

Chapter 2

Single Crystal EPR Studies of Radicals Produced by Radiolysis of Organophosphorus Compounds

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Abstract The main radical species produced by radiolysis of organophosphorus compounds are described in this chapter. Their identification is generally based on an analysis of the g and hyperfine tensors obtained from EPR experiments performed on irradiated single crystals. Special emphasis is placed on the properties of the ^{31}P hyperfine tensor, which is often decisive in determining the structure of these radicals. Radiogenic species mentioned in the beginning of this review correspond to simple phosphorus-centered radicals (PR_2 , PR_3^- , PR_4 , PR_3^+ , and R_2PO). Then, more delocalized systems are reported (allylic structures, captodatively stabilized radicals, symmetrical radical ions containing a P–P bond). The effects of radiolysis on compounds containing low-coordinate phosphorus atoms (e.g. phosphalkenes) are also described as well as the formation of radical pairs in irradiated phosphorylated sugars. The last part of the chapter deals with metallated radicals formed by radiolysis of metallic complexes $\text{M}(\text{CO})_5\text{P}(\text{H})\text{Ph}_2$ (with $\text{M} = \text{Mo}, \text{Cr}, \text{W}$). In some cases, phosphorus-centered radicals are compared with their arsenic analogues. For several systems the focus lies on dynamical effects; this is the case, for example, for the triptycenephosphinyl radical, which undergoes internal rotation around a P–C bond. Molecular rearrangements after radiolysis of some organophosphorus compounds (e.g. diphosphenes) are also reported.

2.1 Introduction

Phosphorus, the 11th most abundant element in the Earth's crust, plays a crucial role in almost all fields of chemistry. It participates in a multitude of industrial processes, is a key element in the life sciences and is involved in the structure of numerous reactants useful in organic synthesis [1]. The ability of phosphorus to adopt several oxidation states and various coordination numbers is the source of its rich and diversified chemistry. This property is especially important for explaining

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the huge variety of reaction intermediates encountered in the radical chemistry of organophosphorus compounds. Without any doubt, EPR is one of the most efficient methods to detect these radicals. A great number of phosphorus-centered radicals, formed by photolysis, chemical reaction or electrochemistry, have been identified by liquid phase EPR [2, 3]. In these experiments, however, due to rapid motion of the radicals, only the average g value and the isotropic component of the hyperfine interactions can be measured. More complete information about the structure of these species is provided by solid state EPR [4]. In most cases, these spectra are recorded after rapid freezing of the reaction medium or by direct radiolysis of a solid sample containing the randomly oriented precursor. All the tensors that participate in the spin Hamiltonian of the radical contribute to the resulting “powder” spectra and, in principle, this technique is well suited for structural interpretation. However, due to frequent overlapping signals, the analysis of these spectra is often quite tedious, especially when several paramagnetic species are simultaneously produced in the sample. Moreover, it cannot be entirely excluded, when line-widths are rather large, that various sets of tensors can lead to similar spectra. All these difficulties are overcome when the radiogenic radical is trapped in a single crystal matrix. The angular dependences of the signals lead to an unambiguous determination of all the tensors of the system and, in favorable cases, additional valuable information can be obtained. As mentioned in this chapter, when the crystal structure of the sample is known, it is possible to directly determine the orientation of the orbital containing the unpaired electron with respect to the undamaged molecule. It is also possible to get a clear description of molecular motion when, after radiolysis, the radical undergoes internal rotation or rearrangement. Contributions of the matrix to stabilizing the trapped radical can be revealed by comparing the principal directions of the EPR tensors with the bond directions given by the crystal structure of the precursor; this approach is particularly pertinent when hydrogen bonds are involved. Specific information about radiation mechanism can also be provided by single crystal EPR in the case of pair wise trapping; for these systems the vector linking the two radicals of the pair can be determined and discussed in relation to the crystallographic data.

Analysis of EPR spectra obtained with radiolyzed single crystals of organophosphorus compounds is greatly facilitated by the magnetic properties of the ^{31}P nucleus. The natural abundance of this nucleus is equal to 100% and its spin is equal to $\frac{1}{2}$. Moreover, the isotropic coupling constant associated with an electron localized in a phosphorus 3s orbital is large ($^{31}\text{P}-A_{\text{iso}}^* = 13306$ MHz) and the dipolar tensor associated with an electron lying in a phosphorus 3p orbital ($2B_0 = 733$ MHz) leads to rather anisotropic hyperfine splittings. The angular variation of signals due to radicals exhibiting hyperfine interactions with ^{31}P is therefore easy to follow, even when several species are simultaneously trapped in the crystal. Many programs have been written in order to extract the g and hyperfine tensors from the angular dependence of signals recorded in a single crystal EPR study or from powder spectra [5, 6]; some of them are commercially available [7]. For some organophosphorus radicals presenting a small ^{31}P hyperfine interaction, assignment of the couplings to the various spin $\frac{1}{2}$ nuclei present in the molecule is not straightforward but can be performed by running single crystal ENDOR spectra.

Interpretation of ^{31}P hyperfine tensors in terms of radical structure is generally performed by comparing the experimental isotropic and anisotropic coupling constants with the expectation values of the Fermi contact and dipolar interactions obtained from *ab initio* calculations or Density Functional Theory (DFT). It is then possible to check if the measured isotropic (A_{iso}) and anisotropic (τ) coupling constants are consistent with the calculated s and p contributions to the SOMO of the postulated radical. A rapid but rather rough method for estimating the phosphorus s and p characters of the SOMO of a radiogenic radical is to merely compare the experimental A_{iso} and τ values with the atomic constants A_{iso}^* and $2B_0$. Several sets of atomic constants have been tabulated in the literature [8, 9]; in the present chapter, for sake of consistency, only the values published by Morton and Preston [10] will be used. The hybridization ratio λ^2 , equal to the ratio of the p character ρ_p over the s character ρ_s has frequently been used to get information about the geometry of a radical. For an AB_3 radical with local C_{3v} symmetry, λ^2 allows calculation of the interbonding angle and the pyramidity (out-of-plane angle) of the radical [9, 11].

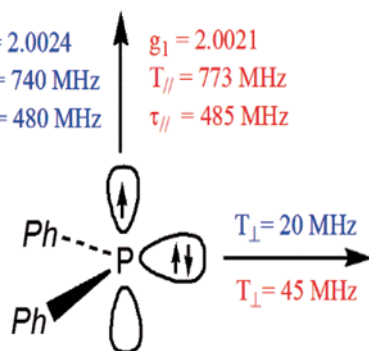
From a chemical point of view it can be interesting to compare phosphorus-centered radicals with other species centered on a heavy atom in group 15. Although considerably less numerous than their phosphorus homologues, some arsenic and antimony radicals will be mentioned in this chapter. For these radicals, structural information is provided not only by the magnetic hyperfine interaction but also by the quadrupolar coupling: ^{75}As : natural abundance = 100 %, $I = 3/2$, $A_{\text{iso}}^* = 14660$ MHz, $2B_0 = 667$ MHz, ^{121}Sb : natural abundance: 57.2 %, $I = 5/2$, $A_{\text{iso}}^* = 35100$ MHz, $2B_0 = 1257$ MHz [10].

The present chapter deals with radicals produced by radiolysis of organic compounds containing a phosphorus atom. However, for historical reasons, pure inorganic radicals, such as PO_3^{2-} or PF_4 , will also be mentioned.

2.2 Phosphinyl Radicals

The first EPR study of a phosphinyl radical was reported almost 50 years ago [12]. It concerned the formation of PH_2 produced by γ -irradiation of PH_3 in a diluted solution in a Kr matrix at low temperature. Due to the rapid motion of this small radical, only the isotropic part of the ^{31}P hyperfine tensor could be measured ($A_{\text{iso}} = 224$ MHz). A few years later, the anisotropic part of the phosphorus coupling could be estimated for PF_2 [13] ($\tau = 626$ MHz) and PCl_2 [14] ($\tau = 605$ MHz) after trapping these species at 4 K in Xe matrices. As shown by Symons et al. [15, 16], powder spectra recorded after γ -radiolysis at 77 K of several trivalent phosphorus derivatives (e.g. $\text{P}(\text{SMe})_3$, $\text{P}(\text{OMe})_3$, Pr_2PCl) revealed the formation of phosphinyl radicals. A full determination of both the g and ^{31}P hyperfine tensors could be obtained for the diphenylphosphinyl radical Ph_2P after trapping of this radical in X-irradiated single crystals of triphenyl phosphine oxide and diphenyl phosphine sulfide at room temperature [17]. The ^{31}P hyperfine tensor presents axial symmetry and is moderately sensitive to the host matrix: (740, 20, 20 MHz in Ph_3PO ; 773,

Fig. 2.1 ^{31}P hyperfine values for Ph_2P trapped in an X-irradiated single crystal of Ph_3PO (data in blue) and in an X-irradiated single crystal of $\text{Ph}_2\text{P}(\text{S})\text{H}$ (data in red)



55, 35 MHz in $\text{Ph}_2\text{P}(\text{S})\text{H}$). Similarly, the g -tensor is not very affected by the nature of the crystal: (2.0024, 2.0052, 2.0124) in Ph_3PO and (2.0021, 2.0039, 2.0094) in $\text{Ph}_2\text{P}(\text{S})\text{H}$. As shown in Fig. 2.1, drawn in the approximation of a perfect cylindrical symmetry of ^{31}P -T, the ^{31}P -T $_{||}$ direction is oriented along the g -eigenvector corresponding to the g value close to that of the free electron. This relative orientation of the g and phosphorus hyperfine tensors agrees with properties predicted by Atkins and Symons for this type of radical with C_{2v} symmetry [9].

Assuming a positive sign for the three ^{31}P coupling eigenvalues leads to isotropic coupling constants of 260 MHz in Ph_3PO and 287 MHz in $\text{Ph}_2\text{P}(\text{S})\text{H}$, respectively. The corresponding s -spin densities are small ($\rho_s = 0.020$ and 0.022) and are mainly due to inner shell polarization. The anisotropic coupling constants $\tau_{||}$ shown in Fig. 2.1 are consistent with a rather large localization of the unpaired electron in the phosphorus $\text{P}\pi$ -orbital ($\rho_p = 0.65$ in Ph_3PO , $\rho_p = 0.66$ in $\text{Ph}_2\text{P}(\text{S})\text{H}$). This identification of the Ph_2P radical was confirmed by uv-photolysis of frozen Ph_2PH at -100°C ; the resulting spectrum could be simulated using the tensors obtained from the Ph_3PO single crystal study. In order to assess the sensitivity of the structure of R_2P to the nature of R, the radical $(\text{PhNH})_2\text{P}$ was trapped in an X-irradiated single crystal of $(\text{PhNH})_2\text{P}(\text{O})\text{H}$; a marked axiality of the ^{31}P coupling tensor was still observed but a variation in the anisotropic components revealed a decrease of $\sim 15\%$ in the phosphorus spin density [18].

Lately, renewed interest has focused on phosphinyl radicals in organic and organometallic chemistry. Due to the use of sterically encumbering substituents, very persistent phosphinyl radicals have been synthesized [19, 20]. A dialkylphosphinyl radical was even obtained as thermally stable crystals [21] and an X-ray diffraction study was performed on a phosphinyl radical bearing a cationic substituent [22].

2.2.1 Arsenic and Antimony Homologues of Phosphinyl Radicals

It is interesting to compare the structures of phosphinyl radicals with those of arsinyl and stibinyl radicals. This is possible for the diphenyl phosphinyl radical since Ph_2As could be produced in an X-irradiated single crystal of triphenylarsine oxid [23], while Ph_2Sb was trapped, after radiolysis or uv-photolysis, in a single crystal

of triphenylantimony [24, 25]. For Ph_2As , both magnetic ($^{75}\text{As-T}$) and quadrupolar ($^{75}\text{As-P}$) hyperfine coupling tensors exhibit cylindrical symmetry. As expected, the direction of T_{\parallel} (628 MHz) aligned along the arsenic p-orbital containing the unpaired electron is perpendicular to the quadrupolar interaction eigenvector P_{\parallel} (−19 MHz), which is oriented along the direction of the lone pair. The tensors g , $^{121/123}\text{Sb-T}$ and $^{121/123}\text{Sb-P}$ obtained for Ph_2Sb are also consistent with this model. Measurements of both the magnetic and quadrupolar interactions with the central atom allow an estimation of the bonding angle: the C–As–C as well as the C–Sb–C angle are close to 98° .

2.2.2 Internal Rotation in Phosphinyl Radicals

During the last two decades considerable efforts have been devoted to the development of molecular rotors and motors [26]. For example, Kelly et al. took advantage of the C_3 symmetry in the triptycene moiety to design a diamagnetic molecular brake in solution [27]. In a similar approach, secondary phosphines containing a barrelene moiety were synthesized and crystallized. In these systems, after radiolysis, a paramagnetic PH bond can rotate around an immobilized phosphorus-barrelene bond [28, 29, 30]. These radicals are shown in Fig. 2.2.

X-irradiation of a single crystal of 9-phosphinotriptycene at room temperature gives rise to a radical characterized by hyperfine couplings with a ^{31}P nucleus and a proton [28]. As shown by experiments performed with deuterated crystals of triptycene- PD_2 [29], the ^1H -coupling is due to a hydrogen atom bound to the phosphorus. Angular variations of the spectrum show that at room temperature, the radical is trapped along a single orientation. The hyperfine eigenvalues for ^1H and ^{31}P are

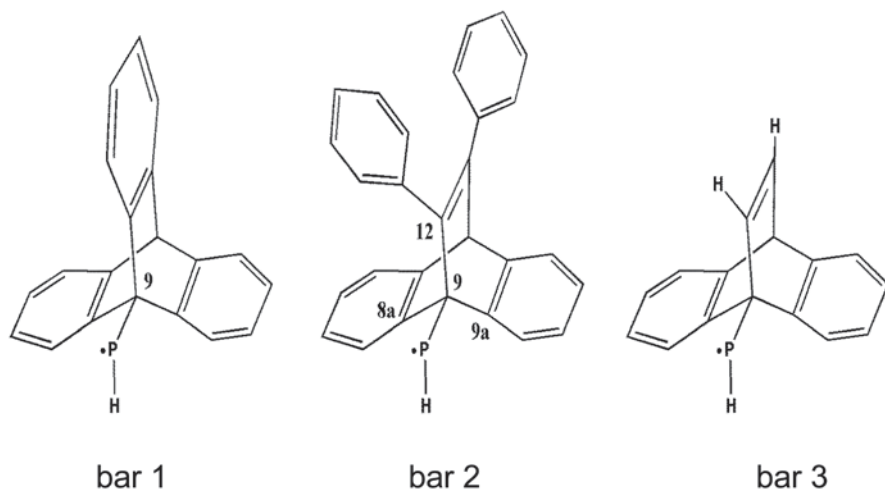


Fig. 2.2 Phosphinyl radicals formed in an x-irradiated single crystal of 9-phosphinotriptycene (bar 1), diphenyldibenzobarrelenephosphine (bar 2), dibenzobarrelenephosphine (bar 3)

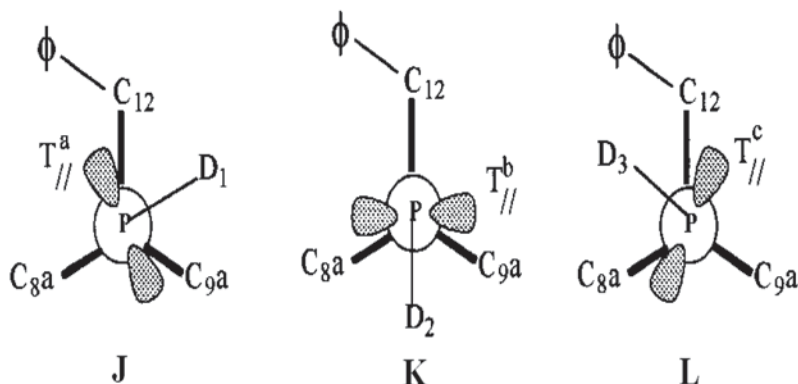


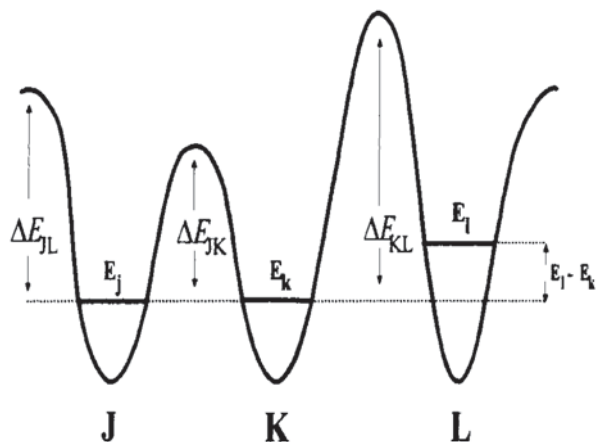
Fig. 2.3 The three staggered configurations of the phosphinyl radical (bar 2) trapped in an irradiated crystal of diphenyldibenzobarrelenephosphine. The figure is adapted from [29] by permission of the American Chemical Society

equal to (38, 39, 61 MHz) and (23, 409, 413 MHz), respectively. Decreasing temperature drastically modifies the spectrum. At 77 K, the radical is trapped along three magnetically non-equivalent sites with new sets of eigenvalues: (37, 42, 67 MHz) for ^1H and (4, 74, 848 MHz) for ^{31}P . The phosphorus isotropic coupling constant is therefore rather small ($A_{\text{iso}} = 308$ MHz) and the anisotropic constant $\tau_{\parallel} = 540$ MHz implies a spin density of 0.73 in a phosphorus p orbital. The component of the g-tensor (2.0036, 2.0102, 2.0134) close to the free electron value is aligned along $^{31}\text{P}-T_{\parallel}$. The angle between the three new $^{31}\text{P}-T_{\parallel}$ eigenvectors is equal to 120° and these three directions are perpendicular to the C–P crystallographic direction. All these features demonstrate that the phosphinyl radical resulting from homolytic scission of a P–H bond is trapped in the crystal and that this radical, immobilized at 77 K, is freely rotating at 300 K around the triptycene-phosphorus bond. In accordance with *ab initio* calculations, the three sites observed at low temperature correspond to the three most stable staggered conformations of the phosphinyl radical (bar 1 in Fig. 2.2). The dynamical process occurring between 77 and 300 K was studied by recording the temperature dependence of the spectrum and analyzing this temperature dependence with density matrix formalism. From the Arrhenius plot $\ln(1/\tau_c) = f(1/T)$, the energy barrier to the rotation of the P–D bond around the P–C bond was found to be about $2.75 \text{ kcal mol}^{-1}$ [29].

In order to assess the factors that influence the motion of the P–H bond in this type of phosphinyl radical, single crystals of deuterated and non-deuterated diphenyldibenzobarrelenephosphine were X-irradiated at 300 K and their EPR spectra studied at various temperatures [29]. As with bar 1, the radical due to the homolytic scission of a P–H bond is trapped in the crystal. Three staggered conformations, denoted **J**, **K**, and **L** in Fig. 2.3, are possible for this phosphinyl radical (bar 2, Fig. 2.2), whose internal rotation of the P–H bond is hindered by the presence of the phenyl ring linked to the ethylenic bond.

However, at 77 K, only conformations **J** and **K** contribute to the EPR spectrum; steric constraints between the phosphinyl deuterium and the phenyl group bound

Fig. 2.4 Variation in the potential energy of the phosphinyl radical bar 2 as a function of the $C_{12}C_9PH$ torsion angle. The figure is reproduced from [29] by permission of the American Chemical Society



to C_{12} preclude occupation of site L. A schematic representation of the energy for the three rotamers is shown in Fig. 2.4. At 100 K, site L begins to be populated and to exchange with site J, while exchange with site K starts only at 130 K. Exchange between J and K begins at 110 K.

The temperature dependence of the EPR spectrum indicates that steric interactions with the phenyl ring bound to the ethylenic carbon C_9 give rise to three different potential wells: $\Delta E_{JL} = 2.46 \text{ kcal mol}^{-1}$, $\Delta E_{JK} = 2.37 \text{ kcal mol}^{-1}$, $\Delta E_{KL} = 2.74 \text{ kcal mol}^{-1}$ and $E_L - E_K = 0.5 \text{ kcal mol}^{-1}$. The role of the environment of the phosphinyl group on the motion of the P–H bond was confirmed by studying the temperature dependence of the EPR spectrum obtained after x-irradiation of a single crystal of dibenzobarrelenephosphine [31]. In the resulting phosphinyl radical (bar 3, Fig. 2.2), there is no group linked to C_{12} and it was necessary to decrease the temperature to 40 K to stop the motion of the P–H bond. The phosphinyl radical was blocked in only two conformations and the motion observed between 45 and 200 K was attributed to jumps between the two corresponding rotamers. The energy barrier associated with this hopping of the phosphinyl proton between two sites was found to be equal to $0.5 \text{ kcal mol}^{-1}$.

The triptycengermany radical (Triptycene- GeH_2) is another example of a radiogenic radical located on a heteroatom bound to triptycene [32]. In this radical, the rotation of the GeH_2 moiety is blocked at 90 K and is free above 110 K. The corresponding rotation barrier is equal to $1.3 \text{ kcal mol}^{-1}$.

2.3 Radical Anion PR_3^-

Earlier studies on non-oriented samples have shown that radiolysis of trivalent tri-coordinated phosphorus compounds leads to a large variety of radical species. The resulting EPR spectra are strongly dependent upon the experimental conditions: polycrystalline or dilute frozen solutions, nature of the solvent (protic or aprotic),

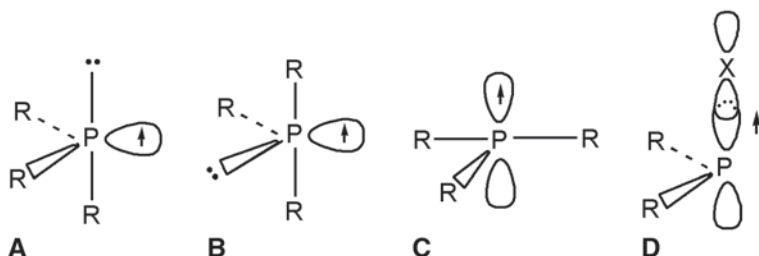


Fig. 2.5 Examples of structures adopted by a radical monoanion centered on a tricoordinated phosphorus atom. The figure is adapted from [33] by permission of Elsevier

temperature of irradiation, and annealing temperature of the irradiated sample [33]. This sensitivity to experimental conditions has been attributed, in part, to the various conformations that the primary radical anion can adopt and to the secondary reactions that this anion can undergo. Trimethylphosphite has been widely studied in this context. Three structures have been proposed for this radical anion. Both structures **A** and **B** are derived from a trigonal bipyramid structure, with a lone pair of electrons in the axial position for **A** and a lone pair of electrons in equatorial position for **B**. Structure **C** corresponds to a planar T-shape structure with the unpaired electron located in a phosphorus p_π orbital (see Fig. 2.5).

One of the first species (called species **1**) formed by γ -irradiation of polycrystalline P(OMe)_3 at 77 K is characterized by ^{31}P hyperfine splittings equal to $T_{\parallel}=1792$ MHz and $T_{\perp}=1464$ MHz. By annealing, this species transforms into a new radical (called species **2**) characterized by $T_{\parallel}=2274$ MHz and $T_{\perp}=1870$ MHz. Hudson and Williams [34] proposed that species **1** corresponds to the radical anion P(OMe)_3^- in conformation **A** and that species **2** results from the rearrangement of structure **A** into structure **B**. However, as shown by Symons et al. [33], the species trapped after radiolysis of polycrystalline P(OMe)_3 are different from those formed by radiolysis of frozen solutions. In MeTHF, a species (called species **1'**) with a hyperfine splitting $T_{\parallel}=748$ MHz is observed immediately after irradiation at 77 K. A slight increase in temperature transforms this species into species **2'** with $T_{\parallel}=812$ MHz. Symons et al. identified species **1'** as being the planar radical anion P(OMe)_3^- with structure **C** and proposed that species **2'** results from a dissociative reaction which gives rise to the phosphinyl radical P(OMe)_2 . In this interpretation, signals observed for species **1** and **2** in polycrystalline samples are attributed to phosphoranyl radicals (*vide infra*).

Phosphorus-centered radical anions resulting from the reduction of a phosphine are rarely observed. The $(\text{PhPMe}_2)^-$ species formed from phenyldimethylphosphine by electrolysis or by reaction with metal alkali exhibits a $^{31}\text{P-A}_{\text{iso}}$ coupling of 5 G, and corresponds, in fact, to a phenyl radical anion bearing a dimethylphosphino group [35].

Electron capture by a R_2PCl compound and subsequent dissociation into a chlorine anion and a phosphinyl radical were clearly observed with an irradiated single crystal of 1,2-phenylenephosphorochloridite (**I**) [36]. The crystal structure of **I** is

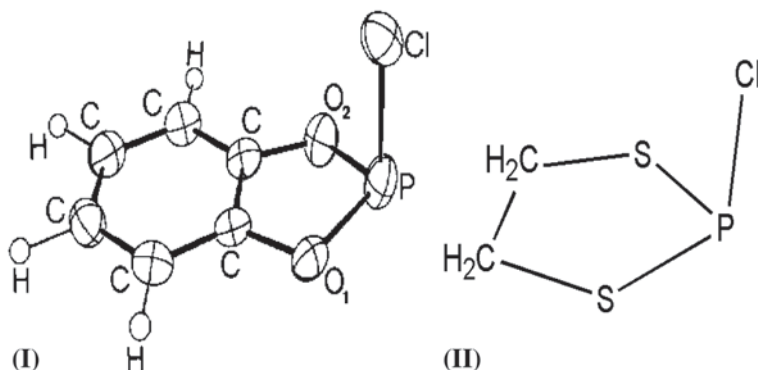


Fig. 2.6 (I) perspective view of 1,2-phenylenephosphorochloridite (from the crystal structure given in [36]. (II) molecule of 2-chloro-1,3,2-dithiaphospholane. The figure is adapted from [36] by permission of the American Chemical society

known (see Fig. 2.6) and confirms the pyramidity of the phosphorus coordination ($\text{OPO} = 95.5^\circ$ and $\text{OPCl} = 99^\circ$). X-irradiation of such a single crystal at 77 K leads to a radical exhibiting hyperfine coupling with both a ^{31}P nucleus (868, 56, 44 MHz) and a ^{35}Cl nucleus (41, (-) 20, (-) 19 MHz). This radical disappears by annealing or photolysis; it is replaced by a new species without ^{35}Cl coupling whose ^{31}P coupling eigenvalues are equal to 755, 111, 93 MHz.

As indicated by the hyperfine interactions, in the first species the unpaired electron is mainly located in a phosphorus p-orbital ($\sim 74\%$) and a chlorine p orbital ($\sim 10\%$, by assuming negative signs for “perpendicular” ^{35}Cl hyperfine eigenvalues). The angle between the two “parallel” eigenvectors is rather small (26°). These properties are consistent with the formation of a radical anion I^- in which the unpaired electron belongs to a phosphorus-chlorine σ^* orbital (Fig. 2.5, structure D). This type of structure has also been observed with selenium-centered radicals [37]. This is also the structure predicted by former *ab initio* calculations for H_2PCl^- whereas a planar T-shape structure was predicted for PCl_3^- .

The ^{31}P coupling of the radical observed after annealing is very anisotropic and indicates a spin density of $\sim 60\%$ in a phosphorus p-orbital. Moreover, its T_{\parallel} eigenvector is oriented along a direction corresponding to g near 2.0023. These properties agree with those expected for phosphinyl radicals and show that a slight increase in temperature causes the dissociation reaction of $(\text{RO})_2\text{PCl}^-$ into $(\text{RO})_2\text{P}$ to occur. Similar results have been obtained with a radiolyzed single crystal of chlorodithiaphospholane (see Fig. 2.6) [38]. The resulting radical anion II^- , trapped at 77 K, also adopts a pyramidal conformation with the unpaired electron localized in a P–Cl σ^* orbital. This is confirmed by the small angle formed by the ^{31}P - T_{\parallel} and ^{35}Cl - T_{\parallel} directions (11°). The presence of the sulfur atoms linked to the phosphorus atoms does not appreciably affect the spin density in the P–Cl bond ($\rho \sim 0.80$). Similar to (I), the phosphinyl radical is observed after annealing. As shown by *ab initio* calculations, the dissociation energy of H_2PCl^- into Cl^- and the phosphinyl radical

is rather low ($\Delta E = 29.3 \text{ kJ mol}^{-1}$). This is probably why the radical anion resulting from electron capture by a chlorophosphine is rarely observed.

It is worthwhile noting that electron addition to compounds containing a pentacoordinated phosphorus has also been reported. PF_5^- has been formed by γ -irradiation of solid solution of PF_5 in neopentane [39] and a $(\text{RO})_4\text{PCl}^-$ radical has been trapped in X-irradiated crystals of a derivative of chlorobenzodioxaphosphole [40]. The structure of this latter species is octahedral with the unpaired electron and the chlorine atom in axial position. In this context, irradiation of a single crystal of Ph_3AsF_2 led to the formation of $\text{Ph}_3\text{AsF}_2^-$ adopting a square base pyramidal structure [41].

2.4 Phosphoranyl Radicals

Formally, in phosphoranyl radicals the unpaired electron is mainly localized on a neutral tetracoordinated phosphorus atom. The exact electronic configuration and the conformation of these radicals have been shown to be very dependent upon the nature of the chemical groups bound to phosphorus [42, 43]. A large number of EPR studies has been devoted to the various structures of these radicals [44] and this species is now well documented. Here, we will focus our attention on results obtained after radiolysis of single crystals.

Early investigations, carried out in liquid solution, concluded that phosphoranyl radicals adopt a trigonal bipyramid structure. Single crystal EPR studies on two halogen-containing phosphoranyls (PF_4 [45] and POCl_3^- [46]) showed, however, that the angular dependences of the spectra were not in accord with a traditional valence bond description, which expects the unpaired electron to occupy one of the five sp^3d -hybridized orbitals. The low anisotropy of the ^{31}P coupling together with the rather large anisotropic coupling with two equivalent halogens were interpreted in terms of a Rundle three-center non-bonding orbital [47]. In this model the two axial ligand p_z -orbitals mix with the phosphorus s and p_x orbitals in an antibonding combination. In this structure most of the *phosphorus* spin density lies in the equatorial plane of a trigonal bipyramid (*structure TBP-e*). As shown by Buck et al., phosphoranyl can also adopt a second type of TBP structure in which the unpaired electron lies in an apical position (*structure TBP-a*) [48]. A third limiting structure was found for some R_3PX phosphoranyls [49]; in this C_{3v} structure, the unpaired electron lies in a σ^* P-X bond as shown in Fig. 2.7.

A simple way to trap a phosphoranyl radical in an oriented matrix is to irradiate a crystalline pentacoordinated phosphorus compound containing a P-H bond. This method was used by Buck et al. to generate phosphoranyl radicals **A** [50, 51], **B** [51] and **C** [52] (see Fig. 2.8). As shown by X-ray diffraction analysis, the conformation of the precursor of **A** corresponds to a trigonal bipyramid with the hydrogen atom in the equatorial position. The resulting EPR parameters are given in Table 2.1. The ^{31}P - $T_{||}$ eigenvector—found to be oriented along the crystallographic P-H direction of the precursor—confirms that this radical adopts a *TBP-e* structure.

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