

## 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

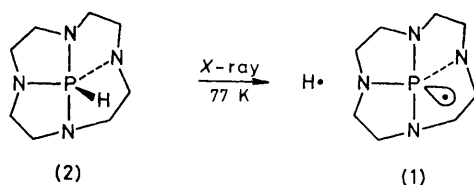
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**Summary** The nitrogen ligands of the title phosphoranyl radical interconvert pairwise *via* an M-1 Berry pseudorotation mechanism in the solid state.

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.<sup>1</sup> 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,<sup>2</sup> it has been suggested that the TBP-e structure is only a poor description of the real structure of the phosphoranyl radical.<sup>1</sup> 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  $\sigma^*$  P-Cl orbital.<sup>3</sup> In recent literature the latter structure has been adopted as an intermediate in ligand exchange processes of TBP-e radicals in solution.<sup>4</sup> However, single crystal e.s.r. studies of phosphoranyl radicals which we published recently,<sup>5,6</sup> indicated that the unpaired electron was a real fifth ligand occurring either in the apical<sup>5</sup> or equatorial<sup>6</sup> position of the TBP structure. Therefore the  $\sigma^*$  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)<sup>7</sup> at 77 K generated the free hydrogen radical  $\text{H}\cdot$  [ $a_{\text{H}}$  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 calculates<sup>8</sup> 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  $^{14}\text{N}$  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).<sup>†</sup> 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.

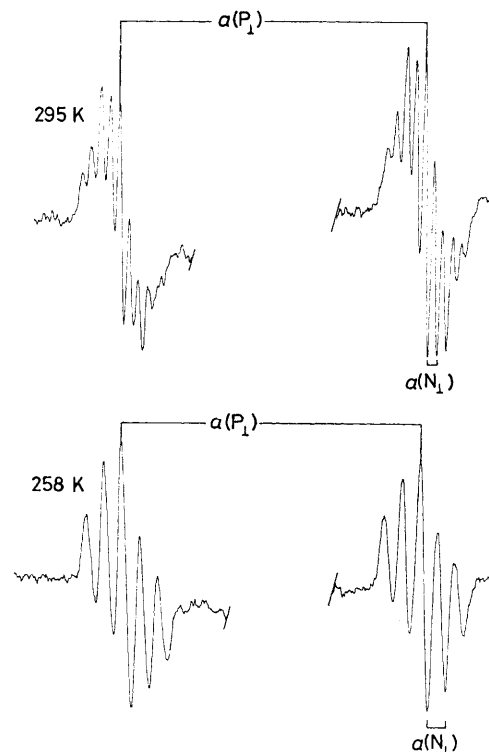
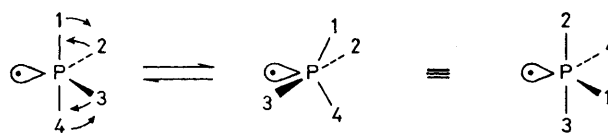


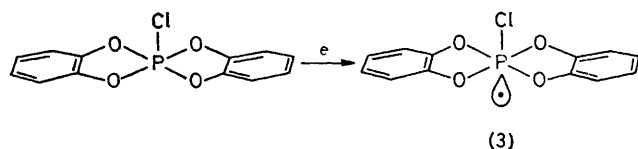
FIGURE. Single crystal e.s.r. spectrum of (1) showing  $a(\text{P}_{\parallel})$  and  $a(\text{N}_{\perp})$ .

Both the  $a(\text{P})$  principal values and their directions remain constant throughout temperature variation, only the  $^{14}\text{N}$  coupling constant varies from 13.3 (4N) to 24.8 G (2N), whereas the anisotropy in  $^{14}\text{N}$  h.f.c. is preserved. From this it is concluded that the nitrogen ligands exchange in a Berry pseudorotation mechanism<sup>9</sup> with the unpaired electron acting as the pivot (m-l).



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,<sup>10</sup> accounting for the existence of four equivalent (anisotropic) fluorines and the isotropic  $^{31}\text{P}$  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  $\dot{\text{P}}\text{F}_4$ .<sup>11</sup> 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.<sup>12</sup> 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

<sup>†</sup> 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.<sup>13</sup> 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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