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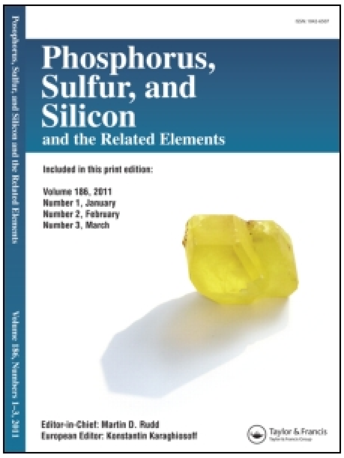

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THE ACCEPTOR PROPERTIES OF SOME PERCHLOROALKYLCHLOROPHOSPHORANES AND THEIR LEWIS ACID DERIVATIVES

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THE ACCEPTOR PROPERTIES OF SOME PERCHLOROALKYLCHLOROPHOSPHORANES AND THEIR LEWIS ACID DERIVATIVES

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The acceptor properties towards some Lewis bases of the perchloroalkylchlorophosphoranes $P(CCl_3)Cl_4$, $P(CCl_3)_2Cl_3$, $P(C_2Cl_5)Cl_4$ and of their salts with strong Lewis acids, have been investigated by means of ^{31}P n.m.r. spectroscopy. The results are compared with those for other alkyl- and aryl-chlorophosphoranes.

Key words: Acceptor (properties); phosphoranes (perchloroalkylchloro); Lewis acid (derivatives).

In a series of papers from this research group we have demonstrated that some aryl-[1] and alkyl-[2]chlorophosphoranes, as well as $P(C_6H_4O_2)Cl_3$ and $P(C_6H_4O_2)_2Cl$,[3] and their derivatives with strong Lewis acids, show acceptor properties towards Lewis bases, such as the chloride ion, or uni- or bi-dentate pyridines. Recently[4] we have compared the effect of the C_6F_5 group, which has strongly electron-withdrawing substituents, with that of the phenyl group, on the acceptor properties of PR_nCl_{5-n} and $[PR_nCl_{4-n}]^+$. It was therefore of considerable interest to extend these studies to alkyl-chlorophosphoranes with strongly electron-withdrawing substituents. It proved more facile from the experimental viewpoint to synthesize the trichloromethyl compounds $P(CCl_3)Cl_4$ and $P(CCl_3)_2Cl_3$ than their perfluoroanalogues. In the present work the acceptor properties of these phosphoranes, and of their salts with strong Lewis acids such as $SbCl_5$, have been investigated, mainly by ^{31}P n.m.r. solution measurements. The phosphorane $P(C_2Cl_5)Cl_4$ has been synthesized for the first time, and similarly studied. The results are compared with those for other alkyl- and aryl-chlorophosphoranes and their derivatives.

RESULTS AND DISCUSSION

(a) Acceptor Properties of $P(CCl_3)Cl_4$ and of the $[P(CCl_3)Cl_3]^+$ ion

The compound $P(CCl_3)Cl_4$ is obtained by chlorination of the analogous phosphine $P(CCl_3)Cl_2$. The latter has been prepared by various methods, including heating white phosphorus and CCl_4 in a sealed tube above 373 K,[11] or reduction of $[P(CCl_3)Cl_3][AlCl_4]$[12,13] by $P(OMe)Cl_2$,[14] both giving low yields, and the chlorination of $PMeCl_2$ in $PPh(O)Cl_2$ as solvent, followed by reduction with $P(OMe)Cl_2$.[6] This last preparative method was adapted to yield $P(CCl_3)Cl_4$ directly, in CH_2Cl_2 as solvent (Experimental section). The ^{35}Cl n.q.r. spectrum at 77 K of the phosphorane has shown that it is molecular, with an axial CCl_3 group,[7,15] in marked contrast with $PMeCl_4$, which has the quasi-phosphonium salt structure $[PMeCl_3]^+$ Cl^- in the solid state and in solution.[10] The ^{31}P solution shifts, both in the present work and from the literature (Table I), also support a molecular structure for $P(CCl_3)Cl_4$.

The phosphorane showed no acceptor properties towards NEt_4Cl in either $PhNO_2$ or CH_2Cl_2, the ^{31}P n.m.r. signal remaining unchanged in shift. When NPr_4Cl was used as the chloride ion source in $PhNO_2$, however, a new signal was observed at -194.6 p.p.m., which increased in intensity with the addition of more chloride. The limiting shift was established as -196.6 p.p.m. when a large excess of chloride was used (Table II), and was attributed to the ion $[P(CCl_3)Cl_5]^-$.[16,17] No adduct formation occurred in CH_2Cl_2, showing that the equilibrium (1)

$$P(CCl_3)Cl_4 + Cl^- \rightleftharpoons [P(CCl_3)Cl_5]^- \tag{1}$$

is markedly cation- and solvent-dependent. It had been previously reported, from analysis of u.v. spectra, that the addition of NMe_4Cl or PBu_3Cl_2 to $P(CCl_3)Cl_4$ in either $CH_2Cl.CH_2Cl$ or MeCN gave a small amount of the $[P(CCl_3)Cl_5]^-$ ion.[17] When the reaction was performed in a 1:1 molar ratio in $PhNO_2$, attempts to isolate the adduct failed, because of the forcing conditions required to remove the high-boiling solvent. When it was removed in vacuo, a cream solid was obtained, but its ^{31}P spectrum in $PhNO_2$ gave a signal at -298.3 p.p.m., readily assigned to the $[PCl_6]^-$ ion.[18] Hence the P—C bond in $[P(CCl_3)Cl_5]^-$ is unstable to this treatment. It has been reported that $P(CCl_3)Cl_4$ is unstable at high temperatures, decomposing in a sealed tube to CCl_4 and PCl_3,[19] which again requires the scission of a P—C bond. Attempts to carry out the preparation in other solvents, including $MeNO_2$ and MeCN, were unsuccessful, with decomposition to $P(CCl_3)Cl_2$ ($\delta^{31}P$

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TABLE I

$\delta^{31}P$ (p.p.m.) for perchloroalkyl-chlorophosphoranes and their Lewis acid derivatives

Compound	$\delta^{31}P$	Lit.	Ref
$P(CCl_3)Cl_4$	-19.9 (CH_2Cl_2)	-18.6 (PhH), -19.8($PhNO_2$), -20.1 ($MeNO_2$)	7
$[P(CCl_3)Cl_3][SbCl_6]$	104.5 ($PhNO_2$), 99.7 (solid)	103.9 ($PhNO_2$), 103.3 ($MeNO_2$)	7
$[P(CCl_3)Cl_3][BCl_4]$	105.2 ($PhNO_2$), 102.9 (solid)	-	-
$[P(CCl_3)Cl_3][ICl_4]$	96.5 ($PhNO_2$)	-	-
$P(CCl_3)_2Cl_3$	29.0 ($PhNO_2$), 32.2 (CH_2Cl_2), 33.8 (solid)	31.3 (PhH), 29.3 ($PhNO_2$)	7
$[P(CCl_3)_2Cl_2][SbCl_6]$	149.0 ($PhNO_2$)	148.9 ($PhNO_2$), 148.4 ($MeNO_2$)	7
$P(C_2Cl_5)Cl_4$	-19.3 ($PhNO_2$), -17.7 (CH_2Cl_2)	-	-
$[P(C_2Cl_5)Cl_3][SbCl_6]$	112.4 ($PhNO_2$), 109.4 (solid)	-	-
$[P(C_2Cl_5)Cl_3][ICl_4]$	112.6 ($PhNO_2$), 112.6 (solid)	-	-

TABLE II

$\delta^{31}P$ (p.p.m.) for six-coordinate derivatives of $P(CCl_3)Cl_4$

Compound	$\delta^{31}P$
$[NPr_4][P(CCl_3)Cl_5]$	-196.6 ($PhNO_2$)
$[P(CCl_3)Cl_3$ phen$][SbCl_6]$	-132.2 ($PhNO_2$)
$[P(CCl_3)Cl_3$ bipy$][SbCl_6]$	-131.9 ($PhNO_2$)

149.6 p.p.m.) occurring in MeCN, but there seems no doubt that the $[P(CCl_3)Cl_5]^-$ ion can be formed in solution, given a suitable cation and solvent. This is confirmed by the successful synthesis of cyano-derivatives of this ion.[16]

The phosphorane showed no acceptor properties towards the bidentate pyridine bases 1,10-phenanthroline (phen) or 2,2'-bipyridine (bipy) in either CH_2Cl_2 or $PhNO_2$, the ^{31}P n.m.r. spectrum remaining unchanged in all instances. When liquid pyridine was added to a solution of $P(CCl_3)Cl_4$ in CH_2Cl_2, a new peak was detected at −46.6 p.p.m., as well as a resonance from the hydrolysis product $P(CCl_3)(O)Cl_2$ at 32.2 p.p.m. The new signal was attributed to the adduct $P(CCl_3)Cl_4 \cdot py$, partially dissociated in solution. The solid isolated from a 1:1 reaction when re-dissolved in $PhNO_2$ gave a broad peak at −39.0 p.p.m., again showing the occurrence of dissociation in solution. The phosphorane $P(CCl_3)Cl_4$ thus shows some acceptor properties towards Lewis bases, but these are weaker than those observed for $PMeCl_4$,[2] $PPhCl_4$[1] or $P(C_6F_5)Cl_4$.[4]

The compound $[P(CCl_3)Cl_3][SbCl_6]$ gave a strong band at 340 cm^{-1} in its i.r. spectrum, assigned to a vibration of the $[SbCl_6]^-$ ion.[20] No ^{35}Cl n.q.r. signals were detected at 77, 195 or 298 K. When a small amount of dry phen was added to a solution of the salt in $PhNO_2$, new resonances were observed at 147.0 ($P(CCl_3)Cl_2$), and −127.0 p.p.m., the latter signal ascribed to one of the two possible isomers of $[P(CCl_3)Cl_3\ phen]^+$. The complex was isolated from a 1:1 reaction, and gave a single signal at −132.2 p.p.m. when redissolved in $PhNO_2$, confirming that one isomer of the cation is formed preferentially (Table II). The shift is similar to those observed for other ions of the type $[PRCl_3\ phen]^+$ (R = Ph,[1] Me,[2] Et[2] or C_6F_5[4]), although in these systems both possible isomers were detected. The compound $[P(C_6F_5)Cl_3\ phen]^+$ $[SbCl_6]^-$ showed the presence of only one isomer when it was re-dissolved in $PhNO_2$, however,[4] so that strongly electron-withdrawing organo-groups may exert a directing effect on the formation of a particular isomer. A similar 1:1 complex was formed with bipy, which when re-dissolved in $PhNO_2$ gave a ^{31}P signal at −131.9 p.p.m. (Table II), again attributed to preferential formation of one of the two possible isomers of the $[P(CCl_3)Cl_3\ bipy]^+$ ion. A strong, broad band for the $[SbCl_6]^-$ ion at 340 cm^{-1} was apparent in the i.r. spectra[20] of both complexes.

The salt $[P(CCl_3)Cl_3][BCl_4]$ gave ^{11}B resonances at −11.2 ($PhNO_2$) and −10.1 (solid state) p.p.m., in good agreement with literature data for the $[BCl_4]^-$ ion.[21-23] A broad band at 650 cm^{-1} in its i.r. spectrum was assigned to a vibration of the BCl_4^- ion.[24] At 77 K, ^{35}Cl n.q.r. signals were detected from each type of chlorine. The CCl_3 group gave three equally intense signals at 41.330, 41.480 and 41.645 MHz. Two resonances attributed to Cl bound to P were observed at 31.600 and 31.950 MHz., in a 2:1 intensity ratio, and four equally intense signals were seen for Cl bound to B, at 20.825, 20.925, 21.367 and 21.550 MHz. Hence the only symmetry apparent at 77 K from the n.q.r. results was the equivalence of two of the chlorines bound to phosphorus. No signals were detected at room temperature. Attempts to form adducts with phen or bipy were unsuccessful, and the only ^{31}P solution signals detected when the bases were added separately to a solution of the salt in CH_2Cl_2 were readily attributable to $P(CCl_3)Cl_4$. The reactions thus appear to follow the course:

$$[P(CCl_3)Cl_3]^+BCl_4^- + L \rightarrow P(CCl_3)Cl_4 + [BCl_2L]^+Cl^- \qquad (2)$$

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(L = phen or bipy)
This conclusion was supported by the ^{11}B spectrum of a solution from the reaction with bipy, which gave a resonance at −10.1 p.p.m., in excellent agreement with the value recorded for $[BCl_2\ bipy]^+Cl^-$.[25] In view of these reactions, the acceptor properties of $[P(CCl_3)Cl_3][ICl_4]$ were not investigated; this compound gave a broad band at 260 cm^{-1} in its i.r. spectrum, ascribed to a vibration of the $[ICl_4]^-$ ion.[26]

(b) *Acceptor Properties of $P(CCl_3)_2Cl_3$ and of the $[P(CCl_3)_2Cl_2]^+$ Ion*

The phosphorane $P(CCl_3)_2Cl_3$ has been prepared previously in poor yield by chlorination of tetramethyldiphosphine disulphide,[27] and in higher yield by chlorination of $P(ClCH_2)_3$.[28] At 77 K three equally intense ^{35}Cl n.q.r. signals were seen,[7,15] at 39.749, 39.609 and 29.458 MHz, the first two assigned to C—Cl and the last one to P—Cl, thus indicating that both CCl_3 groups occupy axial positions. It is a white crystalline solid, stable to air and moisture, which indicates remarkable stability for P—Cl bonds in a five-coordinate phosphorus compound. It was prepared more conveniently in the present work by exhaustive chlorination of PMe_2Cl_3.[2] The n.m.r. data (Table I) confirm its molecular structure in both solution and solid state. It showed no acceptor properties towards the chloride ion (with NEt_4Cl or NPr_4Cl as the chloride ion source) in either CH_2Cl_2 or $PhNO_2$. Similarly it exhibited no tendency to form six-coordinate adducts with either bidentate (phen, bipy) or unidentate (py) pyridines, although its limited solubility in most solvents made the investigation of its properties more difficult.

No ^{35}Cl n.q.r. signals were detected from the compound $[P(CCl_3)_2Cl_2][SbCl_6]$ at 77, 195 or 298 K. When a small amount of phen was added to a solution of the salt in $PhNO_2$, no six-coordinate phosphorus species were apparent in the ^{31}P n.m.r. spectrum, but two signals were seen at 35.4 (ms) and 32.2 (s) p.p.m. A precipitate formed when more phen was added. It thus seems probable that the reaction

$$[P(CCl_3)_2Cl_2]^+[SbCl_6]^- + \text{phen} \rightarrow P(CCl_3)_2Cl_3 + SbCl_5.\text{phen} \qquad (3)$$

occurs. The two signals are interesting, and could arise from two of the three possible isomers of $P(CCl_3)_2Cl_3$. As shown by ^{35}Cl n.q.r.,[15] the stable isomer at 77 K is the one with both CCl_3 groups axial, and the stronger resonance at 32.2 p.p.m. is attributed to this form. It is possible that in solution another metastable isomer, probably with one CCl_3 group axial and the other equatorial, may be formed from the Ψ-tetrahedral $[P(CCl_3)_2Cl_2]^+$ cation. A stoichiometric reaction yielded a solid, which appeared to be a mixture of $P(CCl_3)_2Cl_3$ and $SbCl_5$.phen. This gave a single ^{31}P resonance at 30.9 p.p.m. when re-dissolved in $PhNO_2$, assigned to the normal isomer of the phosphorane. A similar reaction to (3) was observed between $[P(C_6F_5)_2Cl_2][SbCl_6]$ and phen.[4] Comparable behavior occurred with bipy, which showed no evidence for formation of six-coordinate complexes, but gave a signal at 30.3 p.p.m. in $PhNO_2$ from the phosphorane, and one at 14.5 p.p.m., possibly from impurities.

Attempts to prepare salts with the Lewis acids BCl_3 and ICl_3 were unsuccessful, the phosphorane being recovered unchanged in both instances. Hence a very strong Lewis acid is required to remove a chlorine from $P(CCl_3)_2Cl_3$, and the presence of

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the electronegative CCl_3 groups confers considerable stability on the trigonal bipyramidal structure, as also observed by Dmitriev *et al.*[7]

(c) Acceptor Properties of $P(C_2Cl_5)Cl_4$ and of the $[P(C_2Cl_5)Cl_3]^+$ Ion

The phosphorane $P(C_2Cl_5)Cl_4$ had not been described previously; it was prepared as a white solid by exhaustive chlorination of $PEtCl_4$. The n.m.r. shifts (Table I) are in agreement with a molecular Ψ-tbp structure. The compound decomposed in the spectrometer when an attempt was made to record its solid state spectrum, giving several different phosphorus species, including some with no P—C bond such as PCl_3 and PCl_6^-. Similar decompositions have been observed for compounds containing P—CCl_3 groups.[19,29]

When NEt_4Cl was added to a solution of the phosphorane in $PhNO_2$, a ^{31}P signal at 146.3 p.p.m. was observed, and was identified as arising from $P(C_2Cl_5)Cl_2$. Hence decomposition to phosphorus (III) species takes place. When the reaction was performed in CH_2Cl_2, however, a new resonance at -168.9 p.p.m. was recorded (Table III), attributed to the ion $[P(C_2Cl_5)Cl_5]^-$. This anion was unstable, and the signal disappeared on the addition of more chloride, which caused decomposition to $P(C_2Cl_5)Cl_2$ (δ 148.0 p.p.m.). Support for the assignment of the new peak to the six-coordinate anion is provided by using the correlation between the ^{31}P shift difference (Δ_1) between A^+ and AX (the quasi-phosphonium salt and phosphorane) and that (Δ_2) between A^+ and AX_2^-.[30] A value of 112 p.p.m. was recorded for A^+ (Table I) in $PhNO_2$, giving a value of 131 p.p.m. for Δ_1. The predicted[30] value for Δ_2 is in the range 272 ± 10 p.p.m., giving a shift for AX_2^- of -160 ± 10 p.p.m. Nevertheless it is not certain whether the true 'limiting shift' for the $[P(C_2Cl_5)Cl_5]^-$ ion was established in this experiment. NPr_4Cl gave only decomposition products, including $P(C_2Cl_5)Cl_2$ and PCl_6^-, in CH_2Cl_2 or $PhNO_2$, showing the inherent instability of the P—C bond.

Acceptor properties were also displayed towards bidentate pyridines. A 1:1 reaction between the phosphorane and phen in CH_2Cl_2 caused immediate precipitation; the product was sparingly soluble in $PhNO_2$, but a weak resonance at -138.5 p.p.m. was discerned (Table III), and assigned to one of the two possible isomers of the $[P(C_2Cl_5)Cl_3 \text{ phen}]^+$ cation. A similar reaction was observed with bipy, but in this instance the product was insoluble in all common solvents, and no solution spectrum could be obtained. I.r. frequencies between 800 and 200 cm^{-1} (Table IV) are in accordance with formulation of these compounds as new six-coordinate complexes, rather than mixtures of the starting materials. The strong bands at 595 and 560 cm^{-1} observed in the i.r. spectrum of $P(C_2Cl_5)Cl_4$, for example, are absent in the spectra of the complexes.

The hexachloroantimonate gave the expected strong, broad i.r. band[20] at 340 cm^{-1}. When phen was added to a $PhNO_2$ solution of the salt, a new strong resonance at -135.5 p.p.m. was discerned, attributed to one of the isomers of $[P(C_2Cl_5)Cl_3 \text{ phen}]^+$ (Table III). As in other systems in the present work, one isomer seems to form preferentially. A quantitative (1:1) reaction was attempted, but the ^{31}P n.m.r. spectrum showed some unreacted $[P(C_2Cl_5)Cl_3]^+$, giving a weak signal at 112.5 p.p.m., as well as stronger resonances from the six-coordinate cation (-135.5 p.p.m.) and the hydrolysis product $P(C_2Cl_5)(O)Cl_2$ (40.8 p.p.m.). Con-

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TABLE III

$\delta^{31}P$ (p.p.m.) for six-coordinate derivatives of $P(C_2Cl_5)Cl_4$

Compound	$\delta^{31}P$
$[NEt_4][P(C_2Cl_5)Cl_5]$	− 168.9 (CH_2Cl_2)
$[P(C_2Cl_5)Cl_3\ phen]Cl$	− 138.5 ($PhNO_2$)
$[P(C_2Cl_5)Cl_3\ phen][SbCl_6]$	− 135.5 ($PhNO_2$)

TABLE IV

I.R. frequencies for $P(C_2Cl_5)Cl_4$ and derivatives (800-200 cm^{-1})

Compound	I.R. Frequencies
$P(C_2Cl_5)Cl_4$	785w, 655m,br, 595s, 560s, 555sh, 505s, 440sh, 420s, 390m, 350m
$[P(C_2Cl_5)Cl_3][SbCl_6]$	650s,br, 565s, 465m, 340s,br[a]
$[P(C_2Cl_5)Cl_3][ICl_4]$	750sh, 650s,br, 590m, 465m, 385w, 335m, 250s,br[a]
$[P(C_2Cl_5)Cl_3phen]Cl$	770w, 750s, 705s, 655m, 620m, 540s, 525m, 505sh, 500s, 480s, 465sh, 440s,br, 415sh, 350m, 290w
$[P(C_2Cl_5)Cl_3bipy]Cl$	760s, 650w, 620m, 610m, 590m, 540w, 440s,br, 340m

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sequently the complex could not be prepared in a pure state. When bipy was used in a similar reaction, a suspension was formed as soon as the ligand was added, and no solution signals could be obtained in either $PhNO_2$ or MeCN. There is thus no definite proof of the formation of $[P(C_2Cl_5)Cl_3\ bipy][SbCl_6]$, but in view of the results for phen, and the reactions of the phosphorane itself with these ligands, complexation seems highly probable.

An attempt to form a tetrachloroborate did not result in a pure compound, since the cation signal at 112.1 p.p.m. in $PhNO_2$ was accompanied by other weaker resonances at 87.7 (possibly PCl_4^+), 80.2 (unassigned) and 41.1 ($P(C_2Cl_5)(O)Cl_2$) p.p.m. When the product was washed with CH_2Cl_2 and re-dissolved in $PhNO_2$, signals were detected at 220.2 w (PCl_3), 112.6 s ($[P(C_2Cl_5)Cl_3]^+$) and 83.3 m (possibly $[PCl_4]^+$) p.p.m. Hence reactions involving the breaking of the P—C bond take place, and the coordination chemistry of this salt was not investigated. It proved possible to isolate the yellow tetrachloroiodate from CH_2Cl_2 solution, although this compound was unstable at room temperature and rapidly turned to a dark orange liquid. It could be stored without decomposition at low temperature, however. Its coordination chemistry was not investigated in view of its instability.

(d) General Conclusions

It is not easy to compare the acceptor properties of $P(CCl_3)Cl_4$ and $P(C_2Cl_5)Cl_4$ because of the ready scission of the P—C bond in the latter system. A solution-stable anion $[PRCl_5]^-$ was formed by $P(CCl_3)Cl_4$ with NPr_4Cl in $PhNO_2$, the choice of cation and solvent being critical. $P(C_2Cl_5)Cl_4$ gave a similar derivative with NEt_4Cl in CH_2Cl_2, but this was not stable to decomposition. The bidentate pyridine

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bases did not yield adducts with $P(CCl_3)Cl_4$, indicating the stability of the five-coordinate form, although a pyridine adduct, partially dissociated in solution, was obtained. The phosphorane $P(C_2Cl_5)Cl_4$ gave six-coordinate complexes $[P(C_2Cl_5)Cl_3L]^+Cl^-$ with bipy and phen, and these complexes could be isolated. Where solution spectra were obtainable, one of the two possible isomers appeared to form preferentially. The hexachloroantimonates $[PRCl_3]^+[SbCl_6]^-$ ($R = CCl_3$ or C_2Cl_5) yielded similar six-coordinate complexes with bipy and phen, but these could not be isolated in a pure state when $R = C_2Cl_5$. Both phosphoranes produced salts with ICl_3, but a discrete tetrachloroborate was obtained only from $P(CCl_3)Cl_4$. No acceptor properties towards Lewis bases were shown by $P(CCl_3)_2Cl_3$ or its derivative $[P(CCl_3)_2Cl_2]^+[SbCl_6]^-$, the five-coordinate phosphorane being particularly stable in this instance, even to air and water. Indeed the cation reacts with bipy or phen (L) with formation of the phosphorane and the $SbCl_5.L$ complex, while both BCl_3 and ICl_3 failed to remove a chlorine from $P(CCl_3)_2Cl_3$. These results suggest that the order of Lewis basicities of the phosphoranes (to removal of a Cl^- ion) is $P(CCl_3)Cl_4 > P(C_2Cl_5)Cl_4 > P(CCl_3)_2Cl_3$, and that the strengths of the Lewis acids used follow the sequence $SbCl_5 > ICl_3 > BCl_3$.

The replacement of an alkyl group such as Me or Et by a perchloroalkyl group reduces considerably the strength of the P—C bond, and favors the five-coordinate (phosphorane) structure over the four-coordinate (quasi-phosphonium salt) structure adopted by alkylchlorophosphoranes. More stable six-coordinate derivatives are formed by the simple mono-alkyl species $PRCl_3{}^+Cl^-$, but this is not surprising in view of the positive charge on phosphorus, which should make it a stronger Lewis acid. While the presence of electronegative groups (CCl_3, C_2Cl_5) should help to stabilize anionic six-coordinate complexes $[PRCl_5]^-$ by helping to delocalize the formal negative charge on phosphorus, this effect is countered by the instability of the P—C bond in these systems, making isolation of the complexes in a pure state not possible under our experimental conditions.

As in arylchorophosphoranes, electronegative substituents tend to take up axial positions in the Ψ-tbp structures. ^{35}Cl n.q.r. evidence shows clearly that the CCl_3 groups in both $P(CCl_3)Cl_4$ and $P(CCl_3)_2Cl_3$ occupy axial sites at 77 K,[15] just like the C_6F_5 group in $P(C_6F_5)Cl_4$,[31] whereas the phenyl group in $PPhCl_4$ occupies an equatorial position.[10] Interestingly, a second, metastable isomer of $P(CCl_3)_2Cl_3$ may have been formed in the reaction of $[P(CCl_3)_2Cl_2][SbCl_6]$ with phen in $PhNO_2$. The introduction of a more electronegative aryl group has been shown to enhance the acceptor properties of an arylchlorophosphorane,[4] whereas in the present work the introduction of a more electronegative alkyl group has the opposite effect. Since this also causes a change in structure of the phosphorane itself, however, these deductions are not contradictory.

EXPERIMENTAL

All manipulations, including n.m.r., i.r. and n.q.r. sample preparation, were carried out either under an inert atmosphere of dry nitrogen or in vacuo. Solvents were degassed on the vacuum line to remove any oxygen present, and stored over molecular sieves. Tetraalkylammonium salts were dried as described in earlier work.[5] The compound $P(CCl_3)Cl_4$ was prepared from $PMeCl_2$ by a slight modification of the method of Quin and Rolston,[6] which yields $P(CCl_3)Cl_2$ as the product, following reduction by $P(OMe)Cl_2$ of the initially formed phosphorane. The reaction was carried out in CH_2Cl_2 solvent, and the white slurry which resulted was heated at 333–343 K until fully dissolved, before chlorine gas was allowed to flow into the solution. This was continued until a clear yellowish solution was obtained. The solvent and excess Cl_2 were removed in vacuo to yield a fine white solid. ^{31}P n.m.r. data for the phosphoranes and their Lewis acid derivatives prepared in the present work are given in Table I, together with literature values where available. The compound $P(CCl_3)_2Cl_3$ was similarly prepared from PMe_2Cl_3.[2] In this instance the starting material was only partially soluble in the solvent medium, and Cl_2 gas was allowed to flow into the slurry until a clear greenish-yellow solution formed. The product was isolated as above as a fine white solid. The phosphorane $P(C_2Cl_5)Cl_4$ was similarly prepared by chlorination of $P(Et)Cl_4$, and was isolated as a white solid.

Hexachloroantimonates were prepared by dissolving the phosphorane in CH_2Cl_2, and adding an equimolar amount of $SbCl_5$, with constant stirring. The mixtures were left to stir for a few minutes more to complete the reaction, and the solid products were either filtered off if a precipitate had formed ($P(CCl_3)_nCl_{5-n}$, n = 1 or 2), or the solvent was removed in vacuo ($P(C_2Cl_5)Cl_4$). The compounds were washed with a little CH_2Cl_2 and pentane, and dried in vacuo or in a dry nitrogen atmosphere. The salt $[P(CCl_3)Cl_3]^+[BCl_4]^-$ was obtained by dissolving the phosphorane in CH_2Cl_2 and allowing BCl_3 gas to flow in, with constant stirring, until a white precipitate formed. After a further 10 min. of stirring, the product was filtered off and washed with CH_2Cl_2. Similar preparative procedures were used in attempts to obtain tetrachloroborates from $P(CCl_3)_2Cl_3$ and $P(C_2Cl_5)Cl_4$, but in neither case was the desired product obtained in a pure state. These reactions are discussed in more detail in the Results and Discussion section. Tetrachloroiodates were prepared from $P(CCl_3)Cl_4$ and $P(C_2Cl_5)Cl_4$ by treating a solution of the phosphorane in CH_2Cl_2 with an equimolar amount of ICl_3, with constant stirring. A yellowish precipitate formed with $P(CCl_3)Cl_4$, and was isolated as above. The solvent was removed in vacuo after 15 min. stirring to yield the yellow derivative of $P(C_2Cl_5)Cl_4$. No reaction was observed between $P(CCl_3)_2Cl_3$ and ICl_3, and the phosphorane was recovered unchanged.

$[P(CCl_3)Cl_3\,phen][SbCl_6]$. To a suspension of $[P(CCl_3)Cl_3][SbCl_6]$ in CH_2Cl_2 was added an equimolar quantity of 1,10-phenanthroline (phen), with stirring. A yellow solution formed initially, followed quickly by the precipitation of a yellow solid. The solvent was removed in vacuo, then the solid was washed with pentane and dried under N_2.

$[P(CCl_3)Cl_3\,bipy][SbCl_6]$. This complex was similarly prepared from $[P(CCl_3)Cl_3][SbCl_6]$ and 2,2′-bipyridine (bipy). The reaction mixture was left to stir for 1 h. before isolation of the solid product.

$P(CCl_3)Cl_4.py$. $P(CCl_3)Cl_4$ was dissolved in CH_2Cl_2, and an equimolar amount of liquid pyridine was added dropwise, with constant stirring for a further 30 min. Solvent removal in vacuo yielded an off-white solid.

$[P(C_2Cl_5)Cl_3\,phen]Cl$. $P(C_2Cl_5)Cl_4$ was dissolved in CH_2Cl_2, and an equimolar quantity of solid phen was added to the solution, with stirring. After a few minutes, the precipitate which formed was filtered off and washed with CH_2Cl_2 to yield a fine white solid.

$[P(C_2Cl_5)Cl_3\,bipy]Cl$. This complex was similarly prepared from equimolar amounts of $P(C_2Cl_5)Cl_4$ and bipy.

Phosphorus-31 and boron-11 n.m.r. spectra were recorded at 307.2 K on a Fourier transform spectrometer, as described previously.[8] Chemical shifts were measured relative to external 85% H_3PO_4 and $B(OMe)_3$ respectively, with the higher frequency (downfield) direction taken as positive. I.r.[2] and n.q.r.[9,10] spectra were obtained as in earlier work.

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