

Such an effect would not be anticipated in $\text{MeN}(\text{PF}_2)_2$ if the P–N–P backbone were rigid due to nitrogen→phosphorus π bonding.⁹ Extrapolation from the well studied dimethylaminodifluorophosphine, Me_2NPF_2 , substantiates this contention of a p_π – d_π interaction enhanced by the presence of electronegative fluorine atoms. Thus, Nordman's X-ray diffraction study²⁶ has revealed C_s molecular symmetry for Me_2NPF_2 (a mirror plane containing the P–NC₂ moiety and bisecting the FPF angle). The P–N distance at 1.63 Å is in the range of P=N multiple bond distance found in phosphonitrilic derivatives.²⁷ The short bond and the planarity about nitrogen strongly suggest N→P multiple bonding in Me_2NPF_2 .

Since the sign and magnitude of $^2J_{\text{PP}}$ in F_2PSPF_2 and $\text{MeN}(\text{PF}_2)_2$ are the same, it seems reasonable to conclude that similar mechanisms are responsible for the transmission of spin-spin coupling between the phosphorus nuclei in both cases.

We are led to speculate that $3p_\pi$ – $3d_\pi$ bonding, such as that implied for the PSP backbone, is less rigid than the $2p_\pi$ – $3d_\pi$ bonding proposed for the nitrogen homolog. It is not clear, however, whether the size of the orbitals involved in the π backbone, or alternatively,

the number of lone-pair electrons in the bridging moiety affects the rigidity.

A through-space mechanism²⁸ or a through-bond mechanism may be responsible for the transmission of the PP coupling. However, it is difficult to imagine how a through-space effect could be present in F_2PSPF_2 and not in F_2POPF_2 , where the shortness of the P–O bond relative to the P–S bond should offset any expansion of the geminal angle in the oxygen compound. Nevertheless, because of the geometry of these systems, it is reasonable to expect that through-space coupling would only be significant for $^2J_{\text{PP}}$, and thus it might explain why the percentage variations with temperature of the 3- and 4-bond couplings in F_2PSPF_2 are much less than those for $^2J_{\text{PP}}$.

Certainly, structural data on all the P–X–P systems mentioned here will be of considerable value in explaining the nmr results. Also, the preparation and investigation of $\text{F}_2\text{PP}(\text{R})\text{PF}_2$ species should provide data pertinent to the role of p_π orbital size.

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Electron Paramagnetic Resonance Studies of Phosphorus-Containing Reactive Intermediates^{1a}

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Abstract: Several novel phosphorus-containing radicals have been produced at -196° by photolytic methods and characterized by epr spectrometry. In addition to the formation of PCl_2 ($A(\text{P}) = 92$ MHz; $g = 2.018$) in neat parent PCl_3 , a secondary reaction has been observed which yields PCl_4 ($A(\text{P}) = 3398$ MHz; $A'(\text{Cl}) = 175$ MHz; $A''(\text{Cl}) = 21$ MHz; $g = 2.013$). Appropriate modification of the parent matrix by either cocondensation of inert diluent (Xe) or possibly reactive materials (PF_3 , SnCl_4) results in useful additional spectral information. Thus in $\text{PF}_3:\text{PCl}_3$ (1:10) the full anisotropy of PCl_2 is revealed ($A_{\parallel}(\text{P}) = 753$ MHz; $A_{\perp}(\text{P}) = 78$ MHz; $A_{\parallel}(\text{Cl}) = 41.5$ MHz; $A_{\perp}(\text{Cl}) = 0$ MHz; $g_{\parallel} = 2.001$; $g_{\perp} = 2.021$). In contrast to neat PCl_3 , irradiation of $\text{Xe}:\text{PCl}_3$ (9:1) does not result in formation of PCl_4 , presumably from inhibition of $\text{Cl} + \text{PCl}_3 \rightarrow \text{PCl}_4$ by competitive Cl recombination. Irradiation of $\text{SnCl}_4:\text{PCl}_3$ (6:1) results in formation both of PCl_2 and PCl_4 . Several related organophosphines were also irradiated, but only with CH_3PCl_2 was evidence obtained suggesting formation of a four-coordinate radical similar to PCl_4 ($A(\text{P}) = 3015$ MHz, $g = 2.000$). In all cases, however, epr data are consistent with bond scission of the ternary phosphine to produce PCl_2 -like fragments. The above results are discussed in light of their bearing on the role of reactive intermediates in synthetic chemistry, and considerations of molecular geometric and orbital composition are presented with reference to current MO and electrostatic models.

The main group V elements form both neutral three-coordinate compounds and, with the exception of nitrogen, neutral five-coordinate compounds. Both of these types are of interest in terms of (1) their stereochemistry and (2) the nature and orbital composition

of their bonds. The simplest case of a group V atom forming both three- and five-coordinate halogen compounds is phosphorus. Several recent theoretical papers have described the bonding in five-coordinate phosphorus compounds including such aspects as d-orbital participation and the relationship between stereochemistry and relative electronegativities in the mixed halo compounds.^{2,3}

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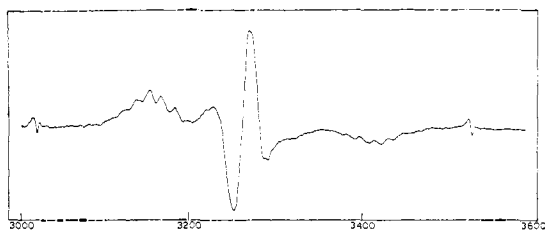


Figure 1. The spectrum of a mixture of $\text{PCl}_3:\text{PF}_3$ in a ratio of about 10:1. The outermost lines are attributed to atomic hydrogen. The abscissa is in units of gauss ($10^4 \text{ G} = 1 \text{ tesla}$).

Since uncharged pentacoordinate phosphorus compounds contain no unpaired electrons, the electron paramagnetic resonance technique cannot be expected to produce any experimental data to verify or dispute theoretical findings. On the other hand, the four-coordinate radical PF_4 is known and believed to be nearly trigonal bipyramidal, with the unpaired electron occupying an equatorial position.^{4,5} Additional data on other trigonal bipyramidal phosphorus radicals should be welcomed at this time not only to compare the results with the PF_4 species, but also to relate these data to the theoretical models for other halogenated species. Such a detailed theoretical analysis of the relationship between the isotropic hyperfine splittings and the molecular structure of the PF_4 radical has appeared.⁶ There, Higuchi has calculated the molecular angles from both a valence bond as well as a molecular orbital point of view. Appreciable hybridization with the phosphorus d orbitals was incorporated in this treatment, although exclusion of d-orbital participation has been proposed by other authors.³

A preliminary account of the generation of new chlorine-containing phosphorus radicals has already appeared,^{1a,7} and the present paper discusses, in addition to the interesting case of PCl_4 , related species which permit consideration of several bonding models including the Higuchi case.

Just as the PX_4 species are believed to have considerable importance in providing data for enhancing the understanding of the PX_3 species, so also is it desirable to obtain data on PX_2 molecules in order to provide some insight into the nature of the electronic distribution in that radical and in the related PX_3 system. The PF_2 radical was first reported by Wan, *et al.*,⁸ as a freely rotating species. Recently, a preliminary spectrum associated with the PF_2 species undergoing hindered rotation was reported by Gendell, Wei, and Current.⁹ The PCl_3 species is known to contain three P-Cl bonds

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(5) R. W. Fessenden and R. H. Schuler, *J. Chem. Phys.*, **45**, 1845 (1966).

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(7) G. F. Kokoszka and F. E. Brinckman, *Chem. Commun.*, 349 (1968).

(8) J. K. S. Wan, J. R. Morton, and H. J. Bernstein, *Can. J. Chem.*, **44**, 1957 (1966).

(9) J. Gendell, M. Wei, and J. Current, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. PHYS 041. The authors wish to thank Professor Current for providing an opportunity to examine his detailed results for the PF_2 radical which will appear in a forthcoming paper.

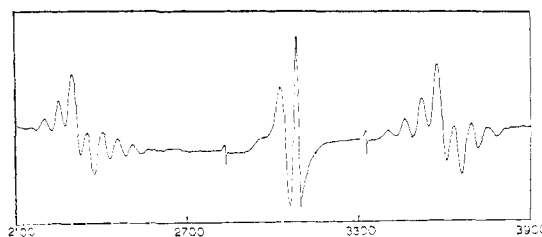


Figure 2. The complete spectrum from neat PCl_3 following 4 hr of irradiation at 253.7 nm. The center portion is attenuated by a factor of 10 for clarity. The lines at about 2800 and 3300 G are attributed to atomic hydrogen. The abscissa is in units of G ($10^4 \text{ G} = 1 \text{ tesla}$).

at roughly right angles to one another, suggesting that each of these bonds contains orbital contributions chiefly from each of the three phosphorus 3p orbitals. Removal of one of the chlorine atoms might then be expected to result in a single unpaired electron residing in a p orbital perpendicular to the molecular plane. Such a result will be shown to be consistent with the experimental data to be presented in this paper. A semi-quantitative estimate of the delocalization of the unpaired electronic density into the chlorine 3p orbitals will also be considered.

Often, useful epr spectra are obtained from studies on radical species embedded in inert host matrices, usually noble gas lattices, where, generally, it is necessary to employ relatively high-energy irradiation (X-rays or γ -rays). In contrast the authors have mostly utilized neat materials or mixtures of neat materials to serve as precursors to and matrices for the radical species. This approach is worthy of more than passing interest since the PCl_4 species is produced as a result of a secondary reaction at -196° , there being no evidence for its formation on irradiation of PCl_3 diluted in a noble gas host lattice. The sources of irradiation utilized in this study are high- and low-pressure mercury lamps. These low-energy sources have proven useful also for generation of radicals from the group IVa organohalides.¹⁰

Finally, the knowledge of whether or not a reactive intermediate, particularly of a free radical type, exists under accessible laboratory conditions can be of significance to the course of synthetic chemistry. An important example is provided by the electric discharge synthesis of B_2Cl_4 . It is now thought that BCl_2 is not an important radical intermediate since spectroscopic studies have failed to reveal its presence even in very small quantities, although it was demonstrated that a neutral BCl intermediate appears important to the reaction.¹¹ The synthetic potentialities of analogous BF have also been demonstrated recently.^{12,12a} The corresponding re-

(10) F. E. Brinckman, G. F. Kokoszka, and N. K. Adams, *J. Res. Nat. Bur. Stand., A*, **73**, 201 (1969).

(11) R. T. Holzmann and W. F. Morris, *J. Chem. Phys.*, **29**, 677 (1958).

(12) P. L. Timms, *J. Amer. Chem. Soc.*, **89**, 1629 (1967).

(12a) NOTE ADDED IN PROOF. Particularly significant to these considerations is the recent report by W. Nelson and W. Gordy, *J. Chem. Phys.*, **51**, 4710 (1969), describing the detection and structural determination of BF_2 radical. These authors generate this C_{2v} species by γ -irradiation of solid xenon containing small amounts of BF_3 , but suggest it would be "possibly feasible to observe the microwave spectrum of BF_2 radicals in the gaseous state." Such a line of investigation is of great interest from the standpoint of elucidating synthetic consequences of treating either gaseous BF or BF_2 intermediates with common substrates. For example, as an interesting alternate route to the postulated formation of B_2F_4 by BF insertion reaction with B-F bonds in BF_3 , it would be instructive to ascertain whether a similar catenation process can occur *via* simple self-condensation of BF_2 .

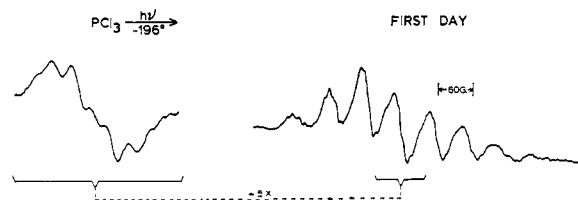


Figure 3. The high-field component of the doublet spectrum associated with PCl_4 is seen at the right. Each of the doublet components is split into a septet. Furthermore, each of the components of the septet is further split into an additional septet. This is more clearly seen in the $5\times$ blow-up on the left-hand side of the figure.

actions can also be related to PCl_3 . The present demonstration of PCl_2 and PCl_4 suggests that other mechanisms can be important in the electric discharge production of P_2Cl_4 or PCl_5 from PCl_3 ,¹³ an analogous consideration obtains for the formation of P_2F_4 and PF_5 from subjecting PF_3 to gaseous discharges.¹⁴

Experimental Section

Samples of commercial reagent grade PCl_3 were purified by standard high-vacuum line techniques. Infrared spectra obtained from the sample material showed that the concentrations of the most obvious impurities (such as HCl and POCl_3) were below the 1% level. That all the impurities were not removed, however, is apparent from the presence in most of the epr spectra of a weak doublet separated by about 1500 MHz¹⁵ (Figures 1 and 2). These lines are attributed to atomic hydrogen¹⁶ and most likely arise from small residual quantities of HCl in the sample. However, presence or absence of H appears not to materially affect the results reported here.

Epr spectra were obtained with a commercially-available X-band spectrometer equipped with 100 kHz modulation and a cavity containing irradiation slot. The ultraviolet irradiation (principally at 370 nm) was produced by a 200-W high-pressure mercury lamp. Some experiments were also done with a low-pressure mercury lamp whose principal output (2.5 W) is at 253.7 nm. No significant differences were noted in these spectra except that the hydrogen lines appeared to be stronger with the latter source. The spectrum shown in Figure 1 was produced by this lamp in order to show these lines more clearly. Many of the irradiations with the high-pressure source and all with the low-pressure source were carried out at liquid nitrogen temperature outside of the cavity with the sample in a finger dewar flask which was later transferred to the epr spectrometer cavity. With the high-pressure lamp, spectra were also obtained as a function of time with the sample in the cavity. The buildup of spectral intensity, I , of the PCl_2 spectrum in neat PCl_3 closely follows the equation $I = I_0[1 - \exp(-t/T_0)]$, where I_0 is the final intensity ($t \rightarrow \infty$) and T_0 is a parameter which, among other things, is characteristic of the experimental configuration. In this case, $T_0 \sim 60$ min. Usually, with samples irradiated outside the cavity, the time of exposure was of the order of 4 hr, which is at least $8T_0$ if one assumes the slits in the cavity wall pass only half of the radiation.

In neat PCl_3 , a reasonably symmetrical doublet centered in the $g = 2.00$ region is observed at liquid nitrogen temperatures (Figure 2). This signal was observed as a function of temperature between -196° and about -100° . The general line shape was seen to vary somewhat with temperature, with the higher field component becoming broader relative to the lower field component. No additional structure was noted in this doublet, as might be expected from interaction of ^{35}Cl and ^{37}Cl isotopes (where $I = 3/2$). Symmetrically disposed about this doublet was another pair of lines, each component of which was a septet of septets. The higher field component is shown in Figure 3, with an enlargement of the central peak of this septet shown at the left in order to more clearly display the smaller splittings.

(13) W. L. Jolly, C. B. Lindahl, and R. W. Kopp, *Inorg. Chem.*, **1**, 958 (1962); A. A. Dandoval and H. C. Moser, *ibid.*, **2**, 27 (1963).

(14) F. E. Brinckman and G. Gordon, Abstracts, 4th Middle Atlantic Regional Meeting of the American Chemical Society, Washington, D. C., Feb 1969, p 41.

(15) One gauss = 1×10^{-4} tesla ≈ 2.8 MHz.

(16) F. J. Adrian, E. L. Cochran, and V. A. Bowers, *Advances in Chemistry Series*, No. 36, American Chemical Society, Washington, D. C., 1962, p 50.

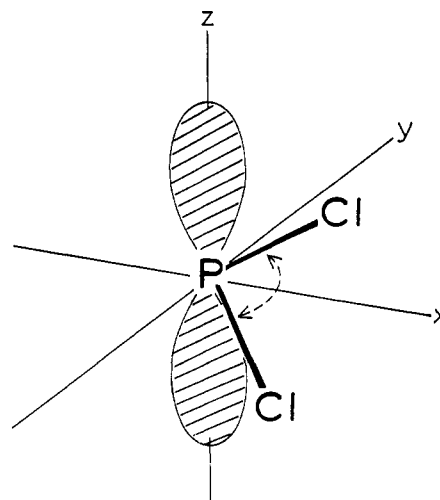


Figure 4. Coordinate system and molecular geometry of the PCl_2 radical.

Another spectrum was observed in the $g = 2.00$ region in frozen mixtures of PCl_3 with PF_3 prepared by cocondensation of the gases in about 10:1, respectively. This is shown in Figure 1. With the usual line shape analysis¹⁷ for randomly oriented $S = 1/2$ species, it is possible to assign the central doublet as the "perpendicular" component of the spectrum and the outermost pair of the lines (with structure) as the "parallel" components. These spectral features suggest that the g and A tensors have nearly axial symmetry.

The authors have also studied compounds of the type $(\text{CH}_3)_n\text{PCl}_{3-n}$, where $n = 1$ and 2. In these cases, the spectra were rather similar to those described above, but with much less structure.

Experimental parameters for the new radicals are summarized in Table I. Due to the anisotropy of the line shape it is believed that the relative measurement within a septet is more precise than the measurement between the outermost doublet components.

Table I. Experimental Parameters^a

	g	$A(\text{P})$, MHz	$A(\text{Cl})$, MHz
PCl_2	2.001 (\parallel)	753 (\parallel)	41.5 (\parallel)
	2.021 (\perp)	78 (\perp)	0 (\perp)
PCl_4	2.013	3398	175
			21
$(\text{CH}_3)_n\text{PCl}_{3-n}$	2.000	3015	b

^a Values are believed to be accurate to within $g \pm 0.005$, $A(\text{P}) \pm 14$ MHz, $A(\text{Cl}) \pm 5$ MHz. ^b Unresolved.

Results

PCl_2 . In the mixture of PF_3 with PCl_3 the spectrum shown in Figure 1 can be analyzed into parallel and perpendicular components for the triatomic radical. A schematic representation of the molecular geometry is shown in Figure 4. The data indicate that the x and y components of the g tensor are essentially identical, as are the x and y components of the phosphorus hyperfine tensor, suggesting a Cl-P-Cl bond angle approaching 90° . No chlorine structure is observed in the perpendicular spectrum. Indeed, the relative narrowness of this spectral region suggests that the value of $A_{\perp}(\text{Cl})$ must be quite small and, in consequence for convenience, has been taken as equal to zero in the rest of this analysis.

(17) G. F. Kokoszka and G. Gordon, "Techniques of Inorganic Chemistry," Vol. VII, H. B. Jonassen and A. Weissberger, Ed., Interscience Publishers, New York, N. Y., 1968, p 205, and references cited therein.

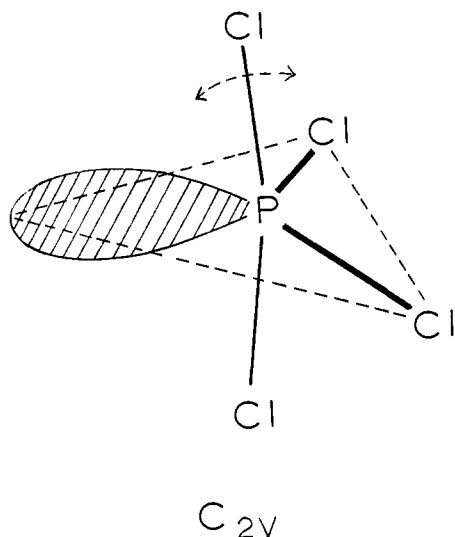
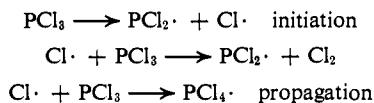


Figure 5. Schematic representation of the PCl_4 radical.

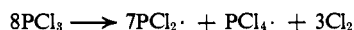
The PCl_2 observed in the neat PCl_3 is broad and displays little structure. The behavior of the spectrum as a function of temperature seems to rule out assignment as the freely-rotating species. The g value measured in this case is also close to that obtained from the PCl_2 in the PF_3 - PCl_3 mixture. It seems likely that the differences in the spectral appearance of the PCl_2 in these matrices are a result of local distortions; the spectrum of PCl_2 in the xenon matrix is identical with that obtained in the neat material. The appearance of the spectrum and the magnetic parameters consequently determined are sensitive to small changes in the local environment, as has been noted in a number of studies.¹⁷

PCl_4 . In the neat PCl_3 , spectral components are found symmetrically disposed about the PCl_2 doublet and are assigned to the species PCl_4 . This assignment is based on the number of hyperfine components found in the spectrum as well as on a comparison of the data obtained for this case with those reported for the radical PF_4 .^{4,5} The spectrum appears to be almost isotropic at liquid nitrogen temperature. In cooling the sample to liquid hydrogen temperatures, the lines became slightly narrower. Thus, in spite of the almost isotropic appearance of the lines, the radical is probably not freely rotating, and careful examination of Figure 2 reveals an asymmetry in the line shape associated with the PCl_4 spectrum.

The ratio of the doubly integrated spectrum of PCl_2 to that for PCl_4 is 7 ± 2 , where the uncertainty is the maximum estimated value. This can be rationalized on the basis of the following reaction scheme.



If it is assumed that the chlorine atom can react with the four constituent atoms of the PCl_3 molecule in a statistical fashion, then the expected ratio is 7, since for the net process

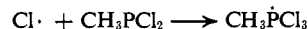
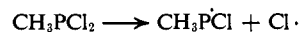


The agreement of the experimental value with the value calculated with a simple reaction stoichiometry scheme suggests that this mechanism is reasonable. However,

it may be noted that $\text{Cl}\cdot$ combination can directly occur, so that the model proposed must be regarded as only a first approximation. When PCl_3 is diluted in Xe in a ratio of 1:9, no evidence for the PCl_4 species is observed. This result suggests that this host lattice serves as an effective means for promoting the combination of two chlorine atoms at the expense of the formation of PCl_4 . In contrast to this, however, dilution in an "inert" matrix may be specific, since preliminary experiments with PCl_3 diluted into an SnCl_4 host lattice revealed formation of the PCl_4 species. Here we may be witnessing an effective chain-transfer mechanism with involvement of formation and scission of $\text{Sn}-\text{Cl}$ bonds.

Organohalophosphines. The compounds studied include CH_3PCl_2 , $(\text{CH}_3)_2\text{PCl}$, $(\text{CH}_3)_3\text{P}$, and CH_3OPCl_2 . The general appearance of the spectra in the $g = 2.00$ region for all of the radicals produced was quite similar to that obtained for the PCl_2 radical in the PF_3 - PCl_3 matrix. The parameters for all these species were similar to that obtained for PCl_2 , but no additional chlorine structure was observed in any of these cases. Also, no spectral evidence for the methyl radical was observed.¹⁰ This could indicate that the organohalophosphines react rather readily with the methyl radical at -196° . An alternate explanation is that only phosphorus-chlorine bonds are cleaved in the chlorine-containing species with this irradiation source; for $(\text{CH}_3)_3\text{P}$ it is presumed that there must be cleavage of the $\text{P}-\text{C}$ bond. In either case, this result is in sharp contrast with results on the organohalo group IV compounds, where the methyl radical quartet was usually the most prominent spectral feature,¹⁰ although secondary reactions resulting in the disappearance of this quartet were noted.

In CH_3PCl_2 a wider doublet was also observed, suggesting a species of the type $(\text{CH}_3)_n\text{PCl}_{4-n}$, where n may be 1 or 2. No chlorine structure was observed in this case. The line width was about 100 G, but varied somewhat as a function of sample preparation and length of irradiation. The lack of any evidence of CH_3 suggests a possible reaction quite analogous to that proposed from the PCl_3 precursor may transpire.



This is an interesting result in connection with frequent postulation of such reactive intermediates in the radical-induced addition of PCl_3 to hydrocarbons.¹⁸

Discussion

Bonding in PCl_2 . An analysis of the stereochemistry and bonding in these phosphorus-containing radicals can be made by comparing the parameters derived from the experimental data with theoretical values. The PCl_2 radical in the mixture PCl_3 - PF_3 revealed the most detailed structure and will be analyzed first.

The phosphorus hyperfine coupling constants, $A_{\parallel}(\text{P}) = 753 \text{ MHz}$ and $A_{\perp}(\text{P}) = 78 \text{ MHz}$, can be written in terms of an isotropic and an anisotropic contribution.

$$A_{\parallel} = A + 2B \quad (1)$$

$$A_{\perp} = A - B \quad (2)$$

Assuming both $A_{\parallel}(\text{P})$ and $A_{\perp}(\text{P})$ to be positive, the val-

(18) J. T. G. Cadogan, *Advan. Free Radical Chem.*, 2, 203 (1967).

ues of $A(P)$ and $B(P)$ are 303 and 225 MHz, respectively. The value expected for $A(P)$, if the electron were entirely within a phosphorus 3s orbital [$A_0(P)$] lies somewhere in the range of 10,178 to 13,000 MHz, while the value of $B(P)$ for an electron entirely within a 3p orbital [$B_0(P)$] on phosphorus is somewhere between 287 and 367 MHz.^{19,20} The small value of $A(P)$ for PCl_2 suggests relatively little 3s character in the unpaired electron wave function,²¹ while the value for the per cent phosphorus 3p character is from about 78 to 61%.²² It seems likely then that as a first approximation, the unpaired electron can be regarded as being primarily in a phosphorus 3p orbital. This orbital is likely to lie perpendicular to the molecular plane, an assignment consistent with that made for the PH_2 radical.²³ Other choices of relative sign might be made in eq 1 and 2. If $A_{\parallel}(P)$ is chosen positive and $A_{\perp}(P)$ negative, then $A(P) = 199$ and $B(P) = -277$. The choice of $A_{\parallel}(P) < 0$, $A_{\perp}(P) > 0$ leads to $A(P) = -199$, $B(P) = 277$; and finally both $A_{\parallel}(P)$ and $A_{\perp}(P)$ negative leads to $A(P) = -303$, $B(P) = -225$. These values obtained for $A(P)$ and $B(P)$ with the experimental parameters of varying sign do not significantly alter the conclusion (*vide infra*) that as a first approximation the unpaired electronic density is in the phosphorus 3p orbital.

With this preliminary analysis, the radical species may be analyzed in terms of the coordinate system defined in Figure 4. The phosphorus-chlorine σ bonds lie in the xy plane. The unpaired electron lies in the p_z orbital perpendicular to this plane. The p_z orbital on phosphorus can form molecular orbitals with the two chlorine p_z orbitals. The amount of time spent by the unpaired electron in these orbitals may also be estimated from the experimental data. From eq 1 and 2 and the previous assumption $A_{\perp}(\text{Cl}) = 0$, the values $A(\text{Cl}) = B(\text{Cl}) = 13.8$ MHz are obtained. If the unpaired electrons were entirely within a 3s orbital on chlorine, a value of about 5000 MHz would be expected for $A(\text{Cl})$, while a value of about 137 to 176 MHz is expected if the unpaired electron is entirely in a chlorine 3p orbital.^{19,20} The values derived from the data suggest about 10% chlorine 3p character but essentially no 3s character. The origin of the small isotropic (s-like) interaction has been discussed by Atkins and Symons in their excellent book,²² and the recent papers of Hunter and Symons²¹ and Higuchi.⁶ These contributions will be further considered below.

The results of a somewhat more detailed analysis of the hyperfine splitting are presented in Table II. The values of B_0' and B_0'' are two theoretical values for total occupancy in the phosphorus or chlorine 3p orbitals using different wave functions.^{19,20} There are four cases to be considered, depending on the value for B as discussed above and the values for B_0 cited elsewhere. Finally, it seemed appropriate to obtain normalized values in the following fashion. With a given $B(P)$, $B(\text{Cl})$, $B_0(P)$, and $B_0(\text{Cl})$, the percentage time spent on the phosphorus atom could be estimated from the ratio $B(P)/B_0(P)$, and on each chlorine atom from the

Table II. π -Bonding Parameters for PCl_2

	B_0' , MHz	B_0'' , MHz
P	367	287
Cl	176	137
Case 1		
$B(P) = 225^a$		
$B(\text{Cl}) = 13.8^a$		
$B(P)/B_0(P)$	0.613	0.783
$B(\text{Cl})/B_0(\text{Cl})$	0.078	0.101
NFSD(P)	0.797	0.795
Case 2		
$B(P) = 277^a$		
$B(\text{Cl}) = 13.8^a$		
$B(P)/B_0(P)$	0.755	0.965
$B(\text{Cl})/B_0(\text{Cl})$	0.078	0.101
NFSD(P)	0.829	0.829

^a MHz.

ratio $B(\text{Cl})/B_0(\text{Cl})$. The sum of $B(P)/B_0(P) + 2B(\text{Cl})/B_0(\text{Cl})$ is generally not equal to one. Since the electron is assumed to be localized on a single molecular fragment, the ratio $[B(P)/B_0(P)] / \{B(P)/B_0(P) + 2[B(\text{Cl})/B_0(\text{Cl})]\}$ = normalized fractional spin density (NFSD) should be a more reasonable measure of the amount of time the unpaired electron spends on the central phosphorus atom. It may be noted that with either set of theoretical values, the normalized fractional spin density (NFSD) is about 0.8. This would suggest that the appropriate terms in the two sets of wave functions are related by a nearly constant scaling factor.²⁰ Thus, if sufficient experimental data are obtained from molecules containing atomic constituents with nonzero nuclear moments, the most reliable value of B_0 may ultimately be an experimental value.

As an additional point of illustration, a similar calculation has also been carried out with the data available for NF_2 .^{24,25} In this case, there are two possible choices for sign for the fluorine hyperfine structure and the values of NFSD(N) range from 0.771 to 0.846. In this case, however, the relative sign is known and the proper value is ~ 0.85 . From a comparative point of view, the NFSD on the P atom in PCl_2 is nearly the same as the NFSD on the N atom in NF_2 .

In PCl_2 , as in NF_2 and PF_2 , the unpaired electron most probably occupies a 2B_1 molecular orbital;^{9,24} this orbital consists of two in-phase chlorine p_z orbitals and an out-of-phase phosphorus p_z orbital. The deviation of the g factor from the free electron value may be considered as due primarily to spin-orbit interactions with orbitals of symmetry B_2 and A_1 . These are expected to cause a deviation of g_x and g_y from the free electron value (g_e) and account for $g_{\perp} > g_e$. On the other hand, Farmer, Gerry, and McDowell²⁴ point out that a deviation of g_z from g_e can occur through an A_2 molecular orbital. In PCl_2 , as in NF_2 , the irreducible representation A_2 in point group C_{2v} does not contain any of the phosphorus s or p orbitals. In agreement with this prediction, the measured value for g_z is g_e .

In the isotropic radical PF_2 , the observed isotropic hyperfine splitting from the fluorine atoms is about 180 MHz.⁸ For PCl_2 , the corresponding isotropic chlorine

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(24) J. B. Farmer, M. C. L. Gerry, and C. A. McDowell, *Mol. Phys.*, **8**, 253 (1964).

(25) P. H. Kasai and E. B. Whipple, *ibid.*, **9**, 497 (1965).

hyperfine splitting is 13.8 MHz or about 5 G. If the PCl_2 and PF_2 radicals had essentially the same structure and the same mechanism was operative in producing halogen hyperfine interactions, then the expected ratio of the isotropic splittings should be about 10. The observed value of 12 can be taken as an indication that the two radicals have a similar geometry and orbital composition.

Bonding in PCl_4 . The spectral components that are associated with the PCl_4 species have the feature of a large hyperfine splitting. Since the contribution from 3p orbital dipolar interaction is expected to be under 400 MHz, the large observed splitting of over 3000 MHz can be taken as an indication of a large contribution from the 3s orbitals in the wave function of the unpaired electron. Comparison of the experimental value of $A(\text{P})$ with the theoretical value of $A_0(\text{P})$, the splitting expected if the electron were totally within a 3s orbital, indicates that the unpaired electron occupies an orbital which contains approximately 33% 3s character. The simplest structure which fulfills this requirement is a trigonal bipyramid with the unpaired electron in an equatorial sp^2 hybrid, as illustrated in Figure 5. The observation of two sets of equivalent chlorines is consistent with this model.

The data do not require that the molecular geometry be rigorously trigonal bipyramidal²⁶ but the orbital composition will first be examined on that basis. Later, deviation from this symmetry will be considered.

Within the framework of a hybrid orbital theory utilizing linear combinations of atomic orbitals and assuming two-center bonding, the five orbitals on the phosphorus can be taken as follows.²⁷

$$\begin{aligned}\phi_1 &= \frac{1}{\sqrt{3}}(s \sin \alpha - d_{z^2} \cos \alpha) + \frac{1}{\sqrt{6}}p_x \\ \phi_2 &= \frac{1}{\sqrt{3}}(s \sin \alpha - d_{z^2} \cos \alpha) - \frac{1}{\sqrt{6}}p_x + \frac{1}{\sqrt{2}}p_y \\ \phi_3 &= \frac{1}{\sqrt{3}}(s \sin \alpha - d_{z^2} \cos \alpha) = \frac{1}{\sqrt{6}}p_x - \frac{1}{\sqrt{2}}p_y \\ \phi_4 &= \frac{1}{\sqrt{2}}(s \cos \alpha + d_{z^2} \sin \alpha) + \frac{1}{\sqrt{2}}p_z \\ \phi_5 &= \frac{1}{\sqrt{2}}(s \cos \alpha + d_{z^2} \sin \alpha) - \frac{1}{\sqrt{2}}p_z\end{aligned}$$

The first three orbitals are along the three equatorial bonds, while the latter two correspond to the axial bonds. For convenience, the orbital containing the unpaired electron will be taken as ϕ_1 , the orbital along the positive x axis. The experimental data may now be examined. As noted previously, the molecule does not appear to be freely rotating at liquid nitrogen temperatures. This circumstance coupled with the incompletely resolved Cl isotopic contributions mentioned earlier, results in diminished resolution of the individual spectral components as compared to that obtained for PF_4 . Thus, the dominant spectral components in Figures 2 and 3 may be associated with the perpendicular portion of the PCl_4 spectrum.

The unpaired electron interacts with the phosphorus

(26) R. W. Fessenden and R. H. Schuler, private communication quoted by Higuchi (ref 6 of this paper).

(27) F. A. Cotton, "Chemical Applications of Group Theory," Interscience Publishers, New York, N. Y., 1963, p 116.

nucleus by means of the Fermi contact term, which produces an isotropic interaction and a dipole-dipole term. The latter term may be associated with the p or d character of the wave function. If the unpaired electron were totally within a p orbital, this interaction would produce a splitting of about 300 MHz. The value of the dipole-dipole interaction between an unpaired electron in a 3d orbital and the phosphorus nucleus has not been calculated, but comparison with typical values for transition metal ions suggests it would be under 600 MHz.²⁸ Thus, the maximum contribution from the p and d portions of the wave function would be significantly lower than the observed value of A . Hence the parallel portion of the spectrum can be separated from the perpendicular portion by at most a few hundred MHz, that is, from eq 1 and 2, a difference of $3B$. It would be difficult to resolve the parallel portions except at one end of the seven-line pattern, and there available signal-to-noise levels preclude direct observation.

Thus, with the wave function listed above, the d portion of ϕ_1 cannot be directly estimated; however, the s portion of the wave function makes up some 30 to 40%. Because of the specified relationship between coefficients in the D_{3h} wave function, the amount of d character must be small if this analysis holds true.

The question of the deviation from trigonal bipyramidal geometry might be considered using a qualitative electrostatic approach.²⁹ In the trigonal bipyramidal geometry, the angle between axial bonds is 180° , while the angle between equatorial bonds is 120° . This is the geometry assumed by five equal point charges constrained to move on the surface of a sphere. If the charge on an equatorial point is reduced to zero, the angle between the "axial" charges would correspondingly decrease from 180° to $109^\circ 54'$ in the plane defined by the "axial" charges and the charge which is being reduced to zero. Similarly, the angle between the two equatorial bonds would decrease from 120° to $109^\circ 54'$. Thus when an "equatorial" charge becomes zero, the four remaining charges have assumed a tetrahedral geometry. Alternatively, if the equatorial charge were not reduced to zero, but rather increased over its original value, it then should be expected that the Cl(axial)-P-Cl(axial) angle will become smaller. In the limit, a square pyramidal geometry (C_{4v}) should be assumed. It is important to emphasize that these data are consistent with a C_{2v} symmetry which can approach either the D_{3h} or C_{4v} limit.

There is some reason to believe that the PCl_4 radical is slightly closer to the C_{4v} extreme than PF_4 . An examination of Higuchi's tables⁶ suggests that a smaller $A(\text{P})$ corresponds to a geometry that tends to less open structure, a conclusion obtained with both valence bond and molecular orbital calculations. However, Higuchi's conclusions concerning 3d orbital participation may not provide the only explanation of this phenomenon. Berry, *et al.*,^{2b} discuss the relation between the simple electrostatic model and the molecular orbital approach, indicating that the relationship between the models is somewhat closer than a cursory examination would suggest. Furthermore, they have considered trigonal bipyramidal \leftrightarrow square pyramidal interconversions in higher symmetry molecules. In the PCl_4 case it should

(28) B. R. McGarvey, *J. Phys. Chem.*, **71**, 51 (1967).

(29) R. J. Gillespie and R. S. Nyholm, *Quart. Rev.*, **11**, 339 (1957).

not be surprising if the geometry were intermediate between these two extremes. Berry, *et al.*, do not believe 3d orbital participation is important in the occupied orbitals.

Bonding in the Organohalophosphines. The argument presented above for the bonding in PCl_4 can also be used for the radical produced in irradiated $\text{CH}_3\text{-PCl}_2$. The large hyperfine splitting of the phosphorus strongly implies a geometry similar to the fully halogenated radicals. This species may be formulated as CH_3PCl_3 , where the dominant contribution to the line width is the unresolved chlorine splittings. It may be noted that some variation of line width was observed, depending on sample history, and is suggestive of important lattice effects. Further, the phosphorus hyperfine splitting is about 10% lower than in PCl_4 . The result may be rationalized with a simple model. Again, it is assumed that the geometry is nearly trigonal bi-

pyramidal and that the orbital composition of the equatorial PCl bond would be expected to be comparable in CH_3PCl_3 and in PCl_4 . The more electropositive P-CH₃ bond would likely have more s character than the P-Cl bond in the remaining equatorial bond.^{2a} Thus, the amount of s character in the orbital or the unpaired electron should be greater for PCl_4 than $\text{CH}_3\text{-PCl}_3$. This is a possible origin of the greater value of $A(\text{P})$ in PCl_4 compared to the organohalo radical. Difference in geometry may also influence the relative values. Again, with reference to the Higuchi tables, the smaller value of $A(\text{P})$ would suggest a geometry slightly closer to C_{4v} for CH_3PCl_3 than for PCl_4 . Indeed, since the values for $A(\text{P})$ decrease for the series PF_4 , PCl_4 , and CH_3PCl_3 , it is not unreasonable to associate this change with relative electronegativities and a sterically more closed structure. The question of 3d orbital participation must be left open as before.

Pentacoordinate Silicon Derivatives. IV.¹ Alkylammonium Siliconate Salts Derived from Aliphatic 1,2-Diols

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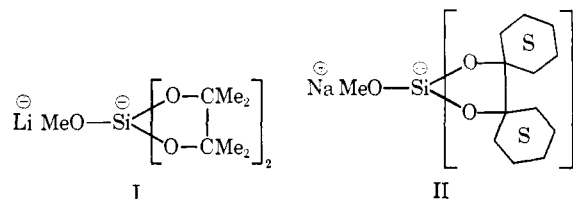
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Abstract: Although stable, easily isolable, extracoordinate silicon derivatives of catechol and other aromatic 1,2-diols are well known, the literature contains relatively little information concerning analogous derivatives of *aliphatic* 1,2-diols. This paper describes the preparation of such a series consisting of alkylammonium siliconate salts derived from 1,2-diols as diverse as ethylene glycol, pinacol, and perfluoropinacol; also included are several examples of related α -hydroxycarboxylic acid derivatives of silicon. Compared to the catechol siliconates, the aliphatic diol siliconates are generally less robust thermally and solvolytically, except for the perfluoropinacol derivatives, in which the pentacoordinate silicon hybridization is maintained even in media as acidic as glacial acetic acid. Because of their extraordinary solvolytic stability, these perfluoropinacol siliconate anions are of special significance, since they should permit solution studies of pentacoordinate silicon species uncomplicated by equilibria involving merely tetracoordinate structure. Especially interesting was the chemistry of the novel strained heterocyclic $\text{Ph}(\text{OMe})\text{Si}(\text{OCMe}_2\text{CMe}_2\text{O})$. In the presence of suitable bases it underwent rapid ligand redistribution to

yield a pentacoordinate siliconate anion bearing two of the bidentate pinacolatoxy moieties (*i.e.*, $\text{PhSi}^-(\text{OCMe}_2\text{-CMe}_2\text{O})_2$). However, with alkanolamine bases possessing the requisite structural features, intermediates bearing only one pinacolatoxy moiety were obtained. These intermediates are believed to be spirocyclic pentacoordinate structures in which a strategically appended donor moiety (*i.e.*, a dangling aminoalkoxy group) has become intramolecularly σ -bonded to the nearby electrophilic silicon center. The extent to which anchimeric coordination of this type occurs was shown to be dependent upon both the length of the aminoalkoxy group and the degree of N-alkylation.

Stable, easily isolable, extracoordinate silicon derivatives of *aromatic* 1,2-diols have been described in considerable detail;² however, the literature contains very little information concerning related derivatives of *aliphatic* 1,2-diols. The presence of such species in solution was inferred by Meerwein³ and convincingly demonstrated by Müller and Heinrich;⁴ the latter

authors also presented evidence for the isolation of two alkali metal pentacoordinate siliconate salts (I and II). Reported herein are facile preparative routes to a related



series of easily isolable crystalline alkylammonium

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(3) H. Meerwein, *Justus Liebigs Ann. Chem.*, **476**, 113 (1929); *Angew. Chem.*, **63**, 489 (1951).