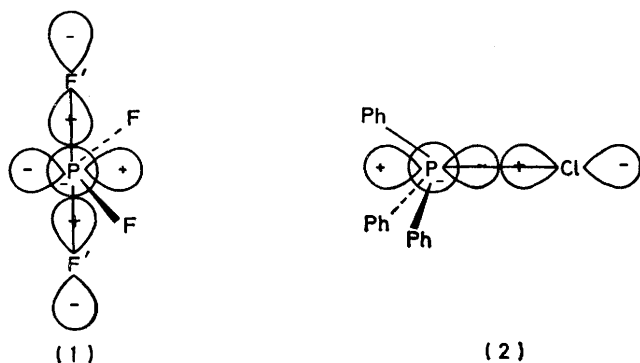


Electron Spin Resonance Studies of Thiophosphoranyl Radicals. The Mechanism of Ligand Permutation in Phosphoranyl Radicals

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A series of thiophosphoranyl radicals have been generated in solution by addition of thiyl radicals (RS^\cdot , from photolysis of $RSSR$ or H_2S) to phosphorus(III) compounds and their e.s.r. spectra have been studied. The phosphoranyl radicals $OCH_2CH_2OP(OR')SR$ have trigonal bipyramidal (TBP) structures in which the ring bridges apical and equatorial sites: the apicophilicity of RS is greater than that of $R'O$. Apical-equatorial (a-e) ring proton exchange is evident from e.s.r. lineshape effects and it is proposed that the exchange takes place *via* a $\sigma^*(P-S)$ intermediate or transition state. In general, the rate of a-e ligand exchange in TBP phosphoranyl radicals appears to increase as the energy difference between TBP and σ^* structures decreases. TBP (C_{2v}) and σ^* (C_{3v}) configurations represent limiting structures for hypervalent phosphoranyl radicals and the geometry between these two extremes adopted by a particular radical appears to depend upon the nature of the ligands. It is suggested that the apicophilicity of ligands in TBP or σ^* isomers is related to the ease of heterolytic dissociation of the P-ligand bonds, rather than to ligand electronegativity alone. The phosphoranyl radicals $Ph_3P^{\cdot}SR$ are hypervalent and probably have $\sigma^*(P-S)$ structures, whereas the RS ligands are equivalent in $(MeS)_2P^{\cdot}Ph_2$ and $(RS)_2P^{\cdot}H_2$, indicating TBP structures. The radical $[Bu^{\cdot}OPPh_3]^{\cdot}$ has a ligand- π -electronic structure and the low-temperature e.s.r. spectrum shows that the unpaired electron is centred on one ring in a π -type orbital. At high temperatures electron exchange between the rings renders them magnetically equivalent.

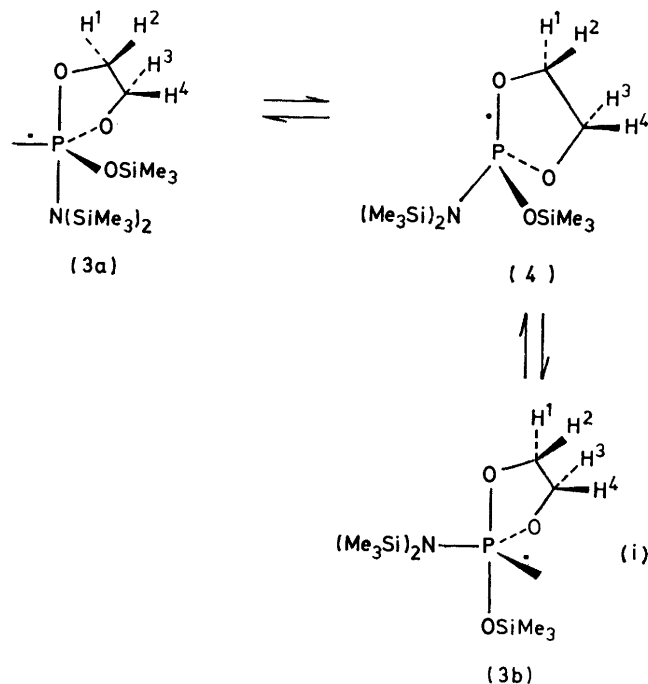
THE structures and electronic configurations of phosphoranyl radicals, $[PX_4]^{\cdot}$, are markedly dependent on the nature of the ligands attached to phosphorus.¹ The e.s.r. spectrum of PF_4^{\cdot} trapped in a single crystal of PF_3 shows that the radical adopts the C_{2v} structure (1), in which the $F'PF'$ angle is close to 180° .² The principal atomic orbitals that contribute to the singly occupied molecular orbital (SOMO) are indicated in (1) and this structure may be described as trigonal bipyramidal (TBP) if the unpaired electron is regarded as the third equatorial ligand. The phosphoranyl radicals $Cl_3P^{\cdot}O^{\ominus}$ ³ and $Cl_2(RO)P^{\cdot}O^{\ominus}$ ⁴ have similar structures and the $Cl_{apical}-PCl_{apical}$ angle is close to 180° in both. In contrast, the chlorotriphenylphosphoranyl radical adopts structure (2), with local C_{3v} symmetry at phosphorus, and the



SOMO is a P-Cl σ^* orbital as shown.⁵ Similarly, an e.s.r. study of the radical $(MeO)_2P^{\cdot}(S)Br$ has shown that this species adopts a $\sigma^*(P-Br)$ structure.⁶ The radicals (1) and (2) may be classified as *hypervalent* because in each the valence shell of the central phosphorus atom contains nine electrons. In principle, it would appear that phosphoranyl radicals may adopt structures anywhere

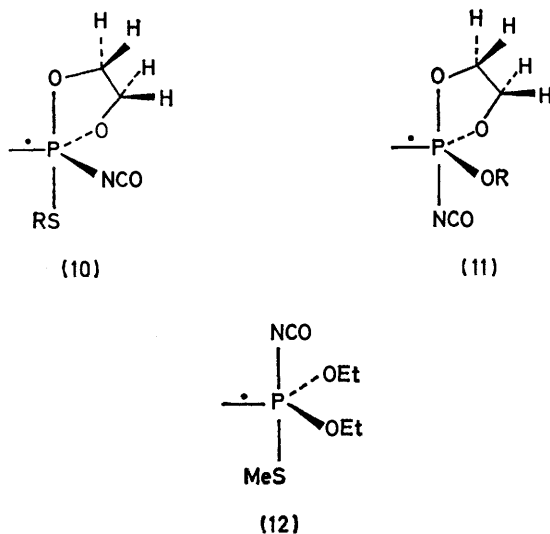
between these TBP and σ^* extremes, depending upon the nature of the ligands attached to phosphorus.

Apical-equatorial (a-e) ligand exchange in many quasi-TBP phosphoranyl radicals takes place at a rate appropriate to give rise to lineshape effects in their e.s.r. spectra¹ and we have suggested^{7,8} that such exchange takes place by way of a σ^* species in which the local symmetry at phosphorus is approximately C_{3v} , as shown for (3) in equation (i).⁸



The observed *mode* of ligand exchange [*i.e.* (3a) \rightleftharpoons (3b)] is consistent with this *mechanism*, in which the apical endocyclic P-O bond in (3a) or (3b) becomes the

A similar spectrum was shown by (10; R = Me) although the large linewidth did not permit observation of proton splitting. Comparison of (10) with the structure (11), adopted¹³ by the adducts of EtO•, Bu^tO•, or Me₃SiO• with (5; X = NCO), leads to the conclusion that the apicophilicities of Bu^tC(O)S and MeS, and presumably of all other



thiyl ligands discussed in this paper, are higher than those of alkoxy- and trimethylsiloxy-substituents. The acyclic analogue of (10; R = Me), (EtO)₂P(NCO)SMe, probably has a structure close to (12) on the basis of the large nitrogen splitting (17.4 G) from the NCO group which is now able to occupy the site *trans*-apical to the MeS group. Hereinafter, when the structure of a TBP thiophosphoranyl radical is not clear from its isotropic e.s.r. spectrum the apicophilicity of the sulphur ligand will be assumed to be greater than that of an alkoxy- or trimethylsiloxy-group.

Addition of HS• to (13) at 144 K gave (14; R = H) the

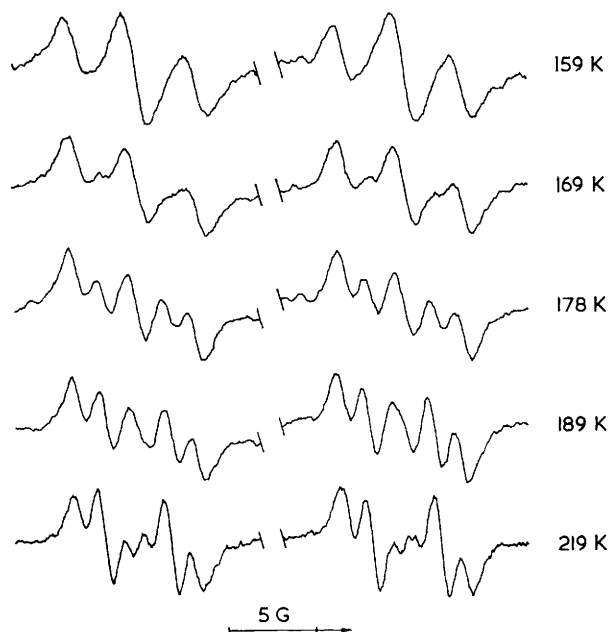
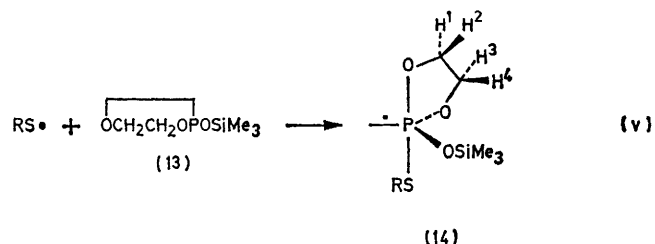


FIGURE 1 E.s.r. spectra of the phosphoranyl radical (14; R = H) in cyclopropane at various temperatures

spectrum of which exhibited a 1 : 2 : 1 splitting with a line spacing of 3.5 G (see Figure 1). This splitting pattern was shown to arise from approximately equal coupling to one ring proton and to the proton of the SH group by generating



the radical (14; R = D) which showed $a(1H)$ 3.5 G at 144 K. At *ca.* 170 K lineshape effects indicated that ring proton exchange was becoming rapid on the e.s.r. time scale and above 183 K coupling to *two* apparently equivalent ring protons (1.5 G) was detected (see Figures 1 and 2). Approxi-

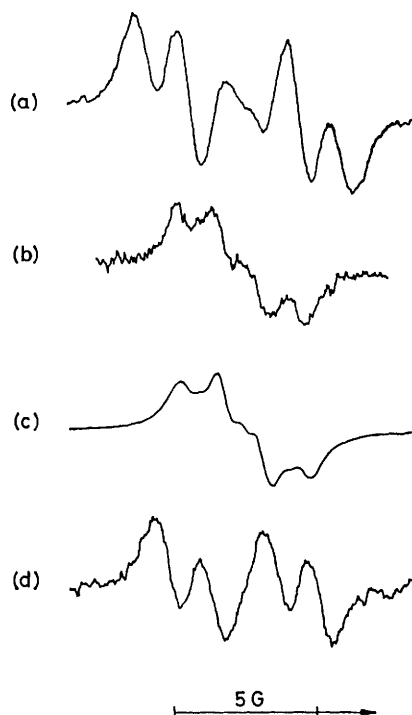
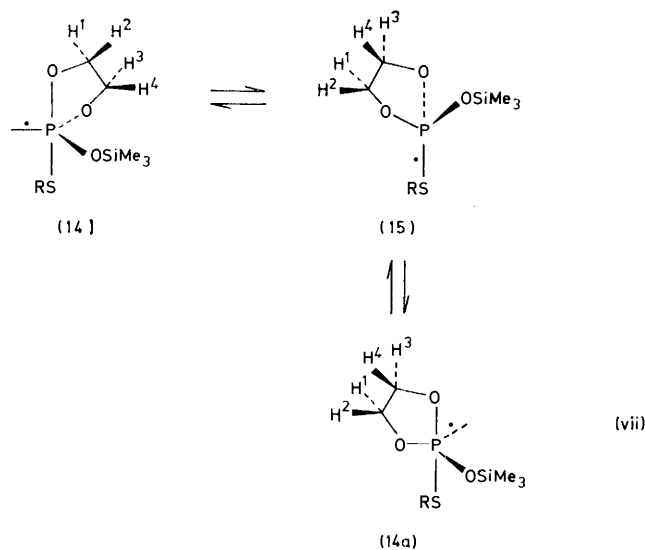


FIGURE 2 E.s.r. spectra of the phosphoranyl radical (14; R = H) and deuterium labelled analogues in cyclopropane at 198 K: (a) (14; R = H); (b) (14; R = D); (c) Computer simulation of (b) using the parameters given in Table 1; (d) $\text{OCH}_2\text{CD}_2\text{OP(SH)OSiMe}_3$. Only the low field [$m_1(^{31}\text{P}) = +\frac{1}{2}$] lines are shown

mate rate constants for ring proton exchange were obtained by computer simulation, assuming that H¹ in (14; R = H) gives rise to a splitting that decreases linearly from 3.32 G at 159 K to 2.75 G at 219 K (see Table 1) and that all other ring proton splittings are zero.¹¹ In the same temperature range $a(\text{SH})$ was assumed to increase linearly from 3.63 to 3.85 G. An Arrhenius plot of these rate constants gave a good straight line corresponding to equation (vi), in which $\theta = 2.303RT \text{ kJ mol}^{-1}$; the errors given are estimates taking account of the approximations made.

$$\log(k_{\text{exch}}/s^{-1}) = (12.7 \pm 0.5) - (16.5 \pm 2.0)/\theta \quad (\text{vi})$$

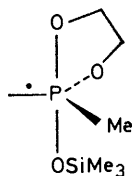
The mode of ligand exchange in (14; R = H) was further defined by generating the deuterium-labelled radical from $\text{OCH}_2\text{CD}_2\text{OPOSiMe}_3$ which showed a 1:1 ring-proton splitting of *ca.* 1.5 G above 183 K, proving that exchange of H with D (rather than of H with H) was occurring^{7-9,11} and thus that exchange of H¹ with H³ or H⁴ takes place in (14; R = H). Ligand permutation by the mechanism shown in equation (vii) [*cf.* equation (i)], proceeding through a $\sigma^*(\text{P-S})$ intermediate (15) would bring about interconversion of (14) and (14a) *i.e.* exchange of H¹ with H³.



The linewidth for [14; R = Bu^tC(O)] was large at very low temperatures, but splitting of 3.1 G from one ring proton was resolved at 182 K. At 203 K and above, a triplet splitting (1.6 G at 203 K) from two apparently equivalent ring protons was observed and thus the radical appears to undergo ligand permutation resulting in exchange of H¹ with H³ at a rate similar to that for (14; R = H).

Photolysis of MeSSMe in the presence of (13) gave rise to a spectrum which we ascribe to (14; R = Me). Optimum resolution was obtained at *ca.* 183 K and the spectrum could be analysed by computer simulation in terms of *a*(1H) 2.8 and *a*(3H) 1.8 G. Between 190 and 210 K the spectrum appeared as a broad singlet, presumably as a result of ring proton exchange, and the radical was not detectable above 210 K. We conclude that exchange of H¹ and H³ in (14) takes place somewhat more slowly when R = Me than when R = H or Bu^tC(O). The radical (14; R = Me) was also obtained by photolysis of dimethyl sulphide in the presence

* Photolysis of dimethyl sulphide affords MeS· and Me·.¹⁴ The spectrum of (A), the adduct of methyl radicals with (13), was also detected in experiments with Me₂S and, above 200 K, with MeSSMe. The radical shows *a*(P) 783.2, *a*(1H) 4.6 G, *g* 2.0023



(A)

at 213 K, and the doublet splitting from one ring proton was much better resolved for the ·CD₃ adduct derived from (CD₃)₂S.

of (13) and when the Me₂S was replaced by (CD₃)₂S the radical (14; R = CD₃) was detected. The spectrum of the deuterium-labelled species showed a 2.8 G doublet splitting from one ring proton (H¹) at 181 K.* An approximate rate constant ($3.5 \times 10^7 \text{ s}^{-1}$ at 201 K) for ring proton exchange in (14; R = Me) was obtained by computer simulation.

The HS· adduct to $\text{OCH}_2\text{CH}_2\text{OPOCH}_2\text{Bu}^t$ undergoes rapid ring proton exchange (presumed to be of H¹ with H³) above 183 K, giving rise to a 1.3 G triplet splitting in the spectrum. Exchange thus takes place at a rate similar to that for (14; R = H) and the rate constant was estimated by computer simulation to be *ca.* $9.7 \times 10^7 \text{ s}^{-1}$ at 187 K. The corresponding adducts with MeS· and Bu^tC(O)S· showed broad lines at all temperatures and proton splittings were not clearly resolved.

(c) *Acyclic Phosphoranyl Radicals*.—E.s.r. spectra assignable to the expected phosphoranyl radical adducts were observed when HS·, MeS·, CF₃S·, EtC(O)S·,¹⁵ or Bu^tC(O)S·¹⁵ were generated photochemically in the presence of trimethyl or triethyl phosphite. On the basis of the isotropic e.s.r. parameters (see Table 2) it is not possible to determine

TABLE 2

E.s.r. parameters of acyclic thiophosphoranyl radicals in cyclopropane

Radicals	<i>T</i> /K	<i>g</i> Factor ^a	Hyperfine splittings (G)	
			<i>a</i> (P) ^a	Others
(EtO) ₃ P(NCO)SMe ^b	171	2.0058	810.2	17.4 (1 N)
(MeO) ₃ PMe ^c	148	2.0057	751.9	1.8 (3 H)
(EtO) ₃ PMe ^d	143	2.0058	753.1	2.0 (3 H)
(MeO) ₃ PSH	151	2.0054	828.9	3.9 (1 H) ^e
(MeO) ₃ PSCF ₃	148	2.0054	844.1	7.6 (3 F)
(MeO) ₃ PSC(O)Et	158	2.0060	886.3	
(MeO) ₃ PSC(O)Bu ^t	143	2.0064	898.1 ^f	
(HS) ₂ P ₂ H ₂	163	2.0067	746.0	5.6 (2 H), 1.9 (2 H)
(DS) ₂ P ₂ H ₂	158	2.0067	744.0	5.6 (2 H)
(Bu ^t S) ₂ P ₂ H ₂	154	2.0090	633.4	6.4 (2 H)
[Bu ^t C(O)S] ₂ P ₂ H ₂	166	2.0085	841.2	6.1 (2 H)
Me ₃ PSH ^g	148	2.0071	619.1	6.0 (1 H), ^h 3.0 (≥ 7 H) ^{h,i}
Me ₃ P ₂ SD	178	2.0071	617.3	3.0 (≥ 7 H), ⁱ 0.9 (1 D)
Me ₃ P ₂ SMe	163	2.0091	547.3	2.8 (≥ 6 H) ^j
Me ₃ PSC(O)Bu ^t ^k	172	2.0074	675.6	3.1 (≥ 7 H) ⁱ
(Me ₂ N) ₃ PSC(O)Bu ^t ^l	154	2.0061	744.5	6.4 (3 N)

^a Calculated using the Breit-Rabi equation. ^b An unidentified secondary product phosphoranyl [*a*(P) *ca.* 700 G] was also detected. ^c Above *ca.* 195 K only (MeO)₃PMe was detected. ^d Above *ca.* 195 K only (EtO)₃PMe was detected [*a*(P) 787.1, *g* 2.0021 at 210 K]. ^e Splitting absent for (MeO)₃P₂SD. The proton splitting increases with temperature; for (EtO)₃PSH, *a*(1H) was 4.2 G at 145 K and 4.9 G at 245 K. ^f Decreases with increasing temperature [in common with *a*(P) for the other radicals of the type (RO)₃P₂SR]; $\partial|a(P)|/\partial T = -140 \text{ mG K}^{-1}$. ^g ΔB_{p-p} 1.1 G. ^h Spectrum analysed with aid of the parameters determined from the spectrum of Me₃P₂SD. ⁱ Odd number of protons. ^j Even number of protons. ^k ΔB_{p-p} 1.7 G at 148 K, 1.3 G at 166 K. ^l ΔB_{p-p} *ca.* 5 G; radical undetectable above 200 K.

whether these adducts are better described as TBP or $\sigma^*(\text{P-S})$ phosphoranyls (see Discussion section). The spectrum of MeS[·]P(OEt)₃ has been reported previously,¹⁶ but the hyperfine splitting from the *S*-methyl protons was not resolved. Above *ca.* 195 K, the radicals MeS[·]P(OR)₃ (R = Me or Et) underwent rapid β-scission to give methyl radicals and only the phosphoranyl MeP(OR)₃ [*a*(P) 786.0, *a*(3H) 0.95 G, *g* 2.0020 at 215 K when R = Me] was detected [equations (viii) and (ix)].¹⁷

In order to obtain more structural information, we attempted to observe spectra of $\text{RS}\dot{\text{P}}\text{F}_3$ and RSPH_3 by photolysis of RSSR (or H_2S) in the presence of PF_3 or PH_3 . No e.s.r. signals were detected with PF_3 and MeSSMe , CF_3SSCF_3 , $\text{Bu}^t\text{C}(\text{O})\text{SSC}(\text{O})\text{Bu}^t$, or H_2S even when the samples were kept below 173 K prior to photolysis in order



to minimise possible thermal reactions. With PH_3 , only secondary radicals of the type $(\text{RS})_2\dot{\text{P}}\text{H}_2$ could be detected using H_2S , Bu^tSSBu^t , or $\text{Bu}^t\text{C}(\text{O})\text{SSC}(\text{O})\text{Bu}^t$. Photolysis of MeSSMe in the presence of PH_3 and PF_3 , it appears likely that addition of $\text{RS}\cdot$ may be relatively slow. The linewidths for these phosphoranyl radicals could be relatively large, due to ligand exchange or other relaxation processes, making detection difficult. The secondary product phosphoranyl $(\text{RS})_2\dot{\text{P}}\text{H}_2$ could originate from a trace impurity of P_2H_4 in the PH_3 and/or from products derived from reactions of PH_3 with thiol radical sources.

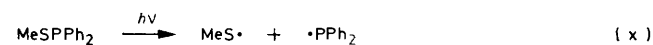
However, reaction of thiol radicals with trimethylphosphine afforded the primary adducts RSPMe_3 . At 172 K the spectrum of $\text{Bu}^t\text{C}(\text{O})\text{SPMe}_3$ showed hyperfine splitting (3.1 G) from an odd number (≥ 7 , presumably 9) of *P*-methyl protons, indicating magnetic equivalence of the methyl groups at this temperature. Even at 148 K, HSPMe_3 showed splitting (3.0 G, ΔB_{p-p} 1.1 G) from ≥ 7 methyl protons. In contrast, the spectrum of Bu^tOPMe_3 shows different splittings [4.6 (3H) and 2.7 G (6H)] from apical and equatorial methyl ligands at *ca.* 160 K, whilst above *ca.* 250 K ligand exchange renders the methyl groups magnetically equivalent.^{17,18} We conclude that either the methyl groups in RSPMe_3 are in essentially identical environments, implying a $\sigma^*(\text{P}-\text{S})$ structure, or that they are significantly non-equivalent (as in a TBP-type structure) but exchanging rapidly on the e.s.r. time scale even at 148 K.

The spectrum of $\text{Bu}^t\text{C}(\text{O})\text{SP}(\text{NMe}_2)_3$ exhibits splitting (6.4 G, ΔB_{p-p} *ca.* 5 G) from three apparently equivalent nitrogen nuclei at 153 K, yet in the phosphoranyl radicals $(\text{Me}_2\text{N})_n\dot{\text{P}}(\text{OR})_{4-n}$ ($n = 1$ or 2) apical and equatorial Me_2N groups give rise to nitrogen splittings of *ca.* 12 and 3 G, respectively.¹² If the amino-groups in $\text{Bu}^t\text{C}(\text{O})\text{SP}(\text{NMe}_2)_3$ are chemically non-equivalent, as in a TBP-type structure, these ligands must be undergoing rapid a-e exchange even at 153 K.

(d) *Phenylphosphoranyl Radicals.*—Prior to commencement of this work two reports of e.s.r. spectra assigned to radicals of the type $\text{RS}\dot{\text{P}}\text{Ph}_3$ existed in the literature. It now appears that certainly one, and possibly both, of these assignments are in error. A radical [$a(\text{P})$ 623 G, no further splitting resolved] detected during photolysis of MeSSMe in the presence of Ph_3P was identified by Davies *et al.*¹⁹ as $\text{MeS}\dot{\text{P}}\text{Ph}_3$ and γ -irradiation of Ph_3PS in sulphuric acid afforded a species [$a(\text{P})$ 391 G] believed by Eastland and Symons²⁰ to be $\text{HS}\dot{\text{P}}\text{Ph}_3$.

We now find that photolysis of MeSSMe in the presence of Ph_3P gives rise to spectra of *two* phosphoranyl radicals.

One radical, present immediately after commencing photolysis, shows $a(\text{P})$ 473 and $a(3\text{H})$ 3.6 G; the other, which shows $a(\text{P})$ 623 and $a(6\text{H})$ 1.2 G, appears to be a secondary product since its concentration increases with the duration of photolysis. The phosphoranyl radical showing the smaller phosphorus splitting is now identified as $\text{MeS}\dot{\text{P}}\text{Ph}_3$ and the other radical (previously¹⁹ thought to be $\text{MeS}\dot{\text{P}}\text{Ph}_3$) is now known to be $(\text{MeS})_2\dot{\text{P}}\text{Ph}_2$. The latter assignment was confirmed by photolysis of MeSSMe in the presence of MeSPPH_2 , when the spectrum of $(\text{MeS})_2\dot{\text{P}}\text{Ph}_2$ was immediately apparent. Photolysis of MeSPPH_2 alone also gave rise to a (weaker) spectrum of this radical, presumably formed as a result of photochemical cleavage of the P-S bond [equations (x) and (xi)].



The route for formation of $(\text{MeS})_2\dot{\text{P}}\text{Ph}_2$ during photolysis of a mixture of MeSSMe and Ph_3P is uncertain, but it appears likely that photochemical cleavage of a P-C bond in the phosphine [equations (xii) and (xiii)] or in $\text{MeS}\dot{\text{P}}\text{Ph}_3$ could lead to MeSPPH_2 and thence to $(\text{MeS})_2\dot{\text{P}}\text{Ph}_2$.

Other thiol radicals add to triphenylphosphine to give $\text{RS}\dot{\text{P}}\text{Ph}_3$ and no secondary radicals of the type $(\text{RS})_2\dot{\text{P}}\text{Ph}_2$ were detected. The spectroscopic parameters are listed in Table 3.

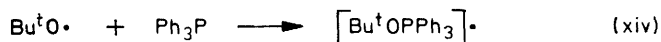
TABLE 3

E.s.r. parameters for phenyl(thio)phosphoranyl radicals in toluene-cyclopropane (1 : 2 v/v)

Radical	T/K	g Factor ^a	Hyperfine splittings (G)	
			$a(\text{P})$ ^a	Others
$\text{MeS}\dot{\text{P}}\text{Ph}_3$	198	2.0086	473.2	3.6 (3 H)
$(\text{MeS})_2\dot{\text{P}}\text{Ph}_2$	198	2.0068	623.2	1.2 (6 H)
$\text{HS}\dot{\text{P}}\text{Ph}_3$	196	2.0074	527.8	6.8 (1 H)
$\text{DS}\dot{\text{P}}\text{Ph}_3$	196	2.0074	527.8	<i>b</i>
$\text{CF}_3\text{S}\dot{\text{P}}\text{Ph}_3$	194	2.0071	540.8	7.8 (3 F)
$\text{EtC}(\text{O})\text{S}\dot{\text{P}}\text{Ph}_3$	193	2.0072	559.5	
$\text{Bu}^t\text{C}(\text{O})\text{S}\dot{\text{P}}\text{Ph}_3$	193	2.0080	563.6	

^a Calculated using the Breit-Rabi equation. ^b Singlet, ΔB_{p-p} 3.2 G.

During the course of our experiments with phenylphosphoranyl radicals, we photolysed a solution of di-*t*-butyl peroxide and triphenylphosphine in cyclopropane-hydrogen sulphide (2 : 1 v/v). No spectrum of $\text{HS}\dot{\text{P}}\text{Ph}_3$ was obtained, but a strong spectrum of $[\text{Bu}^t\text{OPPh}_3]\cdot$ ¹⁹ was observed [equation (xiv)]. Triphenylphosphine is very reactive towards *t*-butoxyl radicals²¹ and apparently competes



effectively with H_2S for these species. However, hydrogen sulphide proved to be a good co-solvent for Ph_3P and permitted the spectrum of $[\text{Bu}^t\text{OPPh}_3]\cdot$, which has a ligand- π electronic structure,* to be observed at lower temperatures than before.¹⁹ At 151 K the spectrum showed $a(\text{P})$ 36.7,

* The unpaired electron is centred on a phenyl ligand in a π^* orbital. Phenylphosphoranyl radicals which have this electronic configuration may be regarded as benzene radical anions carrying a phosphonium substituent, *i.e.* $\text{Ph} - \dot{\text{P}}\text{X}_3$.^{19,22,23}

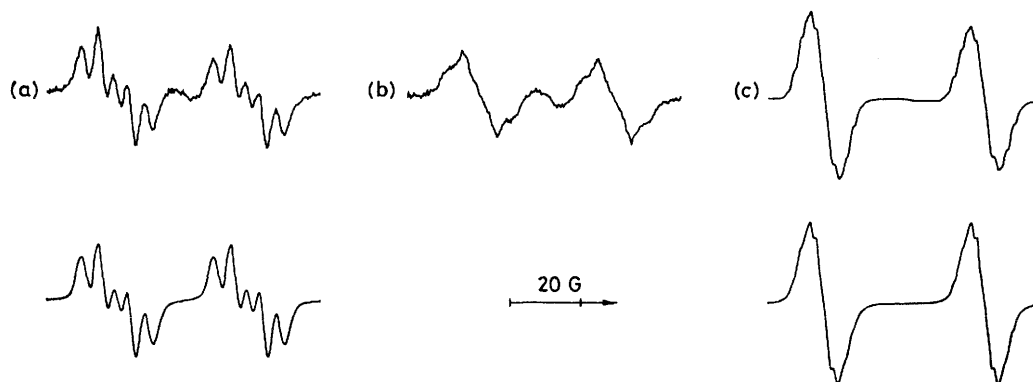
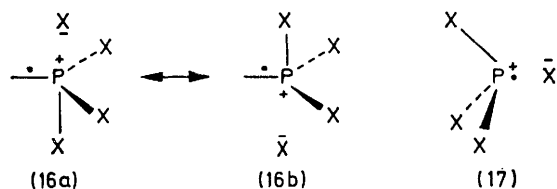


FIGURE 3 E.s.r. spectra of the phosphoranyl radical $[\text{Bu}^t\text{OPPh}_3]$: (a) At 151 K in cyclopropane-hydrogen sulphide (2:1 v/v). (b) At 165 K in cyclopropane-hydrogen sulphide (2:1 v/v). (c) At 216 K in cyclopropane-benzene (3:1 v/v). Computer simulations are also shown for (a) and (c). A permanent signal, originating from the cavity and Dewar insert, is also visible in the central regions of (a) and (b)

$a(1\text{H})$, 7.9, $a(2\text{H})$ 4.4 G, g 2.0031, as expected if the unpaired electron is located on *one* ring rather than delocalised over all three (see Figure 3). At higher temperatures lineshape effects indicated that electron exchange between the rings was taking place on the e.s.r. time scale and at 216 K the spectrum could be analysed in terms of $a(\text{P})$ 44.7, $a(3\text{H})$ 2.92, $a(6\text{H})$ 1.80 G.* Computer simulation of these lineshape effects was not attempted since the *meta*-proton splitting was unresolved at all temperatures and at low temperatures there was a contribution to the linewidth from incomplete averaging of magnetic anisotropy. Similar lineshape changes were apparent in cyclopropane-methyl chloride, which also proved to be a good low-temperature solvent for Ph_3P . A secondary radical, probably $[\text{Ph}_2\text{P}(\text{O}^-\text{Bu}^t)_2]^{\cdot}$, was also detected during photolysis of solutions containing Bu^tOOBu^t and Ph_3P . This radical, which increased in concentration during photolysis, may be formed by routes analogous to those leading to $(\text{MeS})_2\dot{\text{P}}\text{Ph}_2$ (see above).

DISCUSSION

Charge transfer from phosphorus to the apical ligands in TBP and σ^* phosphoranyl radicals is expected to be important in stabilising these species¹ and valence-bond descriptions of the bonding in the limiting TBP (C_{2v}) and σ^* (C_{3v}) structures will involve significant contributions from (16) and (17), respectively. Hence, we might



expect that the preferred structure adopted by a phosphoranyl radical will depend upon the relative ease of heterolytic dissociation of the P-ligand bonds. The apicophilicity (preference for the apical site) of ligand A in a phosphoranyl radical $\text{A}(\text{B})\dot{\text{P}}\text{L}_2$ would be predicted to increase as the value of α_A , which we define in equation

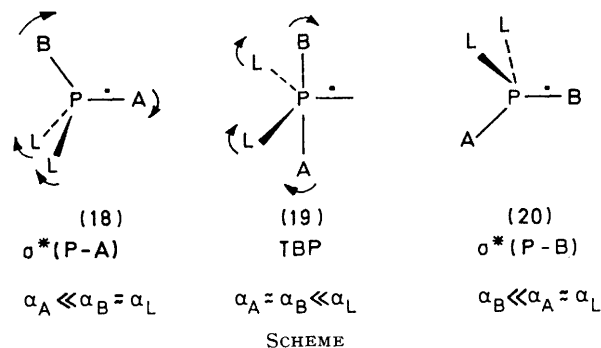
* The previously reported¹⁹ spectrum of $[\text{Bu}^t\text{OPPh}_3]$ [$a(\text{P})$ 45.0, $a(3\text{H})$ 3.1, $a(6\text{H})$ 1.7 G] was obtained in cyclopropane at 225 K and not in propane at 193 K as stated.

(xv), decreases. In this equation the average homolytic bond dissociation enthalpy²⁴ $[\bar{D}(\text{P}-\text{A})]$ in PA_3 is taken

$$\alpha_A = \text{IP}(\text{BPL}_2) - \text{EA}(\text{A}^{\cdot}) + \bar{D}(\text{P}-\text{A}) \quad (\text{xv})$$

as an approximate measure of the strength of an equatorial or basal P-A bond in $\text{A}(\text{B})\dot{\text{P}}\text{L}_2$, $\text{IP}(\text{BPL}_2)$ is the ionisation potential²⁵ of BPL_2 , and $\text{EA}(\text{A}^{\cdot})$ is the electron affinity²⁶ of A^{\cdot} ; α_B and α_L may be defined in an analogous way.

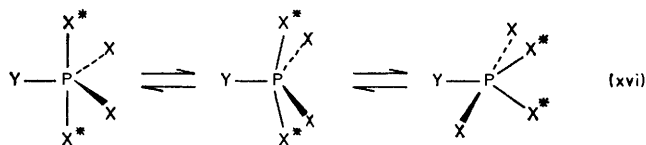
If $\alpha_A \approx \alpha_B \ll \alpha_L$, the radical $\text{A}(\text{B})\dot{\text{P}}\text{L}_2$ would be expected to prefer the TBP structure (19) (see Scheme), since the abilities of A and B to support negative charge in 'no bond' canonical forms of the type (16a and b) are similar. If α for one P-ligand bond is appreciably smaller than those of the other three, we would predict that a σ^* structure [such as (18) or (20)] would be preferred.† These conclusions are summarised in the Scheme, which illustrates the expected changes in ground-state geometry from $\sigma^*(\text{P}-\text{A})$ through TBP to $\sigma^*(\text{P}-\text{B})$ as the ligands change such that initially $\alpha_A \ll \alpha_B \approx \alpha_L$ to a situation where $\alpha_B \ll \alpha_A \approx \alpha_L$.



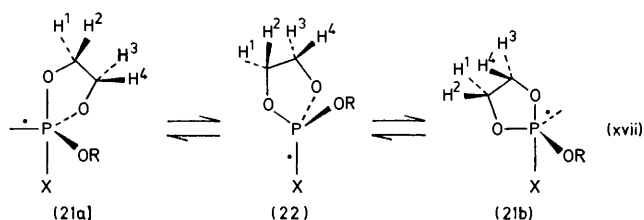
Depending on the nature of the ligands, the ground state structure of a phosphoranyl radical may lie anywhere along the TBP (C_{2v}) \rightarrow σ^* (C_{3v}) distortion coordinate. An analogous situation appears to obtain for

† This is equivalent to saying that an antibonding unpaired electron will be preferentially accommodated in the P-ligand bond(s) which has (have) the lowest associated α_{ligand} value(s).

the phosphoranes, PX_5 , for which geometries ranging from regular TBP to square pyramidal (SP) have been identified and an attempt has been made to describe a structure in terms of its position along the $TBP \rightarrow SP$ distortion co-ordinate.²⁷ Exchange of apical and equatorial ligands in a formally TBP phosphorane is thought to take place *via* an SP transition state (or intermediate)



[equation (xvi)],²⁸ in close analogy with the proposed $TBP \rightarrow \sigma^* \rightarrow TBP$ mechanism* for a-e ligand exchange in TBP phosphoranyl radicals.



The rate constants at 273 K for a-e ring proton exchange in a number of cyclic phosphoranyl radicals of the type (21) [equation (xvii)] are given in Table 4.

TABLE 4
Rates of exchange of H^1 with H^3 in cyclic phosphoranyl radicals of the type (21)

X	R	k_{exch}/s^{-1} ^a (273 K)	α_X ^b (kJ mol ⁻¹)	Ref.
Me ₃ SiO	Me ₃ Si	$< 1 \times 10^6$		c
EtO	Et	$< 5 \times 10^5$	1 058	d
F	Et	$< 6 \times 10^5$	1 036	d
PhC(O)O	Et	6.9×10^6		d
PhC(O)O	Bu ^t CH ₂	5.5×10^6		d
CF ₃ C(O)O	Et	6.4×10^6		d
CH ₃ C(O)O	Et	9.3×10^6		d
MeS	Me ₃ Si	$ca. 1 \times 10^9$	913 ^e	This work
HS	Me ₃ Si	4.2×10^9	868 ^e	This work
HS	Bu ^t CH ₂	$ca. 4 \times 10^9$	868 ^e	This work
Cl	Et	$ca. 6 \times 10^9$	847	d

^a Calculated assuming that $\log(A_{\text{exch}}/s^{-1}) = 13.0$ for all radicals. ^b Calculated using equation (xv), assuming that the ionisation potential of $\overline{OCH_2CH_2OPOR}$ is equal to that²⁵ for $\overline{OCH_2CH_2OPOMe}$ (9.06 eV). ^c Ref. 7. ^d Ref. 11. ^e Calculated assuming $\bar{D}(P-S)$ 218 kJ mol⁻¹ in $(RS)_3P$, R = Me or H.²⁴

It can be seen that the rate of this exchange increases along the series F, RO < R'C(O)O < R''S < Cl. If we assume that ring proton exchange proceeds by way of

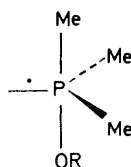
* For certain TBP-type phosphoranyl radicals [e.g.,^{1,12} $(Me_2N)_2\dot{P}(OEt)_2$] a-e ligand exchange takes place much more rapidly than P-ligand bond homolysis (α -scission). If ligand permutation and α -scission are both one-step processes it seems rather unlikely that the *transition states* for the two processes could be different. Hence, we believe that the σ^* structure is an intermediate, rather than a transition state, which can revert to a TBP structure or (less readily) undergo cleavage of the two-centre, three electron bond.

the $\sigma^*(P-X)$ intermediate (22), the rate of exchange should increase as the difference in energy between (22) and the TBP ground state (21) decreases. It follows from the foregoing discussion that this energy difference should decrease as α_X decreases relative to the α values of the remaining ligands. Hence we expect that the rate of ring proton exchange will increase as α_X decreases and it is clear from Table 4 that the predicted correlation is observed experimentally.

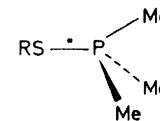
Recent molecular orbital calculations (CNDO/2) by Penkovsky²⁹ provide support for the ligand permutation mechanism illustrated in equations (i), (vii), and (xvii). The σ^* structures $H_3P^-\dot{O}H$, $F_3P^-\dot{F}$, $(HO)_3P^-\dot{O}H$, and $Me_3P^-\dot{O}Me$ were calculated to be only 4–14 kJ mol⁻¹ less stable than the corresponding quasi-TBP ground states and it was predicted that a-e ligand exchange in the latter would proceed *via* the σ^* isomers. For $Me_3\dot{P}F$ the $\sigma^*(P-F)$ structure was calculated to be slightly more stable than the TBP isomer with an apical fluorine.

The relative apicophilicities of the ligands in a TBP phosphoranyl radical should increase in the order of decreasing α values and the available experimental data appear to support this prediction.¹ Previously, it has been assumed that apicophilicity increases with ligand electronegativity¹ and, on this basis, our finding that an MeS group is more apicophilic than RO would be contrary to expectation. Unless the ionisation potential of $\overline{OCH_2CH_2OP}SMe$ is more than 145 kJ mol⁻¹ (1.5 eV) below that of $\overline{OCH_2CH_2OPOR}$, which seems unlikely, the value of α_{MeS} will be smaller than that of α_{RO} (*cf.* Table 4) and hence the order of apicophilicities in $\overline{OCH_2CH_2OP(OR)SMe}$ may be understood.

The *P*-methyl substituents in $Me_3\dot{P}SR$ were magnetically indistinguishable at all temperatures studied, whereas the radicals $Me_3\dot{P}OR$ (R = Et, Bu^t, Pe^v) contain non-equivalent methyl ligands in the TBP-type structure (23).^{17,18} At 163 K the splittings from apical and equatorial methyl protons in (23; R = Bu^t) are 4.6



(23)



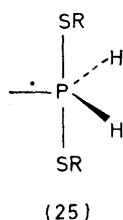
(24)

and 2.7 G, respectively, but above *ca.* 240 K the ligands exchange rapidly on the e.s.r. time scale ($k_{\text{exch}} 4.6 \times 10^6$ s⁻¹ at 203 K) and the weighted average splitting is observed. We conclude that if the methyl ligands in $Me_3\dot{P}SR$ are chemically different (implying a TBP-type geometry) the difference between apical and equatorial methyl proton splittings is smaller than for $Me_3\dot{P}OR$ and/or a-e methyl exchange is more rapid than for $Me_3\dot{P}OR$. This implies that the ground state geometry of $Me_3\dot{P}SR$ lies significantly further along the $TBP \rightarrow \sigma^*$

distortion co-ordinate than that of $\text{Me}_3\dot{\text{P}}\text{OR}$ and, because of the large difference between α_{MeS} and α_{Me} in $\text{Me}_3\dot{\text{P}}\text{SMe}$ [1 055 and 821 kJ mol^{-1} , taking $\text{IP}(\text{Me}_2\text{PSMe}) = \text{IP}(\text{Me}_3\text{P})$ ²⁵], we suggest that $\text{Me}_3\dot{\text{P}}\text{SR}$ adopts a structure close to the $\sigma^*(\text{P-S})$ limit (24) in which the methyl ligands are chemically equivalent.*

Similar conclusions may be drawn from the magnetic equivalence of the three nitrogen nuclei in $(\text{Me}_2\text{N})_3\dot{\text{P}}\text{SR}$ and, whilst one of the Me_2N substituents may well be different from the other two, we suggest that the structure of this radical is distorted from TBP (RS apical) towards $\sigma^*(\text{P-S})$.

The phosphoranyl radicals $(\text{RS})_2\dot{\text{P}}\text{H}_2$ [$\text{R} = \text{H}, \text{D}, \text{Bu}^t, \text{Bu}^t\text{C}(\text{O})$] would be expected to adopt the TBP structure (25) with equivalent apical RS ligands. The e.s.r. parameters (Table 2) are in accord with this assignment



and the splitting from the hydrogen ligands (*ca.* 6 G) is of the magnitude expected ^{17,18} if these occupy equatorial sites.

The phosphoranyl radical $(\text{MeO})_2\dot{\text{P}}(\bar{\text{S}})\text{Br}$ has been studied by Symons ⁶ and shown to adopt a $\sigma^*(\text{P-Br})$ structure. This geometry would be predicted since α_{Br} will be much smaller than α_{MeO} .

It has recently been shown ³⁰ that the hypervalent radical $\text{Ph}_3\dot{\text{P}}\text{Br}$, generated in the solid state by *X*-irradiation of $\text{Ph}_3\text{P}=\dot{\text{N}}\text{H}_2\bar{\text{B}}\text{r}$, adopts a structure more distorted towards TBP than that of $\text{Ph}_3\dot{\text{P}}\text{Cl}$. This would not be expected for the isolated radical in a non-interacting environment, because α_{Br} is smaller than α_{Cl} , and we suggest that crystal forces may be responsible for this anomaly, since the barrier to deformation along the $\text{TBP} \rightarrow \sigma^*$ distortion co-ordinate is in general small.

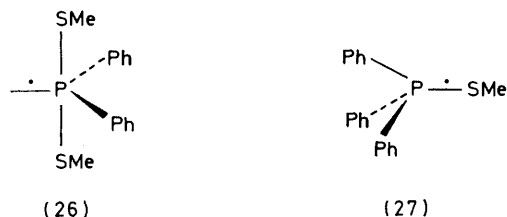
Phenylphosphoranyl Radicals.—Whilst it is very likely that $(\text{MeS})_2\dot{\text{P}}\text{Ph}_2$ is essentially TBP as shown in (26) [*cf.* $\text{Cl}_2\dot{\text{P}}(\bar{\text{O}})\text{OR}$ which has two apical chlorines ⁴], the structure of $\text{MeS}\dot{\text{P}}\text{Ph}_3$ is less certain. By comparison with $\text{Ph}_3\dot{\text{P}}\text{Cl}$ ⁵ which has a σ^* structure, it is unlikely to be TBP and it probably adopts a geometry considerably [or completely, as shown in (27)] along the $\text{TBP} \rightarrow \sigma^*(\text{P-S})$ distortion co-ordinate.

In common with the trend followed by all the other thiophosphoranyl radicals investigated, the values of $a(\text{P})$ for $\text{RS}\dot{\text{P}}\text{Ph}_3$ increase along the series $\text{R} = \text{CH}_3 < \text{H} < \text{CF}_3 < \text{R}'\text{C}(\text{O})$. The phosphorus splitting (528 G) for $\text{HS}\dot{\text{P}}\text{Ph}_3$ is thus in accord with expectation and is very different from that (391 G) shown by the radical previously identified ²⁰ as $\text{HS}\dot{\text{P}}\text{Ph}_3$. Our assignment is

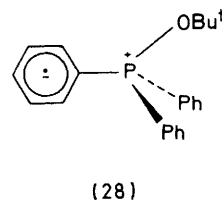
* Studies of the anisotropic e.s.r. spectrum of $\text{Me}_3\dot{\text{P}}^{33}\text{SR}$ in rigid matrices would be required to test this prediction.

further supported by the absence of proton splitting when H_2S was replaced by D_2S .

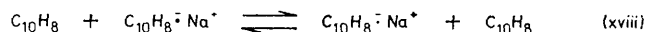
It has been shown previously ¹⁹ that replacement of alkylthio- by alkoxy-ligands results in destabilisation of the hypervalent form of a phenylphosphoranyl radical



with respect to the ligand- π -structure. The low-temperature e.s.r. spectrum of $[\text{Bu}^t\text{OPPh}_3]\cdot$ clearly shows that the unpaired electron is contained in a π orbital centred on *only one* phenyl group as shown in (28). Electron exchange renders the rings magnetically equivalent by 216 K and, although exhaustive computer



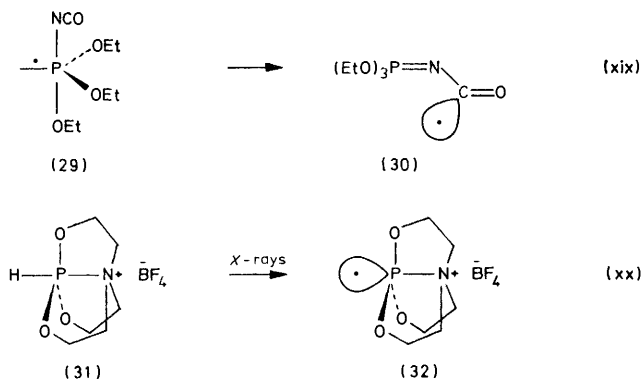
simulation of the spectra was not justified, because the *meta*-proton splitting was unresolved, it is clear that the rate constant for this exchange must be *ca.* 10^7 s^{-1} at 165 K. Electron exchange could take place *via* an intermediate hypervalent isomer, but further speculation would not be justified at this time. Exchange of the unpaired electron between the three phenyl groups in (28) is an intramolecular analogue of the well known radical exchange reaction which occurs between arene radical anions and the neutral arene [*e.g.* equation (xviii)].³¹



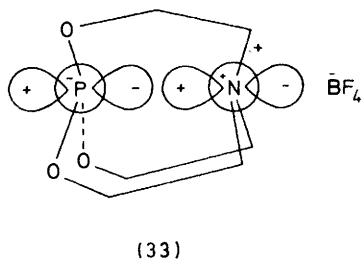
In common with other ligand- π phosphoranyl radicals,³² the phosphorus splitting for (28) is markedly temperature dependent and $\partial|a(\text{P})|/\partial T$ is *ca.* $+75 \text{ mG K}^{-1}$. Thermal population of vibrational states in which the phosphorus atom is out of the nodal plane of the SOMO is probably responsible for this large positive temperature coefficient.

The relatively low value (17.4 G) of the apical nitrogen splitting for $\text{MeS}\dot{\text{P}}(\text{NCO})(\text{OEt})_2$ (12) compared with its value (26.3 G) for the oxygen analogue $(\text{EtO})_3\dot{\text{P}}\text{NCO}$ (29) ¹³ is probably the result of a greater distortion towards a σ^* structure for (12). Whilst the hypervalent species (29) is unstable with respect to the ligand- σ configuration (30),¹³ no analogous rearrangement was observed for (12), probably reflecting the importance of charge transfer to sulphur [see structures (16) and (17)] in stabilising the hypervalent form, in parallel with the observations for phenylphosphoranyl radicals.

In view of our treatment of phosphoranyl radical structure it is important to make some comment on the recent paper by Hamerlinck *et al.*³³ These authors reported that X-irradiation of a single crystal of (31) gave rise to an e.s.r. spectrum which they ascribed to a TBP phosphoranyl radical with the 'unpaired electron in an apical position' as shown in (32). Although the composition of the SOMO is not clear



from (32) and no spectra were shown, it is stated that the ^{14}N splitting (22 G) was 'nearly isotropic' and that it 'probably has a negative sign since it is the result of spin polarisation in the P-N linkage'. If, as the authors conclude, the direction of maximum ^{31}P coupling is close to that of the P-N bond we consider that the electronic configuration (33) [a $\sigma^*(\text{P-N})$ structure] is



more plausible. The phosphoranyl radical is clearly not a cyclic analogue of $\text{Me}_2\text{N}^{\cdot}(\text{OEt})_2\text{OBu}^t$, as suggested, since the apicophilicity of $\text{R}_3\text{N}^{\cdot}$ would be expected to be much greater than that of the R_2N group. The structure (33) is evidently related to those of the σ^* phosphine³⁴ and amine³⁵ dimer radical cations $[\text{X}_3\text{P}^+-\text{PX}_3]^+$ and $[\text{X}_3\text{N}^+-\text{NX}_3]^+$. Finally, we point out that our earlier work^{7,12} on $\text{Me}_2\text{N}^{\cdot}(\text{OEt})_2\text{OBu}^t$ has been misquoted in Hamerlinck's paper.

EXPERIMENTAL

Materials.—Hydrogen sulphide, dimethyl sulphide, dimethyl disulphide, and di-*t*-butyl disulphide were commercial materials used as received. Perfluorodimethyl disulphide (P.C.R.) was purified by preparative g.l.c. before use.¹⁴ Deuterium sulphide was generated by reaction of D_2SO_4 in D_2O with iron(II) sulphide and $(\text{CD}_3)_2\text{S}$ was prepared by ammonium bromide catalysed thermal decomposition of $(\text{CD}_3)_2\text{SO}$.³⁶ Dipropionyl and dipivaloyl disul-

phides^{14,15} were prepared by the method of Gladysz *et al.*³⁷

Phosphine was purified by passage through a trap at -126°C .³⁸ Trimethylphosphine was obtained by heating the solid complex $\text{Me}_3\text{P}\cdot\text{AgI}$ under vacuum. Trifluoro-, triphenyl-, tris(dimethylamino)-phosphines and triethyl- and trimethyl-phosphites were commercial materials which were purified before use.

2-Trimethylsilyloxy-,⁷ 2-trimethylsilyloxy-4,4-dideuterio-,⁷ 2-neopentyloxy-,¹¹ 2-isocyanato-,³⁹ and 2-(2-oxopyrrolidin-1-yl)-¹¹ 1,3,2-dioxaphospholans and diethoxy(isocyanato)phosphine⁴⁰ were prepared by methods described in the literature.

2-Oxopyrrolidin-1-yl(diethoxy)phosphine.—Diethyl chlorophosphite (20.0 g) in ether (50 ml) was added dropwise to a stirred, ice-cooled solution of pyrrolidin-2-one (10.9 g) and triethylamine (13.0 g) in ether (130 ml). After the addition, the mixture was allowed to warm to room temperature and stirred for 1 h. Amine hydrochloride was removed by filtration under dry nitrogen, the ether was evaporated from the filtrate under reduced pressure, and the residual oil was distilled to give the *product*, b.p. $98-99^\circ\text{C}$ at 0.25 Torr (Found: C, 46.9; H, 8.0; N, 7.1; P, 15.2. $\text{C}_8\text{H}_{16}\text{NO}_3\text{P}$ requires C, 46.8; H, 7.9; N, 6.8; P, 15.1%). The proton-decoupled ^{31}P n.m.r. (C_6H_6 - C_6D_6 solvent) showed $\delta +135.2$ p.p.m. downfield from external 85% H_3PO_4 .

Diphenyl(methylthio)phosphine.—Diphenylchlorophosphine (11.0 g) in ether (30 ml) was added dropwise during 0.5 h to a stirred solution of pyridine (4.0 g) in ether (50 ml) through which methanethiol was bubbled slowly. The reaction mixture was maintained at -20 to -25°C during the addition. Stirring was continued at -20°C for 1 h after the addition by which time absorption of MeSH had ceased. The mixture was allowed to warm to room temperature, the pyridine hydrochloride was removed by filtration under dry nitrogen, and the ether was evaporated from the filtrate under reduced pressure. Distillation of the residual oil gave the *product*, b.p. 125°C at 0.05 Torr (Found: C, 67.3; H, 5.7; P, 13.2; S, 13.5. $\text{C}_{19}\text{H}_{18}\text{PS}$ requires C, 67.2; H, 5.6; P, 13.3; S, 13.8%). The proton-decoupled ^{13}P n.m.r. (C_6H_6 - C_6D_6) showed $\delta +30.2$ p.p.m.

E.S.R. Spectroscopy.—The techniques employed for the photochemical generation of transient free radicals for e.s.r. studies have been described previously.^{9,10,14} Computer simulations of lineshape effects resulting from ligand exchange were carried out using the program ESREXN (No. 209) available from Q.C.P.E.

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