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The Diversity of the Stable and Persistent Phosphorus-Containing Radicals

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Stable and persistent phosphorus-containing radicals can be divided into five general categories: phosphinyl, diphosphanyl, 1,3-diphosphaallyl, lithiated tetrakisimidophosphates, and phosphaverdazyl systems. The syntheses, structures, EPR spectroscopic characterization, and sources of stability of these neutral radicals are presented and compared.

Introduction

Though the history of stable radicals dates back to the mid-19th century (1, 2), significant advances in the synthesis of inorganic main group radicals have only been made in the past twenty-five years (3). The recent rapid development of this field coincides with increased interest in radical species as potential magnetic materials (4), polymerization catalysts (5), and spin-labels for biomolecules (6). Stable radicals are also of interest from a more fundamental

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standpoint, in that they challenge one of the basic tenets of chemical theory: that electrons are always present as electron pairs in compounds of the main group elements.

While most radicals are highly reactive transient species due to their open-shell electron configurations, numerous examples of both persistent and stable (7) radicals are now known. Such radicals are generally stabilized by delocalization of the unpaired electron over several electronegative atoms such as oxygen or nitrogen, or by delocalization over a π manifold as is often seen in sulfur-nitrogen ring systems (8). Kinetic stabilization of these systems is also possible; the introduction of bulky substituents can impede the reactivity of a radical considerably, enabling its isolation. Despite these efforts to render them stable, numerous radicals dimerize either in solution or in the solid state in order to remove the instability caused by the presence of unpaired electrons.

Electron Paramagnetic Resonance (EPR) spectroscopy is the single most important technique for characterizing radicals, as hyperfine coupling of the unpaired electron to neighboring spin-active nuclei can be used to deduce its chemical environment. The magnitude of the hyperfine coupling (hfc) constant gives information regarding the location of the unpaired electron both within a molecule and within a particular atomic or molecular orbital. The hfc constant for a particular spin-active nucleus is dependent upon the amount of interaction which occurs between the unpaired electron and that nucleus. The type of orbital in which the electron is located can thus be deduced, as an electron in an s orbital will have a significantly larger nuclear interaction than an electron located in a p or d orbital. In addition, the spin density on a particular atom in a delocalized system can be estimated, as the magnitude of the hfc constant will be directly proportional to the amount of time the unpaired electron resides on that atom. Finally, the value of a hfc constant is also dependent upon the gyromagnetic ratio of the nucleus to which it is coupled.

More recently, researchers have used theoretical calculations in order to confirm and even predict the orbital contributions of various atoms to the singly occupied molecular orbital (SOMO), and to verify experimentally observed hyperfine coupling constants. At the present time, persistent or stable radicals are usually identified through a combination of theoretical calculations and experimental techniques such as EPR spectroscopy.

Among the main group elements, there is particular interest in phosphorus-based radicals since phosphorus has only one isotope (^{31}P , $I = 1/2$) and gives rise to much larger hyperfine couplings than those observed for other abundant spin-active nuclei such as ^{14}N ($I = 1$, 99%). These properties render phosphorus an ideal nucleus for spin-labeling experiments, as the anisotropy or orientation-dependence of the hyperfine coupling to ^{31}P can be used to glean information about rapidly moving molecules (6).

The past decade has witnessed the isolation and characterization of a handful of stable and persistent phosphorus-containing radicals. What is perhaps

most interesting about this group of radicals as a whole is their chemical and structural diversity. Persistent radicals containing both P(III) and P(V) are known; species with one, two, or even three phosphorus atoms have been characterized. In some cases the unpaired electron is localized on one atom, while in others it is delocalized over an extensive π manifold. This article examines the similarities and differences amongst the known persistent and stable phosphorus-containing radicals, including aspects of their synthesis, EPR characterization, and the underlying reasons for their stabilities. Beginning with the simplest $[\text{R}_2\text{P}]^\bullet$ systems, the discussion progresses to related P(III) systems, then on to more complex P(V) radicals, including the heterocyclic phosphaverdazyl radicals. The coverage is limited to *neutral* radicals.

Phosphinyl Radicals $[\text{R}_2\text{P}]^\bullet$

A two-coordinate phosphinyl radical is, from a structural standpoint, the simplest of the phosphorus-centered radicals; it is also one of the most thoroughly understood radicals of the main group elements. Numerous radicals of this type can be produced via the photolytic reduction of the appropriate chloro(dialkyl)phosphine in the presence of an electron-rich alkene (9, 10). The most persistent of the phosphinyl radicals that has been prepared since their initial discovery (11) nearly forty years ago is the bis(trimethylsilyl)methyl derivative $^\bullet\text{P}[\text{CH}(\text{SiMe}_3)_2]_2$ **1** which is stable indefinitely both in solution and in the gas phase (9, 10).

EPR Characterization

The EPR spectrum (9) of a solution of reduced $\text{ClP}[\text{CH}(\text{SiMe}_3)_2]_2$ consists of two 1:2:1 triplets, characteristic of a single unpaired electron coupling to one ^{31}P nucleus and to two equivalent ^1H ($I = 1/2$, 100%) nuclei. This confirms the identity of the radical species as **1**, with coupling to the two methine protons observed. A simulation (12) of this spectrum is shown in Figure 1. The value of the phosphorus hyperfine coupling constant ($a_{31\text{P}} = 96.3$ G) suggests that the unpaired electron is located in an orbital of predominantly p character, presumably the $3p\pi$ orbital of the phosphorus atom.

Interestingly, the intensity of the EPR signal does not decrease over time, indicating that the radical does not dimerize in solution, as most phosphinyl radicals do, to yield the diamagnetic diphosphine $\text{R}_2\text{P-PR}_2$ [$\text{R} = \text{CH}(\text{SiMe}_3)_2$] **2**. This is somewhat surprising for two reasons: first, the unpaired electron is essentially localized on one atom, which should render **1** highly reactive. Secondly, the phosphorus atom is only two-coordinate and thus should not be

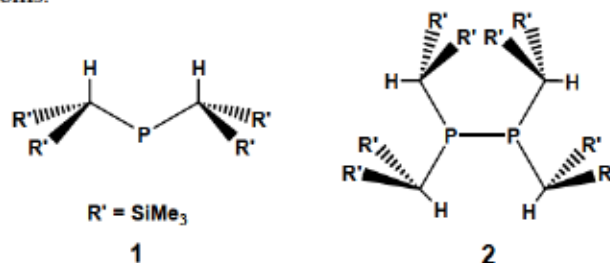


Figure 1. Simulated EPR spectrum of 1.

sufficiently kinetically stabilized to prevent dimerization, its bulky bis(trimethylsilyl)methyl substituents notwithstanding. An investigation of the intensity of the EPR signal as a function of concentration may help to clarify the solution behavior of 1.

Structure and Stability

In order to probe the reasons for the unexpectedly high stability of this radical, a structural study of 1 and its parent diphosphine 2 was undertaken (13, 14) using a combination of X-ray crystallography, gas-phase electron diffraction (GED) and theoretical calculations. The results of this investigation elucidated for the first time the considerable rôle that thermodynamics plays in the stabilization of 1. The structure of 1 was determined by GED measurements, which showed that it exists as a V-shaped species ($\angle\text{CPC} = 104.0^\circ$) with the $\text{CH}(\text{SiMe}_3)_2$ groups oriented exclusively in the *syn,syn* conformation. Density Functional Theory (DFT) calculations were used to confirm this structure. An X-ray crystal structure of 2 showed that, contrary to what is observed in 1, the diphosphine bis(trimethylsilyl)methyl groups adopt a *syn,anti* conformation in the solid state. While this allows for more efficient packing of the $\text{CH}(\text{SiMe}_3)_2$ substituents, it also results in significant crowding of the SiMe_3 groups, both between groups attached to the same phosphorus, and between those bonded to different P atoms.



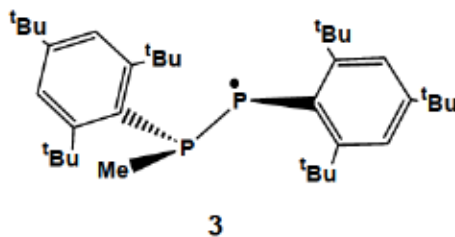
The corollary of these structural data is simply this: the dissociation of the dimer 2 to yield two units of 1 involves not only homolytic cleavage of the

phosphorus-phosphorus bond, but also isomerization of the bis(trimethylsilyl)methyl groups. According to theoretical calculations, the first step in the dissociation process of **2** is homolysis of the P-P bond, which is an endothermic process (95 kJ mol⁻¹). This bond cleavage yields two phosphinyl radicals, both of which are in the *syn,anti* conformation: that is, they are geometrical isomers of the established structure of **1**. Relaxation of the CH(SiMe₃)₂ groups to relieve steric strain, followed by the rotation of one such group about the P-C bond to yield a *syn,syn* radical releases an estimated 67.5 kJ mol⁻¹ for each unit of **1**. Overall, the conversion of the dimer **2** to two fragments of **1** is an exothermic process, releasing approximately 40 kJ for each mole of **2**. Thus the fact that **1** does not dimerize in solution is attributed not to the kinetic stabilization of the bulky ligands, but to the energetic input required for the rearrangement prior to dimerization.

The Diphosphanyl Radical [R₂PPR]•

Related to the phosphinyl radical **1** is the diphosphanyl radical R₂PP•R. While both these species contain a two-coordinate phosphorus atom, the diphosphanyl radical is somewhat more complex in that, as its name implies, it contains a second phosphorus atom. Unlike the phosphinyl radicals, the first stable diphosphanyl radical [Mes*MeP-PMes*]• **3** (Mes* = 2,4,6-tri(*tert*-butyl)phenyl) was synthesized only recently (15), and at present, **3** remains the only such radical known.

The radical **3** was first observed in a cyclic voltammetry experiment with the diphosphene salt [Mes*MeP=PMes*][O₂SCF₃] **4**, which was found to undergo a chemically reversible one-electron reduction. This result prompted an attempt to synthesize the reduction product using chemical means, specifically via an electron transfer reaction from an electron-rich alkene. Reminiscent of the facile reduction of R₂PCl to produce the phosphinyl radical **1** (9) reduction of **4** is effected in an acetonitrile solution containing tetrakis(dimethylamino)ethane at room temperature, yielding yellow crystals of **3**.



Unlike the phosphinyl radicals, **3** is sufficiently stable to be isolated as a solid material; however, magnetic measurements indicate that a small amount of dimerization (~10%) occurs during the liquid to solid transition. Slow decomposition of **3** is observed in the solid state, while in solution, the half-life of this persistent radical is approximately 90 minutes.

EPR Characterization

A solution EPR spectrum of **3** consists of four lines of equal intensities, indicating that the unpaired electron is interacting with two inequivalent ^{31}P nuclei and confirming the identity of **3** as a diphosphanyl radical. The larger of the two coupling constants ($a_{31\text{P}} = 139.3$ G) was attributed to the two-coordinate phosphorus atom, where the larger part of the spin density is thought to be located; the smaller coupling constant ($a_{31\text{P}} = 89.3$ G) was assigned to the three-coordinate phosphorus atom. A simulation (16) of this spectrum is shown in Figure 2.

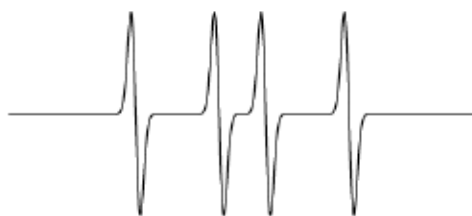


Figure 2. Simulated EPR spectrum of **3**.

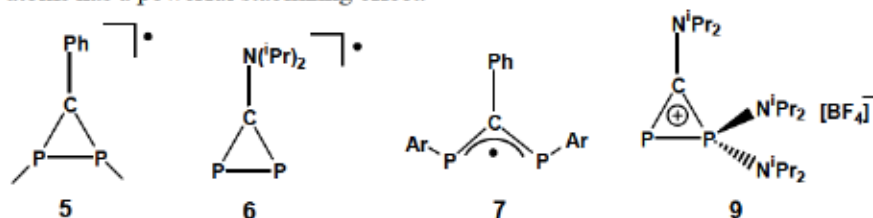
In connection with the growing interest in using ^{31}P -centered radicals as spin-labels, the anisotropy or direction-dependence of the ^{31}P coupling of **3** was examined. By doping **3** into a single crystal of the related diphosphane $\text{Mes}^*\text{MeP-PMes}^*\text{Me}$, solid-state EPR spectra of **3** were obtained, varying the angle of the crystal to the magnetic field. A difference of 420 G between the high- and low-field transitions was observed when the magnetic field is perpendicular to the P-P bond, while a much smaller separation of 130 G was observed with the magnetic field parallel to the P-P bond, i.e. perpendicular to the p orbital in which the unpaired electron resides. The large anisotropies of these phosphorus couplings indicate that diphosphanyl radicals such as **3** may well find use in the future as spin-labels.

Structure and Stability

As is seen for phosphinyl radicals, the phosphorus couplings observed in the EPR spectra of **3** are relatively large, indicating that the unpaired electron resides almost exclusively on the two phosphorus atoms. DFT calculations revealed the expected small *s* contribution (~10%) to the SOMO, while confirming that the largest part (~74%) of the spin density resides in a *p* orbital of the two-coordinate phosphorus atom, while the remaining 15% is located in a *p* orbital of the three-coordinate phosphorus. Consistently, the calculated P-P bond distance (2.18 Å) is only slightly shorter than a typical P-P single bond (2.22 Å); a considerably shorter bond would be expected if the electron were delocalized equally over the two phosphorus atoms, as this would result in a P-P bond order of 1.5. Since minimal delocalization of the unpaired electron occurs in **3**, the stability of this radical is attributed to the steric protection afforded by the Mes* substituents, which reduces the reactivity of **3** making it possible to characterize this species.

A 1,3-Diphosphaallyl Radical [R₂NP(CNR₂)PNR₂][•]

In addition to the diphosphanyl radical, several other species are known which contain a single unpaired electron delocalized over two phosphorus (III) atoms, including the diphosphiranyl **5**, diphosphirenyl **6**, and 1,3-diphosphaallyl **7** radicals. Of these, **5** and **6** are transient species that have been observed in EPR spin-trapping experiments (17) and postulated as reaction intermediates (18). Similar behavior has been noted for the related 1,3-diphosphaallyl radicals, which have widely been considered to be unstable; however, a recent study (19) has shown that the introduction of amino groups on the three ring atoms has a powerful stabilizing effect.



As in the case of the diphosphanyl radical, the stable radical [(ⁱPr₂NP)₂CNⁱPr₂][•] **8** was first observed in a cyclic voltammetry experiment as the product of the one electron reduction of the diphosphacyclopropenium salt **9**. Preparative scale reductions involving either electrolysis or the reduction of **9** with lithium metal led to the isolation of **8** in the form of paramagnetic red crystals. Although the crystals were not suitable for X-ray analysis, a FAB mass

spectrum showed the expected molecular ion. Unlike the phosphinyl and diphosphanyl radicals discussed earlier, **8** can be isolated and shows no sign of decomposition in the solid state over a period of weeks.

EPR Characterization

Solution EPR spectra of **8** were obtained in an attempt to identify the radical species. Each spectrum displayed five broad lines of relative intensities 1:3:4:3:1 as shown in Figure 3; additional hyperfine coupling could not be

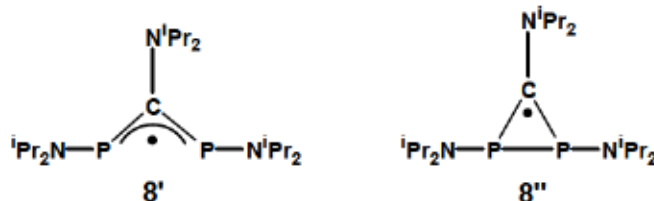


Figure 3. EPR spectrum of **8**. (Reproduced from reference 19. Copyright 1997 American Chemical Society.)

resolved even at low temperature. The increased complexity of this spectrum compared to those of the phosphinyl and diphosphanyl radicals can be attributed to delocalization of the unpaired electron over more spin-active nuclei, specifically ^{14}N . Indeed, the best simulation of this spectrum is obtained by including hyperfine coupling to two equivalent ^{31}P nuclei ($a_{31\text{P}} = 9.4$ G), two equivalent ^{14}N nuclei ($a_{14\text{N}} = 1.5$ G), and a unique nitrogen atom ($a_{14\text{N}} = 9.9$ G). The relatively small value of the ^{31}P coupling constant in **8** compared to those observed in the two P(III) radicals discussed earlier reflects a decrease in the phosphorus character of the SOMO, which results from delocalization of the unpaired electron over the nitrogen centers.

Structure and Stability

Based on the EPR data, two structures **8'** and **8''** can be proposed for the radical **8**. In order to determine the true identity of **8**, *ab initio* calculations were carried out on these two isomers. Structure **8''** was found to be significantly higher in energy (114.6 kJ mol $^{-1}$) than **8'**, essentially precluding the possibility that **8''** is the correct formulation of this radical. In addition, the optimized



geometry of **8''** has the CNⁱPr₂ unit bent out of the plane of the three-membered ring, destroying the symmetry of the molecule; hence, its geometry is not consistent with the observed EPR hyperfine couplings. The stable radical **8** was therefore identified as the 1,3-diphosphaallyl species **8'**; the mechanism of the rearrangement of **9** to yield **8'** has yet to be elucidated. The increased stability of **8'**, compared to that of **1** or **3**, can be attributed to the delocalization of the unpaired electron over a total of five atoms, three of which are highly electronegative.

Dilithiated Tetrakisimidophosphate Radicals

In moving from **1**, **3**, and **8** to a tetrakisimidophosphate radical, the oxidation state of the phosphorus atom increases from those P(III)-based systems to a P(V) species. However, the basic principles of stabilizing the radical through the use of bulky substituents and delocalization of the unpaired electron over several atoms remain unchanged. Like the diphosphanyl radical, the dilithiated tetrakisimidophosphate radical “Li₂[P(N^tBu)₃(NSiMe₃)][•]” **10** was discovered only recently (20). The P(V) radical **10** was prepared via the oxidation of the trilithiated tetrakisimidophosphate Li₃[P(N^tBu)₃(NSiMe₃)] (21) with iodine or bromine in tetrahydrofuran (THF), producing blue solutions that persist for several weeks. From these reactions, paramagnetic blue solids can be isolated that are stable indefinitely in the solid state in the absence of air.

Structure and Stability

In order to identify the radical **10**, the blue solid was crystallized and an X-ray structure was obtained. The crystallographic data showed that, in the solid state, the oxidation product **10** acts to trap a monomeric unit of lithium iodide. The resultant adduct {Li₂[P(N^tBu)₃(NSiMe₃)](LiI)•3THF}[•] **11** exists as a highly distorted PN₃Li₃I cube; an X-ray structure of the isostructural LiO^tBu adduct **12** has also been obtained (22). At present, **11** and **12** are the only inorganic phosphorus-containing radicals to have been characterized by X-ray crystallography.

In order to probe the source of the remarkable stability of these radicals, DFT calculations were carried out (23) to determine the extent of delocalization of the unpaired electron. As expected, nearly all (98%) of the spin density was found to reside on the three cluster nitrogen atoms. Thus, the stability of **11** and **12** can in large part be attributed to the delocalization of spin density over multiple nitrogen centers.

In order to examine the extent of kinetic stabilization in **11** and **12**, the related tetrakisimidophosphates $\text{Li}_3[\text{P}(\text{NAd})_3(\text{NSiMe}_3)]$ **13** and $\text{Li}_3[\text{P}(\text{NCy})_3(\text{NSiMe}_3)]$ **14** were also reacted with halogens (24). Oxidation of **13**, in which the *tert*-butyl-imido groups have been replaced by sterically demanding adamantyl groups, was found to produce stable radicals; however, oxidation reactions of **14**, which contains smaller cyclohexyl-imido groups, result in highly transient radicals. These results indicate that the steric bulk of the alkyl-imido groups plays a critical role in stabilizing the tetrakisimidophosphate radicals.

EPR Characterization

The EPR spectrum of **10** in THF solution is highly dependent upon both temperature and concentration, suggesting that more than one radical may be present in solution. At extreme dilution a limiting spectrum is obtained which contains approximately fifty lines, all of which can be attributed to a single species. The best simulation of the experimental spectrum shown in Figure 4

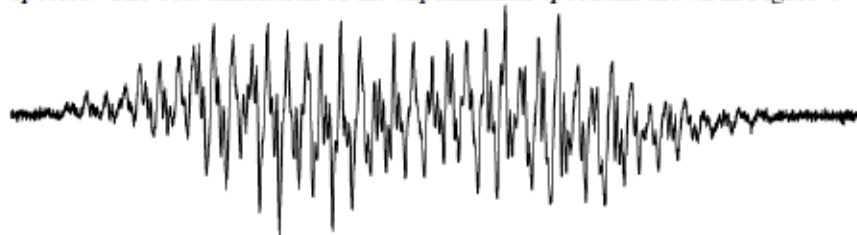
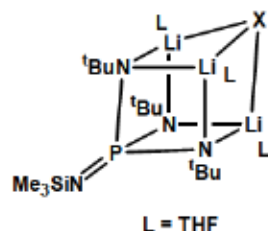
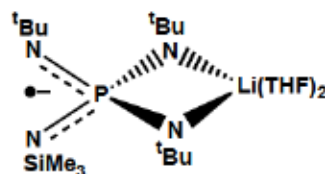


Figure 4. EPR spectrum of **10**. (Reproduced with permission from reference 20. Copyright Wiley-VCH 2004.)

was obtained by including hyperfine couplings to one phosphorus atom ($a_{31\text{P}} = 23.1$ G), two equivalent nitrogen centers ($a_{14\text{N}} = 5.38$ G), two unique nitrogen atoms ($a_{14\text{N}} = 7.38$ G and 1.93 G), and a single lithium nucleus ($a_{7\text{Li}} = 0.30$ G). These EPR parameters are consistent with the formation of the radical monoanion **15** and a $[\text{Li}(\text{THF})_4]^+$ counterion via solvation of the cube **11**. The proposed structure of the solvent-separated ion pair $\{\text{Li}[\text{P}(\text{N}^t\text{Bu})_3(\text{NSiMe}_3)]\}[\text{Li}(\text{THF})_4]^+$ **15** contains two equivalent bridging



11 (X = I); **12** (X = O^tBu)



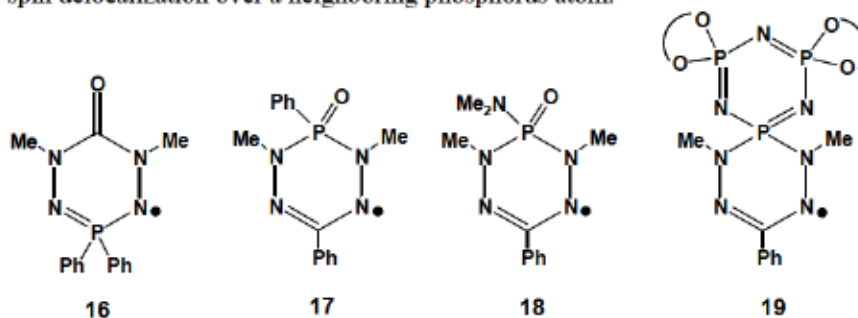
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nitrogen atoms and a single lithium cation, which is consistent with the experimentally obtained EPR spectrum. The ³¹P coupling constant in this EPR spectrum is small compared to the values observed for radicals **1** and **3** in which the spin density is primarily on the phosphorus atom(s). This is in agreement with the DFT calculations, which indicated that the SOMO is predominantly Np in character.

The difference between the solution and solid-state structures of the radical **10** can be explained by the fact that the crystals of **11** were grown from a concentrated THF syrup, while the EPR spectrum corresponding to **15** was recorded in a very dilute THF solution. In dilute solutions, solvation of the lithium cations of **11** occurs, which ruptures the cubic structure forming the solvent-separated ion pair **15** and a molecule of (THF)₃LiI (**20**).

The Phosphaverdazyl Radicals

The phosphaverdazyls represent another example of phosphorus(V)-nitrogen radicals. These species are six-membered heterocycles composed of four nitrogen atoms, one phosphorus atom, and one carbon atom. Since their discovery five years ago, four persistent phosphaverdazyls radicals **16** – **19** have been prepared and characterized (**25**). Like the tetrakisimidophosphate radicals, phosphaverdazyls can be considered nitrogen-centered radicals which exhibit spin delocalization over a neighboring phosphorus atom.



The radicals **16** – **19** are produced via the homolytic cleavage of an N-H bond in the corresponding diamagnetic tetraazaphosphorines using common oxidizing agents such as iodine, periodate, or benzoquinone (26-28). While they can be isolated as red-brown semi-solids, the phosphaverdazyls decompose both in solution and in the solid state over a period of days.

EPR Characterization

The phosphaverdazyl radicals exhibit multiple hyperfine couplings due to interactions of the unpaired electron with neighboring protons, nitrogen atoms, and phosphorus nuclei. This extensive coupling results in numerous overlapping peaks, and frequently produces poorly resolved EPR spectra with quite broad lines. The EPR spectrum of the most complex of these radicals, the spirocyclic cyclophosphazene-phosphaverdazyl hybrid **19**, could not be interpreted without the aid of a double-resonance technique. An electron nuclear double resonance (ENDOR) experiment (28) produced the simplified spectrum shown in Figure 5. The reduced number of lines in the ENDOR spectrum, combined with its superior resolution compared to a traditional EPR spectrum, made it possible to

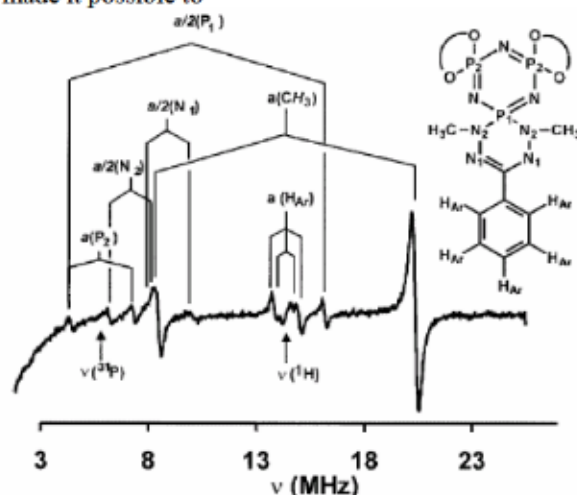


Figure 5. ENDOR spectrum of **19**. (Reproduced with permission from reference 28. Copyright NRC Press 2002.)

unequivocally assign hyperfine coupling constants to the two pairs of equivalent nitrogen atoms in the verdazyl ring ($a_{14N} = 5.18$ G and 6.45 G), the six equivalent protons from the methyl groups attached to the verdazyl nitrogen

atoms ($a_{\text{IH}} = 4.24$ G), and two types of protons on the phenyl ring ($a_{\text{IH}} = 0.40$ G and 0.20 G).

Interestingly, two different ^{31}P couplings were observed: one due to an interaction with the phosphorus in the phosphaverdazyl ring (7.29 G) and one caused by coupling to the two remote phosphorus atoms in the cyclophosphazene ring (1.06 G). Though this second hfc constant is quite small, it indicates delocalization of the unpaired electron not only over the phosphaverdazyl ring, but throughout the cyclophosphazene ring as well. While two other radicals with cyclophosphazene substituents are known (29, 30), coupling in those systems is only observed to the phosphorus nucleus closest to the radical center. The evidence of spin-spin communication between the two rings in **19** suggests that spirocyclic phosphaverdazyls radicals of this type may find applications as magnetic materials.

Structure and Stability

The stability of the persistent phosphaverdazyls radicals **16** – **19** can be attributed to the delocalization of the unpaired electron over at least the four nitrogen atoms of the heterocycle. Detailed theoretical calculations (27) on **16** – **18** confirmed that the SOMOs of these three radicals are fairly similar, with large contributions from the four heterocycle nitrogens and smaller contributions from the phosphorus and other atoms.

The lower stability of **16** – **19** as compared to that of the tetrakisimidophosphate radical in **11** and **12** can be attributed to the lack of kinetic stabilization in the phosphaverdazyls systems. Despite their extensive delocalization, there are no bulky substituents on the heterocycle to hinder the reactions of these species.

Conclusion

Recent investigations have led to the the synthesis and identification of a variety of structurally diverse, stable and persistent phosphorus-containing radicals. To date only one class of these systems, the dilithiated tetraimidophosphates, has been characterized in the solid state by X-ray crystallography. For the other radicals, EPR hyperfine coupling parameters, in conjunction with theoretical calculations, have provided detailed insights into the spin distribution in these paramagnetic systems. Possible applications of these materials as spin labels and in magnetic materials are being considered (25). Although this article has been limited to neutral phosphorus-containing radicals, recent progress in the generation and characterization of

phosphoniumyl radical cations $[R_3P]^{+\bullet}$ by the one-electron oxidation of triarylphosphines is noteworthy (31, 32). Persistent radicals of this type are obtained by using bulky aryl groups with two isopropyl groups in the *ortho* positions. Isotropic EPR hfc's indicate substantial *s* orbital character for the SOMO (32).

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