F_5)Cl_4$, bipy, and $SbCl_5$, which when redissolved in $PhNO_2$ gave one signal only, at −190.2 p.p.m. Hence the thermodynamically more stable *cis* isomer is probably the form isolated, in agreement with the tentative assignment above. When 1,10-phenanthroline was added to a slurry of $[P(C_6F_5)Cl_3][SbCl_6]$ in CH_2Cl_2 a precipitate quickly formed and no solution spectrum could be obtained. A quantitative reaction yielded a cream-coloured solid, which gave one signal at −190.2 p.p.m. when redissolved in $PhNO_2$. Thus only one of the two possible isomers was identified from this system. This again could be the *cis* isomer from the shift, although confirmation is lacking.

A deep yellow solution formed after the addition of pyridine to a solution of $[P(C_6F_5)Cl_3][SbCl_6]$ in $PhNO_2$, and a ^{31}P n.m.r. signal at −178.9 p.p.m. was observed. This rapidly disappeared, with the formation of solid in the tube. The resonance is assigned to one of the three possible isomers of

Table 2. I.r. data (800—200 cm^{-1}) for $P(C_6F_5)_2Cl_3$ and derivatives

Compound	
$P(C_6F_5)_2Cl_3$	770m, 760m, 645 (sh), 640s, 595s, 570s, 540s, 500m, 490m, 460s, 450 (sh), 442s, 410 (sh), 395s, 370s, 345s, 320m, 305m, 270w
$[P(C_6F_5)_2Cl_2][SbCl_6]$	780w, 765w, 650m, 625w, 605m, 595w, 580m, 550w, 535m, 495w, 475w, 435s, 348s, br, 280w
$[P(C_6F_5)_2Cl_2][BCl_4]$	770m, 670m, br, 655w, 650m, 620m, 595w, 535w, 445w, 435m, 410w, 340m
$[P(C_6F_5)_2Cl_2(phen)][SbCl_6]$	765m, 645m, 615w, 600m, 585m, 570w, 530s, 455m, 430m, 340s, br
$[P(C_6F_5)_2Cl_2(phen)][BCl_4]$	760w, 655m, br, 635m, br, 585s, 560m, 530s, 450s, 435m, 390s, 335m, 315w
$[P(C_6F_5)_2Cl_2(bipy)][SbCl_6]$	760s, 640s, 620m, 600m, 590m, 580w, 545s, 535s, 515 (sh), 475m, 465m, 435m, 345s, br
$[P(C_6F_5)_2Cl_2(bipy)][BCl_4]$	760s, 690 (sh), 630m, br, 585m, 550m, 530s, 450m, 435m, 390m, 340m

$[P(C_6F_5)Cl_3(py)_2]^+$. The compound is probably unstable, and converts rapidly into $P(C_6F_5)Cl_4{\cdot}py$ and $SbCl_5{\cdot}py$, [equation (1)], similar to the behaviour of $[PRCl_3(py)_2]^+SbCl_6^-$, where R = Cl,[6] Ph,[1] or Me.[3]

$$[P(C_6F_5)Cl_3(py)_2][SbCl_6] \longrightarrow P(C_6F_5)Cl_4{\cdot}py + SbCl_5{\cdot}py \quad (1)$$

When a small amount of bipy was added to a solution of $[P(C_6F_5)Cl_3][BCl_4]$ in $PhNO_2$, two new signals were seen at −180.6 and −190.2 p.p.m., ascribed to the two isomers of the $[P(C_6F_5)Cl_3(bipy)]^+$ cation. The addition of more bipy caused precipitation, and the resonances could no longer be observed. The solid compound was isolated from a quantitative reaction in CH_2Cl_2. Interestingly, when redissolved in $PhNO_2$ it gave a signal at −182.2 p.p.m., closer to the lower-field signal and possibly arising from the *trans* isomer. It is possible that rapid precipitation favours formation of the kinetically rather than the thermodynamically more stable product. With phen a yellow solid was precipitated, and no solution spectrum could be obtained. The product isolated from a quantitative reaction gave a resonance at −186.2 p.p.m. when redissolved in $PhNO_2$, tentatively assigned to the *cis* isomer. A peak for ^{11}B was also found from this solution at −12.2 p.p.m., in good agreement with literature data for the BCl_4^- ion.[26–28]

(*c*) *The Acceptor Properties of* $P(C_6F_5)_2Cl_3$ *and of the* $[P(C_6F_5)_2Cl_2]^+$ *ion*.—The phosphorane $P(C_6F_5)_2Cl_3$ gave a ^{31}P n.m.r. resonance at −80.7 p.p.m. in both $PhNO_2$ and CH_2Cl_2, in good agreement with the literature value.[13] Its ^{35}Cl n.q.r. spectrum at 77 K consisted of one signal at 35.355 MHz, confirming previous data,[13] and showing that it has a trigonal-bipyramidal structure with axial C_6F_5 groups. No signals were found at 195 K or room temperature. It showed no acceptor properties towards the chloride ion, either with NEt_4Cl in CH_2Cl_2 or with NPr_4Cl in $PhNO_2$, the resonance remaining unchanged. This behaviour parallels that of other phosphoranes PR_2Cl_3, where R = Me,[3] Et,[3] or Ph.[7] Similarly, it showed no acceptor properties towards either unidentate (py) or bidentate (bipy or phen) pyridine bases.

The compound $P(C_6F_5)_2Cl_3$ reacted with the strong Lewis acids $SbCl_5$, BCl_3, and ICl_3 to form ionic derivatives containing the $[P(C_6F_5)_2Cl_2]^+$ ion. The hexachloroantimonate gave ^{31}P n.m.r. signals at 64.6 ($PhNO_2$) and 64.2 ($MeNO_2$) p.p.m., and a broad resonance at 66.2 p.p.m. in the solid state. Its i.r. spectrum showed a strong, broad band for the $SbCl_6^-$ ion,[22,23] with a maximum at 348 cm^{-1}. The tetrachloroborate gave a ^{31}P n.m.r. resonance at 62.7 p.p.m. in $PhNO_2$, and an ^{11}B peak at −11.2 p.p.m., in good agreement with results in this work and elsewhere[26–28] for the BCl_4^- ion. A broad, medium-intensity band with maximum at 640 cm^{-1} in its i.r. spectrum was also assigned to this ion.[12,24] The tetrachloroiodate gave a ^{31}P n.m.r. resonance at 62.9 p.p.m. in $MeNO_2$, and showed a band at 250 cm^{-1} in its i.r. spectrum, attributed to the ICl_4^- ion.[25]

When a small amount of phen was added to a solution of $[P(C_6F_5)_2Cl_2][SbCl_6]$ in $PhNO_2$ a signal was observed at −80.4 p.p.m., ascribed to the phosphorane $P(C_6F_5)_2Cl_3$. A precipitate formed when more phen was added, the solution signal remaining unchanged. The solid isolated from a quantitative reaction gave reasonable analyses, but proved to be unstable in solution in either $PhNO_2$ or $MeNO_2$, where the only ^{31}P n.m.r. resonance detected was that for the phosphorane. The best evidence that the solid was a genuine co-ordination compound containing the ion $[P(C_6F_5)_2Cl_2(phen)]^+$ came from the i.r. spectrum (Table 2), which was not that of a mixture of $P(C_6F_5)_2Cl_3$ and $SbCl_5{\cdot}phen$. {The latter is expected to have the ionic structure $[SbCl_4(phen)]^+Cl^-$}. For example, the phosphorane gives strong bands at 595, 570, 442, 395, and 370 cm^{-1}, which were not present in the spectrum of the complex. The medium-intensity band at 409 cm^{-1} reported[23] for $[SbCl_4(phen)]^+SbCl_6^-$ was also absent. We therefore conclude that a cationic six-co-ordinate complex is formed, probably stabilised by limited solubility in the reaction medium, but that the complex is unstable in solution, reverting to the phosphorane, reaction (2).

$$[P(C_6F_5)_2Cl_2(phen)][SbCl_6] \xrightarrow[\text{or } MeNO_2]{PhNO_2} P(C_6F_5)_2Cl_3 + [SbCl_4(phen)]Cl \quad (2)$$

Similar results were obtained with bipy as the donor; in $PhNO_2$ the only solution signal obtained was that of the phosphorane at −80.9 p.p.m., but a solid product was successfully isolated from a quantitative reaction. Its i.r. data (Table 2) again differed from those expected for a mixture of $P(C_6F_5)_2Cl_3$ and $[SbCl_4(bipy)]^+Cl^-$. Not surprisingly, no stable complex was obtained when pyridine was added to a solution of $[P(C_6F_5)_2Cl_2][SbCl_6]$ in $PhNO_2$, but a resonance at −78.8 p.p.m. was discerned, ascribed to $P(C_6F_5)_2Cl_3$, together with a weak signal at 6.4 p.p.m. from a hydrolysis product. In this case the probable reaction is (3).

$$[P(C_6F_5)_2Cl_2][SbCl_6] + py \longrightarrow P(C_6F_5)_2Cl_3 + SbCl_5{\cdot}py \quad (3)$$

With $[P(C_6F_5)_2Cl_2][BCl_4]$ as the acceptor the reactions with bidentate pyridines followed similar courses. The only ^{31}P n.m.r. resonances detected in solution were from the phosphorane, both from qualitative experiments in $PhNO_2$ solution and on redissolving the solids isolated from stoicheiometric reactions. The i.r. data (Table 2) again support strongly the contention that six-co-ordinate cationic phosphorus complexes are formed in the solid state, rather than mixtures of $P(C_6F_5)_2Cl_3$ and complexes of BCl_3 with the bases. The redissolved products gave ^{11}B n.m.r. resonances at −10.1 p.p.m. (phen or bipy), assigned to the cationic complexes $[BCl_2L]^+Cl^-$, since $[BCl_2(phen)][BCl_4]$ gives ^{11}B signals at −10.3 and −11.2 p.p.m. for the cation and anion respectively.[29] Hence the complexes decompose in solution according to equation (4) (L = phen or bipy).

$$[P(C_6F_5)_2Cl_2L]BCl_4 \longrightarrow P(C_6F_5)_2Cl_3 + [BCl_2L]Cl \quad (4)$$

The above results indicate that $P(C_6F_5)_2Cl_3$ itself shows no

Table 3. I.r. data (800—200 cm^{-1}) for $P(C_6F_5)_3Cl_2$ and derivatives

Compound	
$P(C_6F_5)_3Cl_2$	765s, 755m, 640 (sh), 630s, 585s, 530s, 460 (sh), 440s, 360 (sh), 340s, 310s, 280 (sh)
$[P(C_6F_5)_3Cl][SbCl_6]$	765s, 630s, 600s, 585s, 460 (sh), 445s, 435s, 350s, br, 340 (sh), 310m, 280w
$[P(C_6F_5)_3Cl(phen)][SbCl_6]$	765m, 630w, 580w, 530s, 455m, 440w, 340s, br

Table 4. I.r. data (800—200 cm^{-1}) for $P(C_6F_5)Br_4$ and derivatives

Compound	
$P(C_6F_5)Br_4$	753 (sh), 638m, 630m, 540w, 525s, 495s, 460s, 445w, 423m, 405w, 380w, 345w, 325m
$[P(C_6F_5)Br_3][BBr_4]$	765w, 652m, (625, 605, 560s, br), 528m, 515 (sh), 510s, 432s, 405w, 345m, 325w, 305w
$[P(C_6F_5)Br_3(bipy)]Br$	760s, 638w, 620s, 590w, 560w, 545w, 525s, 495s, 470w, 460w, 435w, 420m, 405m, 380w, 320w

acceptor properties under the experimental conditions used, but that the $[P(C_6F_5)_2Cl_2]^+$ ion is a better acceptor than $[PR_2Cl_2]^+$ (R = Ph,[7] Me,[3] or Et[3]), in keeping with the greater electron-withdrawing ability of the electronegative C_6F_5 groups. Even so the complexes formed are only stable in the solid state, and decompose in solution.

(*d*) *The Acceptor Properties of* $P(C_6F_5)_3Cl_2$ *and of the* $[P(C_6F_5)_3Cl]^+$ *Ion.*—The phosphorane $P(C_6F_5)_3Cl_2$ was initially prepared by the slow (1 d) chlorination of solid $P(C_6F_5)_3$;[30] its ^{31}P n.m.r. shift was measured as -104.7 p.p.m. in C_6H_6. In the present work the synthesis was carried out more conveniently in CH_2Cl_2 solution, and required the passage of dry Cl_2 for only a few minutes to cause precipitation of $P(C_6F_5)_3Cl_2$. It gave ^{31}P n.m.r. signals at -106.4 p.p.m. in CH_2Cl_2, and at -104.5 p.p.m. in $PhNO_2$. As expected, the phosphorane showed no acceptor properties towards the chloride ion, or to uni- or bi-dentate pyridines, the ^{31}P n.m.r. spectrum remaining unchanged in all cases. It readily formed ionic derivatives with the strong Lewis acids $SbCl_5$, BCl_3, and ICl_3. The $SbCl_6^-$ salt gave a ^{31}P n.m.r. signal at 27.3 p.p.m. in $PhNO_2$, and the expected strong, broad i.r. band for the $SbCl_6^-$ ion.[22,23] The tetrachloroborate gave a ^{31}P n.m.r. resonance at 14.5 p.p.m. in $PhNO_2$, and an ^{11}B signal at -12.2 p.p.m. from the BCl_4^- ion.[26–28] There is a marked shift difference between the cations in the two salts, but this is by no means uncommon in ^{31}P n.m.r. spectroscopy.[31] The ICl_4^- salt gave a ^{31}P signal at 25.7 p.p.m. in $MeNO_2$, together with a weaker peak at -8.0 p.p.m. from the hydrolysis product $P(C_6F_5)_3O$, and the expected strong i.r. band at 260 cm^{-1} from the ICl_4^- ion.[25]

The acceptor properties were only investigated for the hexachloroantimonate–phen reaction. No six-co-ordinate peak was detected when phen was added to a solution of $[P(C_6F_5)_3Cl][SbCl_6]$ in $PhNO_2$, but one signal only, at -9.7 p.p.m. A yellowish solid was isolated from a quantitative reaction and gave reasonable analyses, but when redissolved in $PhNO_2$, $MeNO_2$, or MeCN it gave ^{31}P n.m.r. signals at -9.7, -8.0, and -8.0 p.p.m. respectively. The most probable explanation for these signals is an equilibrium between the covalent and ionic forms of $P(C_6F_5)_3Cl_2$, formed by decomposition of the complex as in the $[P(C_6F_5)_2Cl_2]^+$ derivatives [equations (5) and (6)]. Either exchange between $P(C_6F_5)_3Cl_2$ and any unreacted $[P(C_6F_5)_3Cl]^+$, or partial ionisation of the phosphorane, would then give rise to a peak at a position intermediate between 27.3 and -104.5 p.p.m. The alternative possibility of formation of $P(C_6F_5)_3O$ as the only phosphorus-containing species in all solvents seems most unlikely in view of the analyses on the solid product, and the recording of many other spectra in these solvents without major hydrolysis problems. The i.r. data for the complex (Table 3) again support its formulation as containing a six-co-ordinate phosphorus cation, by comparison with the results for $P(C_6F_5)_3Cl_2$ and $2SbCl_5{\cdot}phen$.[23] For example, the spectrum of $P(C_6F_5)_3Cl_2$ showed several strong bands below 650 cm^{-1}, whereas the complex showed only two strong bands in this region, one of them due to the $SbCl_6^-$ ion.[22,23] We therefore conclude that the $[P(C_6F_5)_3Cl]^+$ ion shows weak acceptor properties towards phen, unlike other ions of the type $[PR_3Cl]^+$ (R = Me or Et).[3] The less rigid ligand bipy is likely to be a weaker donor than phen, and its reaction with $[P(C_6F_5)_3Cl][SbCl_6]$ was not investigated.

$$[P(C_6F_5)_3Cl][SbCl_6] + phen \longrightarrow [P(C_6F_5)_3Cl(phen)][SbCl_6] \quad (5)$$

$$[P(C_6F_5)_3Cl(phen)][SbCl_6] \longrightarrow P(C_6F_5)_3Cl_2 + [SbCl_4(phen)]Cl \quad (6)$$

(*e*) *The Acceptor Properties of* $P(C_6F_5)Br_4$ *and of* $[P(C_6F_5)Br_3][BBr_4]$.—The new compound $P(C_6F_5)Br_4$ gave a strong ^{31}P n.m.r. signal at -25.8 p.p.m. in 25% SO_3-oleum solution,[32] assigned to the $[P(C_6F_5)Br_3]^+$ cation. Weak signals at 8.2 and 37.1 p.p.m. were attributed to $[P(C_6F_5)(OH)_3]^+$ and $[P(C_6F_5)Br(OH)_2]^+$ respectively. A strong signal from the cation was also detected in the solid state at -42.0 p.p.m., together with weak resonances at -16.2 [probably $P(C_6F_5)Br_2O$] and 111.3 p.p.m. $[P(C_6F_5)Br_2]$. This result supports the ionic structure $[P(C_6F_5)Br_3]^+Br^-$ for the compound, like other $PRBr_4$ species.[4] Decomposition occurred in organic solvents such as CH_2Cl_2 and $PhNO_2$ to $P(C_6F_5)Br_2$ and bromine, as observed for PBr_5.[4] In liquid Br_2 two signals were detected at -29.1 and -30.7 p.p.m., probably due to the $[P(C_6F_5)Br_3]^+$ cation in two different environments, for example with Br^- and Br_3^- counter ions.

When $P(C_6F_5)Br_4$ was dissolved in liquid pyridine, Br_2 was liberated and the main ^{31}P n.m.r. resonance was at 106.8 p.p.m., due to equilibrium between $P(C_6F_5)Br_2$ (δ 111.3 p.p.m.) and its complex with py. Hence decomposition of the phosphorus(V) species occurs in preference to complexation [equations (7) and (8)]. This behaviour parallels that of $PPhBr_4$ with py.[4] Other

$$P(C_6F_5)Br_4 \longrightarrow P(C_6F_5)Br_2 + Br_2 \quad (7)$$

$$P(C_6F_5)Br_2 + py \rightleftharpoons P(C_6F_5)Br_2{\cdot}py \quad (8)$$

weaker unassigned signals were seen at 82.2 and -42.0 p.p.m. A yellow solid was immediately formed when bipy was added to a slurry of $P(C_6F_5)Br_4$ in a small amount of CH_2Cl_2. The product was isolated from a stoicheiometric reaction, and analysed as the 1:1 adduct. It was unstable in solution, decomposing rapidly in CH_2Cl_2 to give a strong signal at 111.3 p.p.m. $[P(C_6F_5)Br_2]$ and medium-intensity signals at -21.0 and -42.0 p.p.m. In $PhNO_2$ the phosphorus(III) resonance was weaker and the signals at -21.0 and -42.0 p.p.m. stronger, showing that decomposition is slower in this solvent. The peaks at -42.0 p.p.m. are probably from the cation, but the assignment of the resonance at -21.0 p.p.m. is unclear, although it could be from $P(C_6F_5)Br_2O$ as impurity. The solid appeared to be a genuine complex $[P(C_6F_5)Br_3(bipy)]^+Br^-$, rather than a mixture of $P(C_6F_5)Br_4$ and bipy, from its i.r. spectrum (Table 4). Two bands observed at 560 and 545 cm^{-1}

for the complex were not present in the spectra of either component separately, for example.

The tetrabromoborate was prepared by adding BBr_3 to a slurry of the phosphorane in a small amount of CH_2Cl_2. It was unstable in organic solvents; in $PhNO_2$ the ^{31}P n.m.r. spectrum consisted of a signal at 21.1 p.p.m., which was thought to arise from formation of the adduct $P(C_6F_5)Br_2 \cdot BBr_3$, equations (9) and (10). This deduction was checked by treating $P(C_6F_5)Br_2$ with BBr_3 in $PhNO_2$, when a new signal at 22.5 p.p.m. was seen, assigned to this adduct. A solid-state ^{31}P n.m.r. signal was obtained from $[P(C_6F_5)Br_3][BBr_4]$ at -38.0 p.p.m., ascribed to the cation, and the ^{11}B n.m.r. of the $PhNO_2$ solution consisted of a single resonance at -40.6 p.p.m., similar to the value of -39.4 p.p.m. measured for the BBr_4^- ion in $[PMe_3Br]^+[BBr_4]^-$.[29] A ^{31}P n.m.r. signal at -25.8 p.p.m. was also obtained from liquid Br_2 as solvent, again ascribed to the $[P(C_6F_5)Br_3]^+$ cation.

$$[P(C_6F_5)Br_3][BBr_4] \longrightarrow P(C_6F_5)Br_2 + Br_2 + BBr_3 \quad (9)$$

$$P(C_6F_5)Br_2 + BBr_3 \longrightarrow P(C_6F_5)Br_2 \cdot BBr_3 \quad (10)$$

A yellow precipitate formed after a few minutes when bipy was added to a slurry of $[P(C_6F_5)Br_3][BBr_4]$ in CH_2Cl_2. The solid isolated from a stoicheiometric reaction formed a brown solution when solvent was added, showing the liberation of Br_2. Signals were detected at 111.3 [strong, $P(C_6F_5)Br_2$] and -42.0 p.p.m. {medium, $[P(C_6F_5)Br_3]^+$}. The ^{11}B n.m.r. of this solution showed a single peak at -19.8 p.p.m., attributed to the cation $[BBr_2(bipy)]^+$.[29] The compound would not form a mull, and no i.r. spectra could be obtained. Elemental analyses were rather high in carbon and low in bromine (Table 1), probably due to some loss of Br_2, either in the preparation or during the isolation procedure. It seems most probable, however, that the six-co-ordinate complex is formed initially in the solid, and then decomposes according to equation (11). Some loss of Br_2 will occur in the formation of the initial slurry, since $[P(C_6F_5)Br_3][BBr_4]$ is unstable in CH_2Cl_2, and this may well account partly for the low bromine analysis. Similar results were obtained when phen was used as the ligand. A solid compound was isolated, but decomposed readily in solution with liberation of Br_2. The ^{31}P n.m.r. spectrum of the solid redissolved in $PhNO_2$ showed only the signal for $P(C_6F_5)Br_2$ at 111.3 p.p.m., and the ^{11}B resonance at -18.8 p.p.m. was assigned to $[BBr_2(phen)]Br$.[29] The bromine analysis of the solid was again low, and the compound would not mull, like the bipy complex. In an effort to reduce the initial decomposition of the tetrabromoborate, the ligand was dissolved in a small amount of CH_2Cl_2 and solid $[P(C_6F_5)Br_3][BBr_4]$ was added. The bromine percentage in the product increased slightly from 48.2 to 52.1%, but a pure compound was not obtained by this route either. Despite these setbacks, it seems reasonable to conclude that the $[P(C_6F_5)Br_3]^+$ cation shows some acceptor properties towards the bidentate ligands bipy and phen. The complexes, however, are not stable in organic solvents such as $PhNO_2$ to loss of Br_2 and the formation of phosphorus(III) species.

$$[P(C_6F_5)Br_3(bipy)][BBr_4] \longrightarrow P(C_6F_5)Br_2 + [BBr_2(bipy)]Br + Br_2 \quad (11)$$

Conclusions

The results described above indicate that pentafluorophenylphosphorus(V) compounds do show acceptor properties towards Lewis bases. Direct quantitative comparison with other systems is not facile, but analysis of the shifts in the $PRCl_4$–$[PRCl_5]^-$ exchanging systems suggests that $P(C_6F_5)Cl_4$ is a somewhat better chloride-ion acceptor than $PPhCl_4$, as expected with a more electronegative organic substituent. Rather surprisingly, $P(C_6F_5)Cl_4$ did not react under the experimental conditions with PCl_5, where formation of $[P(C_6F_5)Cl_3][PCl_6]$ was expected, or with $PPhCl_4$ or $PMeCl_4$. It seems that strong Lewis acids such as $SbCl_5$, BCl_3, or ICl_3 are required to break a P–Cl bond in $P(C_6F_5)Cl_4$ and form the quasi-phosphonium ion $[P(C_6F_5)Cl_3]^+$, and that PCl_5 is not a strong enough acceptor to do this. The phosphoranes with two or three C_6F_5 groups present did not show any acceptor properties, in common with other species of the type PR_2Cl_3 or PR_3Cl_2, but Lewis-acid behaviour was shown by the cations $[P(C_6F_5)_2Cl_2]^+$ and $[P(C_6F_5)_3Cl]^+$ towards phen and/or bipy. The products were stabilised by precipitation, and dissolved with decomposition in organic solvents. No Lewis-acid properties have been demonstrated previously for $[PR_2Cl_2]^+$ or $[PR_3Cl]^+$, for example in the systems where R = Me or Et and the phosphoranes themselves exist in the ionic form in the solid state.[3] It was not easy to study the co-ordination chemistry of the $[P(C_6F_5)Br_3]^+$ ion because of the instability of the starting materials $[P(C_6F_5)Br_3]Br$ or $[P(C_6F_5)Br_3][BBr_4]$ in organic solvents, but there was again evidence for the formation of six-co-ordinate complexes, even though these could not be isolated in a pure state, and were unstable in solution. Hence it is reasonable overall to conclude that the replacement of an organic substituent with a more strongly electron-withdrawing group on phosphorus(V) enhances its potential Lewis-acid ability.

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