Unstable Intermediates. Part CLX.[1] An Electron Spin Resonance Study of PCl_4, PCl_5^-, PCl_6^{2-}, and PCl_6 Radicals in Irradiated Phosphorus Pentachloride

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Exposure of phosphorus pentachloride (PCl_4^+ PCl_6^-) to ^{60}Co γ-rays at 77 K gave PCl_4 and PCl_5^- radicals in comparable yields, together with a species thought to be PCl_6^{2-} in lower yield. The isotropic ^{31}P hyperfine coupling increases in this order (*ca.* 1 310 G, 1 617 G, and 1 815 G respectively). At 77 K PCl_4 has two inequivalent chloride ligands (A_{iso} *ca.* 35 G and 0 G respectively). The PCl_5^- species exhibited a smaller, poorly resolved, splitting interpreted as coupling to four equivalent chloride ligands. The species thought to be PCl_6^{2-} also exhibited a multiple splitting from several chloride ligands but overlap of features made accurate assessment impossible.

Similar spectra for PCl_4 and PCl_5^- radicals were obtained from solutions in carbon tetrachloride and toluene, in which PCl_5 molecules are present, but the outer features assigned to PCl_6^{2-} were absent.

Well resolved central features obtained from the pure material indicated hyperfine coupling to one phosphorus and two equivalent chlorine nuclei. This species is thought to be a strongly distorted PCl_6 radical.

THE first phosphoranyl radical to be studied by e.s.r. spectroscopy was PF_4 in sulphur hexafluoride.[2] This species, which exhibited hyperfine coupling to two inequivalent pairs of fluorine nuclei, was thought to be the slow-interchange version of a species containing four equally coupled fluorine nuclei in irradiated hexafluorophosphates.[3,4] However, it is now thought that the latter species was really PF_5^-, formed by dissociative electron capture:[5]

$$PF_6^- + e^- \longrightarrow PF_5^- + F^- \qquad (1)$$

The radical PCl_4, containing two inequivalent pairs of chlorine atoms, was first detected in phosphorus trichloride either exposed to u.v. light,[6] or in a subsequent study by exposure to ^{60}Co γ-rays.[7] However, we know of no previous study of phosphorus pentachloride, nor of any previous report of the radicals PCl_5^-, PCl_6^{2-}, or PCl_6.

Since this study was largely completed, the sulphur analogues, SF_5 and SF_6^-, have been reported by Morton and his co-workers.[8,9] The radical SF_5, previously thought to be SF_4^+,[2] had four equivalent fluoride ligands exhibiting a large isotropic hyperfine coupling, and one which, fortuitously, had undetectably small coupling.[8] The radical SF_6^-, tentatively identified previously,[2] had six equivalent fluoride ligands and a remarkably large isotropic coupling to ^{33}S, suggesting a 3*s* orbital population of *ca.* 66.4%.[9]

EXPERIMENTAL

Phosphorus pentachloride was reagent grade and was sublimed *in vacuo* before use. Solutions were prepared in a dry atmosphere using dried, reagent grade, solvents. Samples were irradiated at 77 K as powders or as small glassy beads in a Vickrad ^{60}Co γ-ray cell at a dose rate of 1.7 MCi h^{-1} for up to 2 h.

E.s.r. spectra were measured on a Varian E3 spectrometer at 77 K. Samples were annealed by decanting the liquid nitrogen from the insert Dewar and continuously monitoring the e.s.r. spectra. Liquid nitrogen was added whenever significant changes were observed and spectra were obtained at 77 K.

RESULTS AND DISCUSSION

Data extracted from the e.s.r. spectra together with our interpretation are given in Table 1 and selected e.s.r. spectra are shown in the Figures. Identifications and structural considerations are discussed below for each radical of interest.

The PCl_4 *Radical.*—This radical has been reported previously,[6,7] and our present spectra are quite comparable. However, the chlorine hyperfine features are particularly well defined in the case of the pure ionic solid (Figure 1) and we are able to offer an improved analysis. In the early studies of chlorophosphoranyl radicals in the solid-state, powder spectra seemed to be almost isotropic and hence $A_{iso}(^{35}Cl)$ was set equal to *ca.* 60—70 G.[6,7,10] However, it has recently been appreciated that these spectra were misinterpreted,[11,12] and the re-analysis in terms of anisotropic interaction has yielded isotropic hyperfine couplings (to the axial chlorine atoms) of *ca.* 30—40 G, in good agreement with liquid-phase data.[13] Our present analysis for PCl_4, shown in Figure 1 and justified previously,[12] yields

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[1] Part CLIX, S. P. Mishra and M. C. R. Symons, *J.C.S. Perkin II*, 1975, 1492.

[2] R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, 1966, **45**, 1845.

[3] J. R. Morton, *Canad. J. Phys.*, 1963, **41**, 706.

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[6] G. F. Kokosyka and F. E. Bruickman, *J. Amer. Chem. Soc.*, 1970, **92**, 1199.

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[8] J. R. Morton and K. F. Preston, *Chem. Phys. Letters*, 1973, **18**, 98.

[9] J. R. Morton, K. F. Preston, and J. C. Tait, *J. Chem. Phys.*, 1975, **62**, 2029.

[10] C. M. L. Kerr and F. Williams, *J. Phys. Chem.*, 1971, **75**, 3023.

[11] T. Gillbro and F. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 5032.

[12] D. Nelson and M. C. R. Symons, *J.C.S. Dalton*, 1975, 1164.

[13] D. Griller and B. P. Roberts, *J.C.S. Perkin II*, 1973, 1339.

results in close agreement. This shows that the hyperfine interaction to axial chlorine atoms is not very dependent upon the nature of the two equatorial groups.

Another significant fact is that the small 'perpendicular' coupling to chlorine nuclei is found partly on the larger, parallel, coupling to ^{31}P, whereas the large parallel coupling to chlorine nuclei is clearly on the perpendicular phosphorus features (Figure 1a). This is in accord with expectation for structure (I) provided that delocalisation is primarily *via* the P–Cl σ-bonds rather than *via* the chlorine π-orbitals. This is strongly supported by the fact that axial hydrogen atoms have a relatively high spin density,[14,15] since, in this case, only σ-delocalisation is possible.

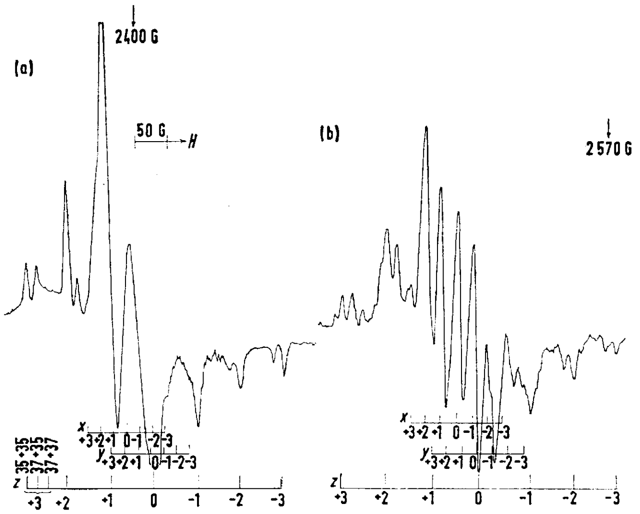
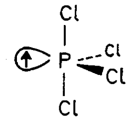
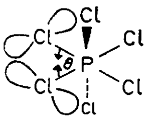


FIGURE 1 First derivative X-band e.s.r. spectra for (a) PCl_5 and (b) $POCl_3$, after exposure to ^{60}Co γ-rays at 77 K, showing the $M_I(^{31}P) = +\frac{1}{2}$ feature for (a) PCl_4 and (b) $POCl_3^-$ radicals



(I)



(II)

TABLE 1

		Hyperfine coupling (G) [a]						
		^{31}P [b]				^{35}Cl [c,d]		
System	Radical	$A_{\parallel}$	$A_{\perp}$	A_{iso}		$A_{\parallel}$	$A_{\perp}$	A_{iso}
$PCl_4^+ PCl_6^-$	PCl_4	1 350	1 290	1 310	Cl_1	65	~20	35
					Cl_2	~0	~0	~0
	PCl_5^-	1 650	1 600	1 617		30 [f]	~10	~23.3
	PCl_6^{2-}			1 815				~37
	PCl_6 [e]	110	110	110		77	0 ± 10	25.7 ± 4
PCl_5–CCl_4	PCl_5^-		*ca.* 1 628			30 [f]	~10	~23.3
PCl_5–Toluene	PCl_4	1 280	1 210	1 233		65	~20	35
	PCl_5^-		*ca.* 1 622			30 [f]	~10	~23.5
PCl_3	PCl_4	1 270	1 200	1 223		63	~20	~34.3
PCl_3	$POCl_3^-$	1 417	1 355	1 375.7	Cl_1	69	24	39
$POCl_3$ [g]	$POCl_3^-$	1 371 (isotropic)			Cl_1	70	25	40

[a] G = 10^{-4}T. [b] Corrected using the Breit Rabi equation: $g_{\parallel}$ 2.00, $g_{\perp}$ 2.02 ± 0.01 except for PCl_6. [c] ^{37}Cl gave the correct parameters when features resolved. [d] g Values close to but always slightly greater than 2.0023. [e] $g_{\parallel} = 2.000$, $g_{\perp} = 2.029$. [f] Measured value of 30 G is set equal to $(A_{\parallel} + A_{\perp})/2$ to obtain A_{iso} (see text). [g] Ref. 11.

If these arguments are correct, then the simple bonding scheme proposed[11] for $POCl_3^-$ and related species, in which a lone-pair of electrons is placed in the third equatorial site and the unpaired electron in a σ-orbital along the axial direction, seems less satisfactory than the model normally used, based upon representation (I), for which σ-delocalisation is implicit. To verify that these arguments indeed apply to $POCl_3^-$, we have re-examined the powder e.s.r. spectra for this species, both in the pure compound and in solvents carbon tetrachloride and toluene. The resulting spectra proved to be remarkably similar to that for PCl_4 (Figure 1). In both cases, for the $M_I = +\frac{1}{2}(^{31}P)$ feature shown, the $M_I = +3(^{35}Cl)$ parallel feature is more intense than the -3 feature. As the reconstruction shows, this must mean that the coupling for chlorine on the ^{31}P parallel component is relatively small, as required by the present bonding scheme. The close similarity between these spectra and those for the dichlorides previously reported[12] suggest that in both cases the hyperfine coupling to equatorial chlorine ligands is small. However, in the case of $POCl_3^-$ there are extra, weak, wing lines which may be due to hyperfine interaction with the equatorial chlorine atom, the odd intensities arising because of a quadrupole effect to be expected when the hyperfine interaction is small.

The PCl_5^- *Radical.*—Unfortunately, the hyperfine coupling to chlorine was always less well resolved than that for PCl_4 radicals (Figure 2). This is largely because the splittings are smaller. We have analysed the low-field feature in terms of coupling to four equivalent chlorine nuclei only, since this accords with the results for the isoelectronic SF_5 radical.[8] (The high-field feature for this and for the postulated PCl_6^{2-} radical are overlapped by that for PCl_4 and, hence, are more difficult to analyse.) In this case, the coupling to chlorine on the parallel ^{31}P features should be perpendicular, whilst that on the perpendicular ^{31}P features is expected to be

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[14] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

[15] A. J. Colussi, J. R. Morton, and K. F. Preston, *J. Chem. Phys.*, 1975, **62**, 2004.

equal to 0.5 $(A_{\parallel} + A_{\perp})$.[16] This gives, very approximately, $A_{\perp}(^{35}Cl) \approx 10$ G, and 0.5 $(A_{\parallel} + A_{\perp}) \approx 30$ G. (These values are a synthesis gleaned from the best features obtained for PCl_5^- in the various environments and at various temperatures.) The results given in Table 1, show that the orbital of the unpaired electron is remarkably similar for PCl_4 and PCl_5^- radicals. This is brought out by the spin-density values listed in Table 2, which are very approximate values obtained in the usual manner from computed atomic values for the orbitals concerned.[17] These show that phosphorus uses more 3*s* and less $3p_z$, but that the spin is distributed between phosphorus and chlorine about equally in the two radicals.

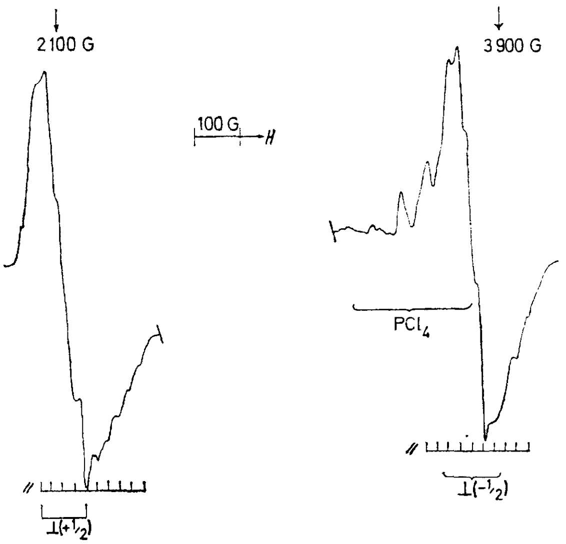

FIGURE 2 First derivative *X*-band e.s.r. spectrum for PCl_5 in CCl_4 solvent after exposure to ^{60}Co γ-rays at 77 K, showing the $M_I = \pm\frac{1}{2}$ features assigned to PCl_5^- radical anions

TABLE 2

Approximate orbital populations

Radical	Orbital populations 3*s*(P)	3*p*(P)	3*p*(Cl)
PCl_4	0.36	0.19	0.30 (2)
PCl_5^-	0.44	0.16	0.14 (4)
PCl_6^{2-}	0.50	*a*	*a*
PCl_6			0.51 (2Cl)
$POCl_3^-$	0.37	0.20	0.30 (2Cl)

a Not determinable from the data.

The PCl_6^{2-} *Radical.*—This species was only obtained from the pure material (PCl_4^+ PCl_6^-), and our identification rests heavily upon this fact. The low-field component was poorly defined initially at 77 K, but resolution was improved on partial annealing, prior to irreversible loss (Figure 3). Because of overlap with the features for PCl_5^- we are unable to estimate the number of coupled chlorine nuclei. Results for SF_6^- [9] suggest that we should observe features for six equivalent chlorine nuclei. As our reconstruction shows, this is certainly possible. The strength of the central component suggests that the coupling to chlorine nuclei is still anisotropic. (If the coupling to ^{31}P and the *g*-tensor were isotropic, we would expect to detect only the isotropic coupling to chlorine in the powder spectrum.)

The derived spin densities, which must be taken as being tentative, suggest that the trend to an increased 3*s* contribution and decreased 3*p* contribution from phosphorus is continued. Indeed, if there is no major distortion of the octahedral structure of PCl_6^- ions, then only 3*s* is expected to contribute, the orbital of the unpaired electron being purely σ* in character.

(The fact that the spin density, summed over all nuclei, is greater than unity is commonly found in this type of approximate calculation, even for the simple diatomic V_K centres.[17] This arises, in part, because of the neglect of spin polarisation of inner orbitals, and of overlap effects.)

Comparison with the results for SF_6^- suggests an increased delocalisation onto the ligands for PCl_6^{2-}. This reflects the fall in electronegativity differences on going from S–F to P–Cl bonding, and is as expected for an electron in an anti-bonding orbital.

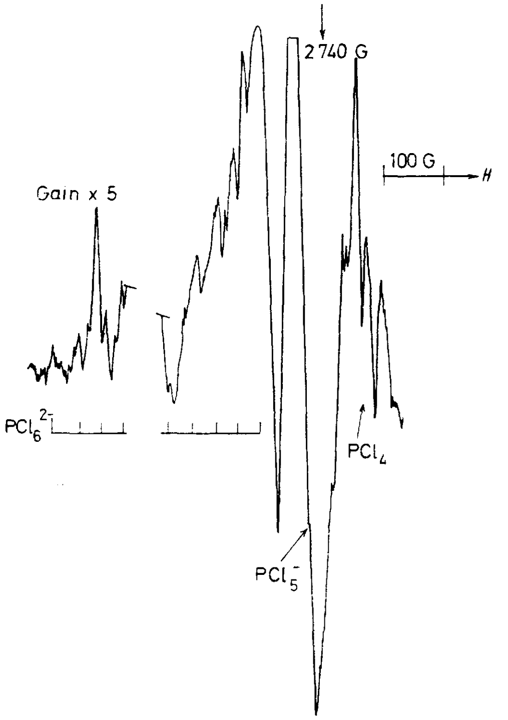

FIGURE 3 First derivative *X*-band e.s.r. spectrum for PCl_5 after exposure to ^{60}Co γ-rays at 77 K, and slight annealing, showing the $M_I = +\frac{1}{2}$ features assigned to PCl_6^{2-} (together with those for PCl_5^- and PCl_4 which overlap the PCl_6^{2-} spectrum)

The PCl_6 *Radical.*—This species, only detected in the pure material after irradiation, had a well defined e.s.r. spectrum showing hyperfine coupling to two equivalent chlorine atoms and one phosphorus atom (Figure 4 and

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[16] C. M. Guzi, J. B. Raynor, and M. C. R. Symons, *J. Chem. Soc. (A)*, 1969, 2299.

[17] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

Table 1). This resembles the powder spectrum for Cl_2^- radicals in several respects.[18] The most probable electron-loss centre is PCl_6, and we consider this to be the most reasonable assignment, since the form of the coupling to ^{31}P and of the g-tensor components accord with expectation.[19] We suggest that the electron is confined to two chlorine ligands because these have moved together to form a loose Cl–Cl bond as in (II). In this case, the observed hyperfine splittings will not, in general, correspond to principle values. In fact, the only well defined splitting is on the 'parallel' features, so $A_{\parallel}(^{35}Cl)$ must, in fact, be greater than that observed by an amount dependent on the magnitude of θ in (II). The isotropic coupling to ^{31}P is, however, surprisingly large for this structure. It is thought to arise primarily from spin polarisation of the σ-bonding electrons, in which case the 3s contribution (^{31}P) to this bonding must be unusually large.[19,20]

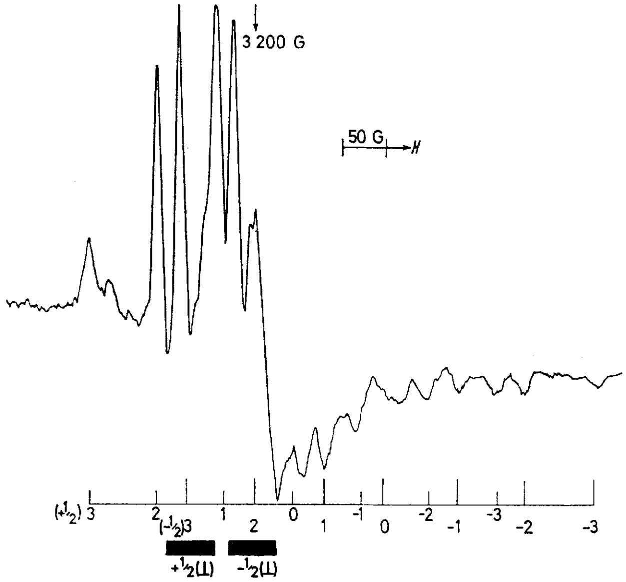

FIGURE 4 First derivative X-band e.s.r. spectrum for PCl_5 after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to PCl_6 radicals

Aspects of Mechanism.—For the pure solid, we suggest:

$$PCl_6^- \xrightarrow{\gamma\text{-rays}} PCl_6 + e^- \quad (2)$$

$$PCl_6^- + e^- \longrightarrow PCl_6^{2-} \quad (3)$$

$$PCl_4^+ + e^- \longrightarrow PCl_4 \quad (4)$$

$$(PCl_6^{2-}) \longrightarrow PCl_5^- + Cl^- \quad (5)$$

This scheme satisfactorily explains the products detected. For the solution, in which phosphorus pentachloride is known to be molecular rather than ionic,[21] we suggest:

$$\text{Solvent} \longrightarrow \text{Solvent}^+ + e^- \quad (6)$$

$$PCl_5 + e^- \longrightarrow PCl_5^- \quad (7)$$

$$(PCl_5^-) \longrightarrow PCl_4 + Cl^- \quad (8)$$

as a reasonable scheme to explain the paramagnetic products. Since we needed to anneal the materials well above 77 K before detecting the loss of PCl_6^{2-} and especially of PCl_5^- we suggest that processes (5) and (8) occur as directly competitive to the electron-addition steps (3) and (7). In other words, two alternative distortions occur when the electron interacts initially, one leading to trapping, (3) and (7), and one to chloride loss, (5) and (8).

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[18] I. Marov and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1971, 201; I. S. Ginns and M. C. R. Symons, *J.C.S. Dalton*, 1972, 143.

[19] A. Begum, S. Subramanian, and M. C. R. Symons, *J. Chem. Soc.* (*A*), 1970, 1323.

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[21] R. W. Suter, H. C. Knackel, V. P. Petro, J. H. Howatson, and S. G. Shore, *J. Amer. Chem. Soc.*, 1973, **95**, 1474.