Solid-state Phosphorus-31 Nuclear Magnetic Resonance and Chlorine-35 Nuclear Quadrupole Resonance Studies of some Alkyl- and Aryl-chlorophosphoranes and their Addition Compounds with Lewis Acids

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The ^{31}P n.m.r. and ^{35}Cl n.q.r. spectra (where observable) of a number of solid methyl-, ethyl- and phenyl-chlorophosphoranes and of their ionic 1 : 1 adducts with Lewis acids X, such as PCl_5, $SbCl_5$, BCl_3, $AlCl_3$, or ICl, have been recorded. The results show that the compounds PMe_nCl_{5-n} ($1 \leqslant n \leqslant 3$), PEt_2Cl_3, PEt_3Cl_2, and PPh_3Cl_2 have ionic structures of the type $[PR_nCl_{4-n}]Cl$ in the solid state, whereas PPh_2Cl_3 and $PPhCl_4$ are molecular. The adducts all have structures of the type $[PR_nCl_{4-n}][XCl]$. The symmetries of the species present are discussed.

ARYL- and alkyl-halogenophosphoranes, PR_nX_{5-n}, are of considerable interest since various alternative structures are possible. The compounds may be molecular trigonal bipyramids, as found for PF_5, they may be ionic with the structure $[PR_nX_{4-n}][PR_nX_{6-n}]$, as in the ionic form of PCl_5, or they may have the simpler phosphonium salt structure $[PR_nX_{4-n}]X$, as in solid PBr_5. ^{35}Cl N.q.r. and ^{31}P n.m.r. spectroscopy are potentially powerful and complementary techniques for solid-state structure determinations of phosphorus chloro-compounds, as shown previously for hexachlorophosphates.[1] High-resolution solid-state ^{31}P n.m.r. spectroscopy has also shown that PBr_2Ph_3 and PPh_3I_2 have phosphonium-salt structures.[2]

Solution studies of chlorophenylphosphoranes have led to confusing and sometimes contradictory structural conclusions,[3-7] partly because the presence of impurities such as HCl or chlorine, or indeed a change of solvent, may cause changes, and partly because labile equilibria between the ionic and covalent forms may occur, as shown by the most recent work of Denney *et al.*[7] Whitehead and his co-workers[8,9] observed two ^{35}Cl n.q.r. signals of equal intensity at 77 K for solid $PPhCl_4$, at 33.58 and 33.74 MHz, and one line only for PPh_2Cl_3, at 33.45 MHz. They therefore concluded that these compounds possess ionic structures $[PPh_nCl_{4-n}]Cl$. Svergun *et al.*[10] observed further ^{35}Cl n.q.r. frequencies, at 25.51 and 24.61 MHz for $PPhCl_4$ and at 22.34 MHz for PPh_2Cl_3, and assigned these to the axial chlorines of a trigonal-bipyramidal structure, the lines seen by Whitehead being ascribed to the equatorial chlorines. The compounds were thus deduced to be molecular, with the phenyl groups occupying equatorial sites.

We have re-examined the ^{35}Cl n.q.r. spectra of these compounds and confirm the results of Svergun. The spectroscopic investigations have been extended to PPh_3Cl_2, for which no ^{35}Cl n.q.r. signals were observable, and to ionic adducts of the chlorophenylphosphoranes with Lewis acids. A preliminary account of some of the n.q.r. results has been given.[11] The chloromethylphosphorane series PMe_nCl_{5-n} ($1 \leqslant n \leqslant 3$) and the ethyl analogues PEt_2Cl_3 and PEt_3Cl_2, together with some Lewis-acid derivatives, have also been studied. Previous workers had deduced from vibrational-spectroscopic measurements that $PMeCl_4$,[12,13] PMe_2Cl_3,[12] and PMe_3Cl_2[14] have ionic structures in the solid state, although a molecular structure for $PMeCl_4$ is possible in solution.[13] The symmetries of the species present, as deduced from the n.q.r. results, are discussed.

EXPERIMENTAL

All manipulations were made under an atmosphere of dry nitrogen. Chemicals of the best available commercial grade were used, in general without further purification, except as described below. Triphenylphosphine was recrystallised from acetone, and dichlorophenylphosphine was redistilled before use. Aluminium chloride was purified by sublimation. The compounds $PPhCl_4$, PPh_2Cl_3, and PEt_3Cl_2 were prepared by chlorination of the corresponding phosphine with dry gaseous chlorine in a solvent such as methylene chloride or carbon tetrachloride. After removal of excess of solvent, the solid was filtered in an inert-atmosphere box, washed with low-boiling light petroleum (except for $PPhCl_4$ which was soluble in this medium), and dried *in vacuo*; PPh_2Cl_3 was also prepared by chlorination of chlorodiphenylphosphine with a stoicheiometric quantity of phosphorus(V) chloride.[15] Considerable difficulty was experienced in obtaining a sample of PPh_3Cl_2. The chlorination of PPh_3 by gaseous chlorine in chlorocarbon solvents invariably produced compounds containing more chlorine and less carbon and phosphorus than required by the formula. At first this was ascribed to the uptake of more chlorine to give PPh_3Cl_4, formulated as $[PPh_3Cl]Cl_3$, or a mixture of this compound with PPh_3Cl_2. The white solids isolated did not lose chlorine on strong pumping *in vacuo* at room temperature, however, in contrast with the known properties of compounds containing the tri-

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chloride ion.[16] The solids did lose weight on heating and pumping, with a corresponding decrease in the chlorine percentage, but chlorine loss continued beyond the PPh_3Cl_2 stage, presumably because of decomposition, making control difficult. The ^{35}Cl n.q.r. spectrum of a solid isolated from carbon tetrachloride solution was then recorded, and showed two doublets, one on each side of the normal range of frequencies for CCl_4,[17] in addition to a signal from $[PPh_3Cl]^+$ (Results section). Elemental analyses for PPh_3Cl_4 and $PPh_3Cl_2{\cdot}0.5CCl_4$ were very similar, but the n.q.r. results provide clear evidence for the presence of carbon tetrachloride in the lattice. Claims in the early literature [18,19] for the preparation of PPh_3Cl_2 by direct chlorination in chlorocarbon solvents may well be in error, since the usual method of identification was to hydrolyse the compound to PPh_3O, which was then characterised. This hydrolysis product would be expected in any case, whether solvent was present in the compound or not. Attempts to prepare PPh_3Cl_2 from the action of chlorine on PPh_3 dissolved in nitrobenzene also gave products containing 24—25% chlorine, presumably because of some trichloride formation. The compound PPh_3Cl_2 was finally obtained by reaction of PPh_3 with phosphorus(V) chloride (1 : 1) in nitrobenzene.[15]

Tetrachloromethylphosphorane was synthesised by reduction of the complex $[PMeCl_3][AlCl_4]$ according to the procedure of Komkov *et al.*,[20] followed by chlorination of the $PMeCl_2$ thus produced. The complex itself and the corresponding ethyl compound were prepared by the method of Parshall.[21] Dialkyltrichlorophosphoranes were produced by chlorination of tetra-alkyldiphosphine disulphides, $R_2(S)PP(S)R_2$.[12,22] Dichlorotrimethylphosphorane was prepared by reaction of thionyl chloride with trimethylphosphine oxide,[14,23] produced from methylmagnesium bromide and freshly distilled phosphorus oxychloride.[24]

Tetrachloroborates were obtained by treating a solution or suspension of the phosphorane in methylene chloride with a slight excess of BCl_3, previously weighed into a cooled ampoule with a Rotaflo valve. After removal of solvent and excess of BCl_3, the compounds were washed with low-boiling light petroleum and dried *in vacuo* when necessary. The i.r. spectra of the compounds contained the expected broad bands for the tetrachloroborate ion in the 660—700 cm^{-1} region.[25] Hexachloroantimonates were obtained either by reaction between the stoicheiometric quantities of phosphorane and antimony(V) chloride, or by direct reaction of 2 mol of antimony(V) chloride with 1 mol of the corresponding phosphine according to the method of Ruff.[26] Hexachlorophosphate derivatives of the chlorophenylphosphoranes were prepared directly from the phosphines by reaction with 2 mol of PCl_5.[15,27] Chlorotriphenylphosphonium tetrachloroaluminate was obtained from the stoicheiometric quantities of PPh_3Cl_2 and $AlCl_3$ in nitrobenzene solution. The complex was precipitated by addition of a large quantity of dry diethyl ether, separated, washed with light petroleum, and dried *in vacuo*. Dichloroiodates were prepared by treating a slurry of the

TABLE 1

Elemental analysis (%)

Compound	Found					Calc.				
	C	H	P	Cl	I	C	H	P	Cl	I
$PPhCl_4$	28.45	2.50	12.45	55.0		28.85	2.00	12.4	56.75	
$[PPhCl_3][BCl_4]$	19.35	2.20	8.40	67.0		19.65	1.35	8.45	67.6	
$[PPhCl_3][SbCl_6]$	12.35	1.45	5.40	56.9		13.15	0.90	5.65	58.15	
$[PPhCl_3][PCl_6]$	16.05	1.40	13.8	69.5		15.75	1.10	13.5	69.65	
PPh_2Cl_3	48.95	4.15	11.10	37.0		49.45	3.45	10.6	36.50	
$[PPh_2Cl_2][BCl_4]$	33.95	2.30	7.80	51.3		35.25	2.45	7.60	52.05	
$[PPh_2Cl_2][SbCl_6]$	23.5	1.70	5.15	47.6		24.4	1.70	5.25	48.05	
$[PPh_2Cl_2][PCl_6]$	28.4	1.90	12.65	56.7		28.85	2.00	12.4	56.75	
PPh_3Cl_2	64.7	4.65	9.10	20.6		64.9	4.55	9.30	21.3	
$PPh_3Cl_2{\cdot}0.5CCl_4$	54.45	3.90	8.35	34.5		54.2	3.70	7.55	34.6	
$[PPh_3Cl][BCl_4]$	48.7	3.45	6.85	39.6		48.0	3.35	6.90	39.35	
$[PPh_3Cl][SbCl_6]$	33.85	2.85	4.95	39.2		34.2	2.40	4.90	39.25	
$[PPh_3Cl][AlCl_4]$	45.95	3.60	6.25	36.65		46.35	3.25	6.65	38.0	
$PMeCl_4$	6.30	2.25	16.4	75.05		6.40	1.60	16.5	75.5	
$[PMeCl_3][AlCl_4]$	3.40	1.00	9.25	77.45		3.75	0.95	9.65	77.25	
$[PMeCl_3][ICl_2]$	3.00	1.30	9.40	50.4	36.3	3.45	0.85	8.85	50.6	36.25
PMe_2Cl_3	14.35	3.50	19.1	63.4		14.35	3.60	18.5	63.55	
$[PMe_2Cl_2][BCl_4]$	8.45	2.10	11.55	75.2		8.45	2.15	10.9	74.75	
$[PMe_2Cl_2][SbCl_6]$	5.54	1.40	6.65	61.7		5.15	1.30	6.65	60.8	
$[PMe_2Cl_2][ICl_2]$	7.00	2.15	9.90	42.4	37.6	7.30	1.85	9.40	43.0	38.5
PMe_3Cl_2	24.2	6.35	21.4	47.55		24.5	6.15	21.05	48.25	
$[PMe_3Cl][BCl_4]$	14.05	3.20	11.65	65.0		13.65	3.45	11.75	67.1	
$[PMe_3Cl][ICl_2]$	11.9	3.30	9.90	34.45	41.05	11.65	2.95	10.0	34.4	41.0
$[PEtCl_3][AlCl_4]$	7.05	1.85	8.95	73.45		7.15	1.50	9.25	74.05	
PEt_2Cl_3	24.3	5.55	15.55	54.5		24.6	5.15	15.85	54.4	
$[PEt_2Cl_2][BCl_4]$	15.95	3.30	9.65	65.05		15.35	3.20	9.90	68.05	
PEt_3Cl_2	38.5	8.05	16.05	37.35		38.1	8.00	16.4	37.5	
$[PEt_3Cl][BCl_4]$	23.6	4.60	9.30	56.9		23.55	4.95	10.1	57.9	

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TABLE 2

^{35}Cl N.q.r. frequencies for chlorophenylphosphoranes and derivatives at 77 K

Compound	$\nu(^{35}\text{Cl})$/MHz (Equatorial)	Average	$\nu(^{35}\text{Cl})$/MHz (Axial)	Average
$PPhCl_4$	33.74	33.66_5	25.51	25.06
	33.59		24.61	
PPh_2Cl_3	33.45	33.45	22.34	22.34
	$\nu(^{35}\text{Cl})$/MHz (Cation)		$\nu(^{35}\text{Cl})$/MHz (Anion)	
$[PPhCl_3][BCl_4]$	31.12	31.12	21.63	21.31
			21.09	
			20.91	
$[PPhCl_3][SbCl_6]$	31.03	31.03	24.95	24.95
$[PPh_2Cl_2][BCl_4]$	30.42	30.19	21.45	21.23
	29.96		21.22	
			21.13	
			21.10	
$[PPh_2Cl_2][SbCl_6]$	30.51	30.15	24.81	24.47
	30.45		24.62	
	30.28		24.33	
	30.14[a]		24.13	
	30.01			
	29.87			
	29.78			
$PPh_3Cl_2\cdot 0.5CCl_4$	30.12	30.12	41.39[b]	40.44[b]
			41.22	
			39.70	
			39.44	
$[PPh_3Cl][BCl_4]$	30.08	30.08	21.50	21.33
			21.37	
			21.27	
			21.18	
$[PPh_3Cl][SbCl_6]$	29.98	29.92	25.60_5	25.48
	29.86		25.49	
			25.35	
$[PPh_3Cl][AlCl_4]$	30.15	30.15	11.28	10.97
			11.07_5	
			10.85	
			10.66	
	$\nu(^{35}\text{Cl})$/MHz			
$[PPhCl_3][PCl_6]$[c]	30.90			
	30.79			
	30.68			
	30.62			
	30.1 (br, m)			
$[PPh_2Cl_2][PCl_6]$[c]	30.23 (m)			
	29.58			
	29.49			
$[PPh_3Cl][PCl_6]$[c,d]	31.15			
	30.44			
	29.93			
	29.76			
	29.59			
	29.53			
	29.33			

[a] Double intensity line. [b] CCl_4 lines. [c] Assignment difficult because cation and anion both contain P–Cl bonds. [d] See ref. 1.

phosphorane in dichloromethane with an equimolar quantity of iodine chloride. The mixture was stirred to complete reaction, and the yellow products isolated as above. Elemental analyses (C, H, P, Cl, and I) for the compounds prepared are given in Table 1.

^{31}P N.m.r. spectra (and ^{11}B spectra where appropriate) were recorded at 307.2 K on a Perkin-Elmer R10 spectrometer operating at 24.29 MHz (or 19.25 MHz for ^{11}B) with a Digiac signal-averaging accessory, using stationary sample tubes (outside diameter, 8.4 mm). The technique of high-resolution spectroscopy for solids containing ^{31}P (ref. 28) or ^{11}B nuclei [29] has been described previously. Phosphorus-31 chemical shifts were measured relative to external P_4O_6, but are quoted with respect to 85% phosphoric acid. Boron-11 chemical shifts were measured relative to external trimethyl borate. Values were reproducible to ±2 p.p.m. in most cases (see Tables 3 and 5). ^{35}Cl N.q.r. spectra were recorded at 77 K on a Decca spectrometer, using Zeeman modulation. Sideband suppression was used to aid the identification of closely spaced resonances. Samples were enclosed in glass tubes of either 13- or 24-mm outside diameter, and resonance frequencies were reproducible to better than ±10 kHz.

RESULTS AND DISCUSSION

Chlorophenylphosphoranes and their Derivatives.—The ^{35}Cl n.q.r. frequencies measured for the chlorophenylphosphoranes and their addition compounds are given in Table 2, together with the mean values averaged over all the solid-state splittings. Chlorine-35 resonances were confirmed by observation of the corresponding

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^{37}Cl lines where these were of sufficient intensity. (A preliminary account of this work has been given,[11] and the unassigned frequencies for [PPhCl$_3$][PCl$_6$] [30] and [PPh$_3$Cl][PCl$_6$] [1] have also been reported.) The results for PPhCl$_4$ and PPh$_2$Cl$_3$ are completely in accordance with those of Semin and his co-workers,[10] and we concur with their conclusions that these compounds have trigonal-bipyramidal structures with the phenyl groups occupying equatorial sites. No chlorine n.q.r. signals were observed from PPh$_3$Cl$_2$ at either 77 or 293 K, but the adduct of approximate composition PPh$_3$Cl$_2$·0.5CCl$_4$ showed a single P–^{35}Cl frequency at 30.12 MHz, compatible with an ionic structure containing [PPh$_3$Cl]$^+$ cations. Two doublets were observed in the C–Cl region (Table 2). Their displacement from the usual range of ^{35}Cl frequencies for CCl$_4$ suggests that the latter is not randomly distributed in the lattice but is associated with the chloride ions. Similar adducts of tetra-alkylammonium halides with carbon tetrahalides have been reported.[31-33] A solid-state ^{31}P n.m.r. spectrum was recorded for PPh$_3$Cl$_2$ and confirmed the ionic formulation [PPh$_3$Cl]Cl, by comparison both with the chemical shifts for other salts of this cation (Table 3), and with the expected shift for the covalent form which should be at least 11 p.p.m. from solution studies.[7]

TABLE 3

Phosphorus-31 and ^{11}B chemical shifts for solid chlorophenylphosphoranes and derivatives

Compound	δ(^{31}P)/p.p.m. (from 85% H$_3$PO$_4$)	δ(^{11}B)/p.p.m. [from B(OMe)$_3$]
PPhCl$_4$		
[PPhCl$_3$][BCl$_4$]	−101 ± 2	12.6 ± 2
[PPhCl$_3$][SbCl$_6$]	−88 ± 2	
[PPhCl$_3$][PCl$_6$]	−96.9 ± 2 296.4 ± 2 [a]	
PPh$_2$Cl$_3$		
[PPh$_2$Cl$_2$][BCl$_4$]	−93.6 ± 5	12.3 ± 1
[PPh$_2$Cl$_2$][SbCl$_6$]	−92 ± 2	
[PPh$_2$Cl$_2$][PCl$_6$]	−89.7 ± 2 294.8 ± 2 [a]	
PPh$_3$Cl$_2$	−62 ± 8	
[PPh$_3$Cl][BCl$_4$]	−81 ± 3	12 ± 1
[PPh$_3$Cl][SbCl$_6$]	−65 ± 2	
[PPh$_3$Cl][PCl$_6$] [b]	−64.3 ± 2 305 ± 3 [a]	
[PPh$_3$Cl][AlCl$_4$]	−67 ± 7	

[a] [PCl$_6$]$^-$ Ion. [b] See ref. 1.

These structural conclusions for the phosphoranes are confirmed by the results for the 1 : 1 adducts with Lewis acids (Table 2). With the exception of [PPh$_3$Cl][PCl$_6$], there is a close similarity in the average frequency for each ionic species. This is not unusual for compounds containing complex ions, since the major contribution to the electric-field gradient (e.f.g.) at a nuclear site is generated by the charge distribution within the ion itself. The observed n.q.r. frequencies are thus often insensitive to the nature of the counter ion. The additional ^{35}Cl resonances observed at lower frequency are consistent with the previously reported values for the anions [BCl$_4$]$^-$, [AlCl$_4$]$^-$, [PCl$_6$]$^-$,[1] and [SbCl$_6$]$^-$. The observed frequencies for [PPhCl$_3$][PCl$_6$] also agree very well in general with the unassigned values reported by Semin *et al.*[30]

In the case of [PPh$_3$Cl][PCl$_6$] there are two possible assignments for the resonance at 31.15 MHz. If this signal is assigned to the cation, the average frequency of the remaining resonances is 29.76 MHz, in good agreement with the average [PCl$_6$]$^-$ frequencies in other compounds which lie in the range 29.65—29.85 MHz.[1] The assignment of this resonance to the cation is not consistent, however, with the values for [PPh$_3$Cl]$^+$ in the parent compound (30.12) or in its [SbCl$_6$]$^-$ (29.92), [BCl$_4$]$^-$ (30.08), or [AlCl$_4$]$^-$ salts (30.15 MHz). The alternative possibility is that the high-frequency line is one of the signals from the hexachlorophosphate anion. Previous studies of this ion have suggested some distortion of the octahedral structure in the solid state, since up to six lines are observed.[1] The resonance at 31.15 MHz could thus conceivably arise from the presence of a considerably distorted [PCl$_6$]$^-$ ion. (The previous highest ^{35}Cl n.q.r. frequency reported for [PCl$_6$]$^-$ is 30.67 MHz.) If the resonance at 29.93 MHz is assigned to the cation, in agreement with the values for [PPh$_3$Cl]$^+$ in the other compounds, the average frequency of the remaining resonance is 29.97 MHz, in reasonable agreement with the average frequencies for [PCl$_6$]$^-$ quoted above.

The ^{31}P and ^{11}B n.m.r. chemical shifts for these compounds in the solid state are given in Table 3. Signals could not be obtained from the five-co-ordinate species PPhCl$_4$ and PPh$_2$Cl$_3$, possibly because of splitting and broadening caused by the asymmetry of the species, but were detectable for the tetrahedral and octahedral ions. Unlike the n.q.r. frequencies, there is some variation of shift with counter ion, particularly for the tetrahedral cations; this type of behaviour has been observed previously for halogenophosphonium cations in the solid state.[34] The results compare well with reported solution shifts of between −103 and −102 p.p.m. for [PPhCl$_3$]$^+$, −93.2 p.p.m. for [PPh$_2$Cl$_2$]$^+$, and between −67 and −62 p.p.m. for [PPh$_3$Cl]$^+$.[1,4,6,7] The values for the [PCl$_6$]$^-$ ion are also as expected from both solid-state and solution work (ref. 1 and refs. therein). Furthermore, the ^{11}B shifts for the [BCl$_4$]$^-$ ion are in excellent agreement with previous determinations for solids and solutions.[29,35] The ionic nature of the adducts, and of dichlorotriphenylphosphorane, is thus amply confirmed.

Table 4 summarises the symmetry information which is consistent with the ^{35}Cl n.q.r. data. Since the space groups of the compounds are unknown, some ambiguity

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is unavoidable. Columns 4 and 5 give the most probable cation and anion point symmetries, on the assumption that all resonances from crystallographically distinct chlorine atoms have been detected. The multiplets observed for $[PPh_2Cl_2][PCl_6]$ and $[PPhCl_3][PCl_6]$ were too weak for individual lines to be identified.

TABLE 4

Symmetry information for chlorophenylphosphonium salts from the n.q.r. spectra at 77 K

	Independent Cl sites		Crystallographically independent molecules	Possible symmetry	
	In cation	In anion		cation	anion
$[PPhCl_3][BCl_4]$	1	3	1	C_3 [a]	C_s
$[PPhCl_3][SbCl_6]$	1	1	1	C_3 [a]	O_h
$[PPhCl_3][PCl_6]$	←Total of 7→		1	C_3 [a]	C_1
$[PPh_2Cl_2][BCl_4]$	2	4	1 or 2	C_1 C_2	C_1 C_2
$[PPh_2Cl_2][SbCl_6]$	7 [b]	4	4	C_1	
$[PPh_3Cl][BCl_4]$	1	4	1		C_1
$[PPh_3Cl][SbCl_6]$	2	3	2		
$[PPh_3Cl][PCl_6]$	←Total of 7→		1		C_1
$[PPh_3Cl][AlCl_4]$	1	4	1		C_1

[a] See text. [b] One line of double intensity (Table 2).

The single ^{35}Cl resonance observed for the trichlorophenylphosphonium cation in $[PPhCl_3][BCl_4]$ and $[PPhCl_3][SbCl_6]$ is somewhat unexpected since the three-fold axis of symmetry suggested by the spectrum is inconsistent with the two-fold symmetry of the phenyl group. A single mirror plane relating two of the three chlorine atoms should give rise to a doublet of relative intensities 2 : 1. The spectral multiplicities of two related species are both greater than one; two ^{35}Cl resonances of 2 : 1 relative intensities are observed for the ion $[PMeCl_3]^+$, at 30.82 (S : N 5 : 1) and 31.3 MHz (S : N 11 : 1) (this work), and the 77 K spectrum of $[AsPhCl_3]^+$ in the compound $[AsPhCl_3][BCl_4]$ shows similar relative intensities [33.94 (S : N 22 : 1) and 34.32 MHz (S : N 10 : 1)].[36] The n.q.r. spectra of both these ions are thus consistent with the presence of a mirror plane relating two of the three chlorine atoms. The single line for $[PPhCl_3]^+$ is therefore difficult to explain in terms of ionic symmetry. Rotation of the phenyl groups at 77 K is unlikely; the non-detection of a second line from the ion is possible, but the observed resonance for $[PPhCl_3][BCl_4]$ was very intense (S : N 30 : 1). The accidental coincidence of two resonance frequencies from crystallographically unrelated chlorine atoms is improbable in view of the high resonance-frequency range : linewidth ratio of n.q.r. spectroscopy, but this possibility cannot be entirely ruled out.

Alkylchlorophosphoranes and their Derivatives.—The observed ^{35}Cl resonance frequencies for the methyl- and ethyl-chlorophosphoranes and their derivatives at 77 K are given in Table 5, together with their ^{31}P and ^{11}B n.m.r. chemical shifts in the solid state. ^{35}Cl N.q.r. frequencies of 29.74, 29.58, and 29.38 MHz at 195 K, and of 29.43, 29.26, and 29.05 MHz at 294 K, were also obtained for PEt_2Cl_3. No n.q.r. signals could be detected from the ionic derivatives of the chloromethylphosphoranes except for $[PMe_2Cl_2][ICl_2]$, or from PEt_3Cl_2, although satisfactory ^{31}P n.m.r. spectra were recorded in each case. This may be due to disorder phenomena in the solids, possibly caused by random orientations of the alkyl and chloro-groups in the pseudo-spherical cations. It is noteworthy that the only methyl derivative for which signals were observed has the most symmetrical cation and a linear anion. Similarly, replacement of a methyl by an ethyl group in Lewis-acid adducts, $[PR_nCl_{4-n}][XCl]$, where the anion is pseudo-spherical, appears to be sufficient to give a preferred orientation, thus making observation of the n.q.r. spectrum possible. Signals were not detected for the $[ICl_2]^-$ ion in $[PMe_2Cl_2][ICl_2]$. Difficulty in obtaining spectra from this and similar ions with large cations has been found in other compounds.[36,37]

TABLE 5

N.q.r. and n.m.r. data for alkylchlorophosphonium compounds

Compound	$\nu(^{35}Cl)$ (MHz) at 77 K for Cation	$\nu(^{35}Cl)$ (MHz) at 77 K for Anion	$\delta(^{31}P)$/p.p.m. (from 85% H_3PO_4)	$\delta(^{11}B)$/p.p.m. [from $B(OMe)_3$]
$PMeCl_4$	31.31 30.82		−119 ± 2	
$[PMeCl_3][AlCl_4]$			−117 ± 1	
$[PMeCl_3][ICl_2]$			−116.5 ± 1	
PMe_2Cl_3	29.88		−124 ± 5	
$[PMe_2Cl_2][BCl_4]$			−119.5 ± 2	12.8 ± 3
$[PMe_2Cl_2][SbCl_6]$			−123 ± 4	
$[PMe_2Cl_2][ICl_2]$	30.13		−121 ± 1	
PMe_3Cl_2	29.09		−87 ± 4	
$[PMe_3Cl][BCl_4]$			−87 ± 1	12 ± 3
$[PMe_3Cl][ICl_2]$			−86.7 ± 1	
$[PEtCl_3][AlCl_4]$	31.20 30.87 30.67	11.34 11.25 10.99 10.91	−124.4 ± 1	
PEt_2Cl_3	29.92 29.60 *		−138.7 ± 2	
$[PEt_2Cl_2][BCl_4]$	29.84	21.36 (m) 21.02	−137.4 ± 2	12.5 ± 1
PEt_3Cl_2			−105.2 ± 2	
$[PEt_3Cl][BCl_4]$	28.80 28.69	21.66 21.45 21.31 21.20	−105.0 ± 2	11.9 ± 1

* Close doublet.

No widely separated ^{35}Cl resonances were detected for the remaining parent compounds, as expected for axial and equatorial chlorines in a trigonal-bipyramidal structure, and the spectra were comparatively simple. A molecular structure for PMe_3Cl_2 with the methyl groups all occupying equatorial sites could give rise to a single ^{35}Cl n.q.r. frequency, but this should be much lower (*ca.* 20 MHz) than the observed value of 29.09 MHz if only axial chlorines are present. The alternative possibility of the chlorines both occupying equatorial sites seems very unlikely. In addition the ^{31}P n.m.r. spectra of all the alkylchlorophosphoranes consisted of

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[36] K. B. Dillon, R. J. Lynch, and T. C. Waddington, *J.C.S. Dalton*, in the press.

[37] E. F. W. Riedel, Dissertation, Washington State University, 1973 (*Diss. Abs.*, 1973, **33**, 5757).

single peaks lying unequivocally in the four-co-ordinate region for phosphorus(V) compounds. The phosphonium-salt structure $[PR_nCl_{4-n}]Cl$ deduced from vibrational spectroscopy for the methyl compounds [12-14] is thus confirmed.

Further support is provided by the n.m.r. and n.q.r. (where obtained) results for the adducts (Table 5), which agree well in all instances with those of the parent compounds. The ^{11}B chemical shifts for the tetrachloroborates are also in excellent agreement with literature values,[29,35] showing that the adducts are ionic, rather than acceptor–donor complexes such as those formed by PCl_3O. The same cations $[PR_nCl_{4-n}]^+$ are thus present in the derivatives, and alternative molecular, ionic, or polymeric structures for the solid alkylchlorophosphoranes studied may be safely discounted.

The number of n.q.r. lines again gives an indication of the ionic symmetries in the solid state. The trichloromethylphosphonium ion possesses two crystallographically equivalent chlorine atoms, showing the presence of a symmetry plane (C_s). Similarly the dichlorodimethylphosphonium ion must have C_2 or C_s symmetry. The single resonance from $[PMe_3Cl]^+$ in PMe_3Cl_2 gives no point-symmetry information; only one molecule per crystallographic asymmetric unit is to be expected from the data. Of the ethyl derivatives, only the dichlorodiethylphosphonium ion in $[PEt_2Cl_2][BCl_4]$ appears to have any special symmetry associated with the chlorine sites in the crystal. In this case a single resonance line indicates the same two-fold symmetry as found in the $[PMe_2Cl_2]^+$ cation. The results for the $[PEtCl_3]^+$ ion show that all three chlorine sites are crystallographically independent, and those for $[PEt_3Cl][BCl_4]$ indicate that there must be two independent cations in the asymmetric unit of the unit cell. In all three derivatives the $[AlCl_4]^-$ and $[BCl_4]^-$ anions do not appear to have full T_d symmetry, parallel with that of the phenyl-substituted derivatives.

The n.q.r. spectrum of trichlorodiethylphosphorane is consistent with three independent chlorine sites in the crystal. The average frequency is very close to that found in $[PEt_2Cl_2][BCl_4]$, and we conclude that the compound is ionic, $[PEt_2Cl_2]Cl$. The ^{31}P n.m.r. shift is also as expected for this structure. Three chlorine resonances, although unusual for an ion of this type, would be consistent with a trigonal or hexagonal crystal structure in which the asymmetric unit contains three molecules, each of which possess a cation with two-fold symmetry relating the chlorine atoms to each other.

The results show the value of using the complementary techniques of n.q.r. and n.m.r. spectroscopy for structural determination, with a consequent reduction in the risk of erroneous conclusions from incomplete data. Unequivocal molecular or ionic structures have been assigned to all the compounds studied on this basis, and some symmetry information has also been deduced. A fuller discussion of the trends in the n.q.r. frequencies for various structural types will follow in a subsequent paper [36] dealing with some similar arsenic compounds and related species.

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