

Single Crystal E.S.R. Study of the Octahydro-2a,4a,6a,8a-tetra-aza-8b-phospha(v)pentaleno[1,6-*cd*]pentalen-8b-yl Radical. Evidence of Ligand Exchange *via* a Berry Pseudorotation Mechanism

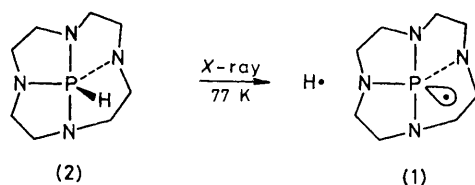
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Summary The nitrogen ligands of the title phosphoranyl radical interconvert pairwise *via* an M-1 Berry pseudorotation mechanism in the solid state.

A NUMBER of e.s.r. studies concerning the structure of phosphoranyl radicals and their modes of ligand exchange in solution have been published recently.¹ Usually a

trigonal bipyramidal structure with the unpaired electron in an equatorial position (TBP-e) has been assigned. However, on the basis of a single crystal e.s.r. study of $\dot{\text{P}}\text{OCl}_3^-$ in which the unpaired electron is assumed to reside in the axial axis of the TBP structure,² it has been suggested that the TBP-e structure is only a poor description of the real structure of the phosphoranyl radical.¹ Analogously,

the unpaired electron in the $\text{Ph}_3\dot{\text{P}}\text{Cl}$ radical, which possesses a C_{3v} structure, is also believed to reside in a σ^* P-Cl orbital.³ In recent literature the latter structure has been adopted as an intermediate in ligand exchange processes of TBP-e radicals in solution.⁴ However, single crystal e.s.r. studies of phosphoranyl radicals which we published recently,^{5,6} indicated that the unpaired electron was a real fifth ligand occurring either in the apical⁵ or equatorial⁶ position of the TBP structure. Therefore the σ^* intermediate in ligand exchange remains questionable. In order to get more insight into this matter we investigated the structure of (1) by means of a single crystal e.s.r. study. Remarkably, this phosphoranyl radical shows fast ligand exchange in the solid state.



X-Irradiation of a powdered sample of (2)⁷ at 77 K generated the free hydrogen radical $\text{H}\cdot$ [a_{H} 509 G]. On annealing to 200 K a phosphoranyl radical was detected with $a(\text{P}_{\parallel})$ 715, $a(\text{P}_{\perp})$ 606 G and additional hyperfine coupling $a(\text{N}_{\parallel})$ 26.3, $a(\text{N}_{\perp})$ 24.0 G due to two nitrogen atoms. From these values one calculates⁸ an $a(\text{P}_{\text{iso}})$ of 642 G, which indicates a phosphorus 3s spin density of 0.18, and a 3p spin density of 0.35, giving a total spin density of 0.53 on phosphorus. The nearly isotropic ^{14}N h.f.c. $a(\text{N}_{\text{iso}})$ of 24.8 G indicates a spin density of 0.05 in its 2s orbital. The small anisotropic contribution (0.8 G) can be attributed to dipole-dipole interaction. From this a TBP-e structure is derived with two apical nitrogen atoms accounting for the observed high h.f.c. and two equatorial nitrogens with small h.f.c. values (< 5 G).[†] On further raising of the temperature (to 295 K) an e.s.r. spectrum was obtained which consisted of the same $a(\text{P}_{\parallel})$ and $a(\text{P}_{\perp})$ values as found at low temperatures, and additional h.f.c. due to four equivalent nitrogen atoms [$a(\text{N}_{\parallel})$ 14.4 and $a(\text{N}_{\perp})$ 12.7 G]. These changes in the e.s.r. spectrum are reversible as indicated by the appearance of the initial spectrum on cooling. Therefore this phenomenon has to be attributed to a rapid pairwise interconversion of the nitrogen ligands.

Additional evidence was obtained by a single crystal e.s.r. study of (1). The e.s.r. spectra of an X-irradiated single crystal of (2) at room temperature show that two identical radicals with an angle between their $a(\text{P}_{\parallel})$ components of $34 \pm 2^\circ$ are present. These spectra were temperature-dependent in the same way as found for the powder sample; at 295 K four equivalent nitrogens were observed, whereas on cooling to 258 K only two nitrogen couplings appeared, with the principal $a(\text{P})$ values at exactly the same positions as found at 295 K (see Figure). Unfortunately the single crystal became polycrystalline at 253 K, showing the features of the powdered sample with enhanced resolution.

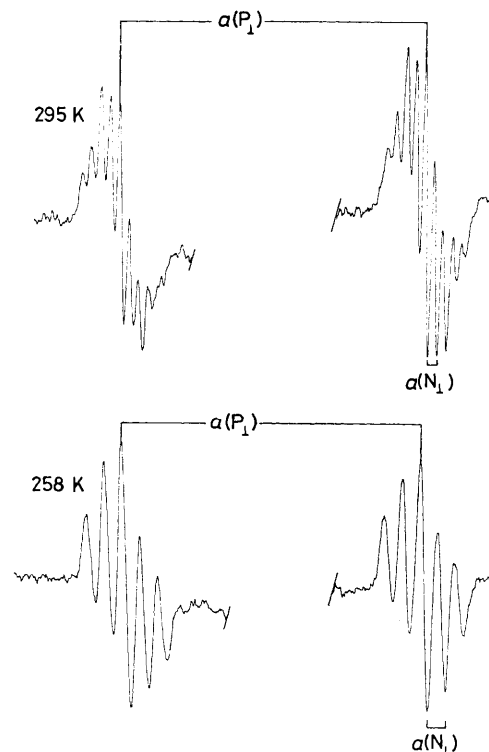
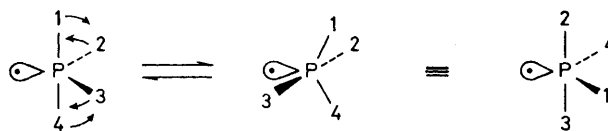


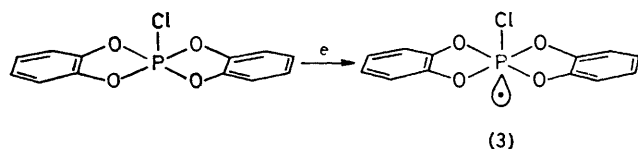
FIGURE. Single crystal e.s.r. spectrum of (1) showing $a(\text{P}_{\parallel})$ and $a(\text{N}_{\perp})$.

Both the $a(\text{P})$ principal values and their directions remain constant throughout temperature variation, only the ^{14}N coupling constant varies from 13.3 (4N) to 24.8 G (2N), whereas the anisotropy in ^{14}N h.f.c. is preserved. From this it is concluded that the nitrogen ligands exchange in a Berry pseudorotation mechanism⁹ with the unpaired electron acting as the pivot (m-1).



A similar mechanism may play a role in other phosphoranyl radicals *e.g.* $\dot{\text{P}}\text{F}_4$. Initially this radical was thought to rotate in the solid matrix,¹⁰ accounting for the existence of four equivalent (anisotropic) fluorines and the isotropic ^{31}P h.f.c. However, a reassignment has been made in which it was assumed, on the basis of a near zero h.f.c. due to the fifth fluorine ligand, that the radical detected should be $\dot{\text{P}}\text{F}_5^-$ instead of $\dot{\text{P}}\text{F}_4$.¹¹ It is believed that the fifth ligand in such C_{4v} geometries (*e.g.* $\dot{\text{P}}\text{F}_5^-$, $\dot{\text{S}}\text{F}_5$, and $\dot{\text{P}}\text{Cl}_5^-$) possesses an almost zero h.f.c. as a general rule.¹² However, recently we showed for the $\text{Cl}\dot{\text{P}}(\text{O}_2\text{C}_6\text{H}_4)_2$ radical anion (3), which has a similar C_{4v} symmetry, that the odd electron and chlorine

[†] Estimated from line width; equatorial nitrogen h.f.c.s were not resolved.



are located in the axial positions with chlorine having an h.f.c. value comparable to those found for apical chlorine in P^V phosphoranyl radicals.¹³ On this basis and regarding the evidence presented here in this paper, we suggest that $\dot{P}F_5^-$ is really $\dot{P}F_4$ which undergoes ligand exchange accord-

ing to a mode of pseudorotation in which the unpaired electron is not acting exclusively as a pivot, explaining the isotropic ^{31}P h.f.c. The permutational mode of (1) is very distinct, probably as a result of crystal and molecular constraints imposed on this radical, representing an unique example of an M-1 Berry pseudorotation mechanism.

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- ¹ J. W. Cooper, M. J. Parrott, and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1977, 730.
- ² T. Gillbro and F. Williams, *J. Am. Chem. Soc.*, 1974, **96**, 5032.
- ³ T. Berclaz, M. Geoffroy, L. Ginet, and E. A. C. Lucken, *Chem. Phys. Lett.*, 1975, **36**, 677.
- ⁴ R. S. Hay and B. P. Roberts, *J. Chem. Soc., Perkin Trans. 2*, 1978, 770.
- ⁵ J. H. H. Hamerlinck, P. Schipper, and H. M. Buck, *J. Am. Chem. Soc.*, 1980, **102**, 5679.
- ⁶ J. H. H. Hamerlinck, P. Schipper, and H. M. Buck, *J. Chem. Soc., Chem. Commun.*, 1981, 104.
- ⁷ J. E. Richman and T. J. Atkins, *Tetrahedron Lett.*, 1978, 4333.
- ⁸ M. C. R. Symons, 'Chemical and Biological Aspects of Electron-Spin Resonance Spectroscopy,' Van Nostrand-Reinhold, New York, 1978, pp. 26-30.
- ⁹ R. S. Berry, *J. Chem. Phys.*, 1960, **32**, 933.
- ¹⁰ P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967, pp. 200-206.
- ¹¹ S. P. Mishra and M. C. R. Symons, *J. Chem. Soc., Chem. Commun.*, 1974, 279.
- ¹² J. R. Morton, K. F. Preston, and S. J. Strach, *J. Magn. Reson.*, 1980, **37**, 321.
- ¹³ J. H. H. Hamerlinck, P. Schipper, and H. M. Buck, *Chem. Phys. Lett.*, in the press.