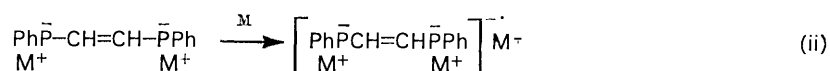
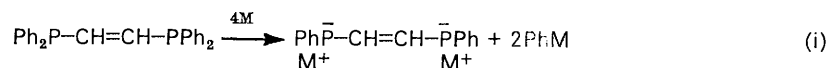


Reactions of Radical Anions. Part XV.¹ An Electron Spin Resonance Study of the Radical Anions derived from *cis*- and *trans*-1,2-Bis(diphenylphosphinyl)ethylene

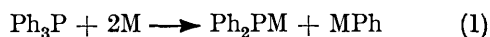
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The radical anions produced by the passage of tetrahydrofuran or 2-methyltetrahydrofuran solutions of *cis*- or *trans*-1,2-bis(diphenylphosphinyl)ethylene (DPPE) over various alkali metal films at -80° have been studied. Their production occurs by a two-stage process (i) and (ii). Computer simulation of the e.s.r. spectra together

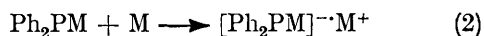


with chemical evidence show that the radical anion produced is as in equation (ii). The e.s.r. spectra also show that the unpaired electron is delocalised over the whole molecule. The nature of the e.s.r. spectra was dependent on the metal used. When Cs^+ was the gegenion, metal splitting due to two caesium ions was observed. We find no metal splitting for the third Cs^+ ion. The radical anion produced from *cis*-DPPE was the same as that from *trans*-DPPE.

THE radical anions of phosphorus have received little attention. Hanna² reported that the reaction of triphenylphosphine with alkali metals in tetrahydrofuran (THF) produced the radical anion $\text{Ph}_3\text{P}^{\cdot-}\text{M}^+$. Since the cleavage (1) of phenyl groups from triphenylphosphine by alkali metals in THF is a well known reaction,³ Britt and



Kaiser⁴ re-investigated this reaction and found that the radical was produced by the reduction of the diphenylphosphide by a further mole of metal [reaction (2)]. The



¹ Part XIV, A. G. Evans, J. C. Evans, and P. Pomery, *J.C.S. Perkin II*, 1974, 1385.

² M. W. Hanna, *J. Chem. Phys.*, 1962, **37**, 685.

³ D. Wittenberg and H. Gilman, *J. Org. Chem.*, 1958, **23**, 1063; K. Issleib and H. O. Frolich, *Z. Naturforsch.*, 1959, **14b**, 349; L. Maier, *Progr. Inorg. Chem.*, 1964, **5**, 54; A. M. Aguir, J. Beisler, and A. Mills, *J. Org. Chem.*, 1962, **27**, 1001.

radical was characterised by both chemical and e.s.r. techniques.

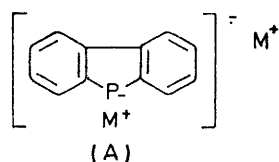
Issleib⁵ made an extensive study of the cleavage of alkyl and aryl groups from tertiary phosphines by alkali metals. He concludes that when mixed phosphines ($\text{R}^1\text{R}^2\text{R}^3\text{P}$) are employed, cleavage occurs at that carbon-phosphorus bond which leads to the ejection of the most 'electronegative' group and the formation of an organophosphide containing at least one aromatic group. Continuing these investigations, Britt and Kaiser studied the reactions of biphenyl-2,2'-diyl(phenyl)phosphine with alkali metals in THF.⁶ Chemical and e.s.r. evidence indicated the cleavage of the phosphorus-phenyl bond, and the production of radical anion (A). More recently Hnoosh and Zingaro have observed the radical anions

⁴ A. D. Britt and E. T. Kaiser, *J. Phys. Chem.*, 1965, **69**, 2775.

⁵ (a) K. Issleib, *Z. Chem.*, 1962, **2**, 163; (b) K. Issleib and H. Völker, *Chem. Ber.*, 1961, **94**, 392; (c) K. Issleib and A. Tzschach, *ibid.*, 1959, **92**, 1118.

⁶ A. D. Britt and E. T. Kaiser, *J. Org. Chem.*, 1966, **31**, 112.

produced when trinaphthylphosphine⁷ and 4,4'-bis(diphenylphosphinyl)biphenyl⁸ reacted with alkali metals



in THF and dimethoxyethane. Again naphthyl and phenyl cleavage was observed, and the radicals $[(C_{10}H_7)_2PM]^{-\cdot}M^+$, and $[PhMP(C_6H_4)_2PMPPh]^{-\cdot}M^+$ were characterised by their e.s.r. spectra.

When the phosphine contains only one aromatic group bonded to the phosphorus atom, however, radical anions can be produced which do not arise from cleavage reactions. Cowley and Hnoosh⁹ observed the e.s.r. spectrum from $[Me_2P(C_6H_4)_2PMe_2]^{-\cdot}M^+$ in THF at -80° , whilst Gerson¹⁰ has prepared $[Me_2PPh]^{-\cdot}$ by electrolysis of dimethyl(phenyl)phosphine in dimethylformamide, and by reduction with Na or K in dimethoxyethane.

tetraphenylboron was prepared and isolated by the standard method described in ref. 14.

Procedure.—Tetrahydrofuran solutions of bis(diphenylphosphinyl)ethylene were made and passed over the appropriate alkali metal film in a high vacuum apparatus at -80° using techniques similar to those described earlier.¹⁵

Saturated solutions of potassium tetraphenylboron were also made and mixed with solutions of the phosphinylethylene radical anion in the high vacuum apparatus. The resulting solution was then filtered before examination.

E.s.r. spectra were obtained on a Varian E-3 spectrometer fitted with a Varian E-4557-9 temperature controller. U.v.-visible spectra were obtained on a Pye-Unicam SP 800 spectrophotometer fitted with a variable temperature cell compartment and a scale expansion accessory. Computer-simulated spectra were obtained from empirically determined hyperfine and linewidth parameters on an I.C.L. system 4-70 computer with 286 kbytes main store. The spectra were plotted on a Calcomp drum plotter. An Evans Electroelenium Ltd. flame photometer was used to measure the concentration of alkali metal in the various solutions, and this instrument was calibrated by using a standard aqueous solution of the appropriate alkali metal chloride.

TABLE I
Absorption maxima (λ_{max} , nm) for the *cis*- and *trans*-dianion at $+20$ and -100°

Solvent	Metal	<i>trans</i>			<i>cis</i>		
		λ_{max} , $+20^\circ$	λ_{max} , -100°	$10^{-4}\epsilon$, $+20^\circ$	λ_{max} , $+20^\circ$	λ_{max} , -100°	$10^{-4}\epsilon$, $+20^\circ$
THF	Potassium	451	456	2.0	451	456	2.0
	Rubidium	454	460	2.5	454	460	2.5
	Caesium	457	461	2.0	457	461	2.0
2-Methyl-THF	Potassium	446	450	2.5	447	450	2.5
	Rubidium	450	456	2.5	450	456	2.5
	Caesium	456	462	2.5	457	461	2.5

This paper reports similar cleavage processes in the reactions of *cis*- and *trans*-1,2-bis(diphenylphosphinyl)ethylene (DPPE) with alkali metals in THF and 2-methyl-THF at low temperature. The effect of the metal ion on the radical anion has also been studied and a contribution of the *d* orbitals of the phosphorus atom to the transmission of the unpaired electron through the molecule has been postulated.

EXPERIMENTAL

Materials.—*cis*- and *trans*-1,2-bis(diphenylphosphinyl)ethylene (Strem Chemicals Ltd.) were used without further purification, m.p. (*cis* and *trans*) 125 – 126° (lit.,¹¹ 125 – 126°). Potassium, rubidium, and caesium (B.D.H.) films were made as previously described.¹² Tetrahydrofuran (B.D.H.) was purified and used as described earlier.¹³ 2-Methyltetrahydrofuran was dried over Na–K alloy and used under high vacuum conditions as for tetrahydrofuran. Potassium

The radical anions derived from *cis*- or *trans*-bis(diphenylphosphinyl)ethylene were treated at -80° by the addition, under vacuum conditions, of a mixture of degassed ethanol with a trace of acetic acid. The products formed were isolated and identified at room temperature using a Pye 104 chromatography apparatus with 10% SE 52 on 60–80 Mesh Diasopert-S column, a Varian T60 n.m.r. spectrometer, and a Varian mass spectrometer.

RESULTS AND DISCUSSION

Dianions.—When a dilute THF or 2-methyl-THF solution ($10^{-4}M$) of *cis*- or *trans*-1,2-bis(diphenylphosphinyl)ethylene was passed at -80° over a potassium, rubidium, or caesium film, a solution was obtained, after filtering off the metal, which was orange-yellow and had no e.s.r. spectra. These solutions were stable with time

⁷ M. H. Hnoosh and R. A. Zingaro, *J. Amer. Chem. Soc.*, 1970, **92**, 4388.

⁸ M. H. Hnoosh and R. A. Zingaro, *Canad. J. Chem.*, 1969, **47**, 4679.

⁹ A. H. Cowley and M. H. Hnoosh, *J. Amer. Chem. Soc.*, 1966, **88**, 2595.

¹⁰ F. Gerson, G. Plattner, and H. Bock, *Helv. Chim. Acta*, 1970, **53**, 1629.

¹¹ A. M. Aguir and D. Diagle, *J. Amer. Chem. Soc.*, 1964, **86**, 2299.

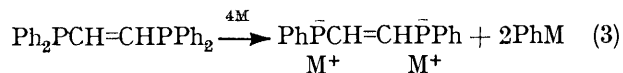
¹² A. G. Evans and J. C. Evans, *Trans. Faraday Soc.*, 1965, **61**, 1202.

¹³ J. E. Bennett, A. G. Evans, J. C. Evans, E. D. Owen, and B. J. Tabner, *J. Chem. Soc.*, 1963, 3954.

¹⁴ A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' Longmans, London, 1961, p. 561.

¹⁵ A. G. Evans, J. C. Evans, and E. H. Godden, *Trans. Faraday Soc.*, 1967, **63**, 136.

and with increase of temperature, and were unaffected by the addition of further bis(diphenylphosphinyl)ethylene. The λ_{max} values at $+20$ and -100° are given in Table 1 for both the *cis*- and *trans*-derivatives in both solvents. A plot of $1/(r_c + 2)$ (r_c = radius of cation) against $\bar{\nu}$ gives a good straight line for both temperatures and both solvents, showing that the dianions exist as contact ion pairs. The metal : phosphine ratio was found for both the *cis*- and the *trans*-solutions in both solvents to be 4.09 : 1 and the products of the reaction on opening to air were identified as benzene, bisphenylphosphinylethylene, and the metal hydroxide. These observations are consistent with reaction (3) in which two phenyl



groups are cleaved from the parent compound resulting in the phenylmetal and the dianion. This elimination of phenyl groups is consistent with the observation of other workers^{3,4} on aromatic phosphines.

Radical Anions.—When a more concentrated THF or a 2-methyl-THF solution ($\geq 10^{-3}\text{M}$) of *cis*- or *trans*-bis(diphenylphosphinyl)ethylene was quickly passed over a potassium, rubidium, or caesium film at -80° , a solution was obtained which had no e.s.r. spectra and had u.v.-visible absorption similar to that obtained for the dianion. If, however, the solution in either solvent was continually passed over the metal film at -80° the colour changed from orange-yellow to deep red and an e.s.r. signal was obtained (see Figure 1) which decayed rapidly with time if the temperature was increased to $> -50^\circ$. Identical e.s.r. spectra were obtained for both *cis*- and *trans*-bis(diphenylphosphinyl)ethylene.

Reaction Products.—The only compounds obtained on reacting the radical species, formed from *cis*- or *trans*-bis(diphenylphosphinyl)ethylene with ethanol at -78° , were benzene, *trans*-bis(phenylphosphinyl)ethylene, and the respective metal hydroxide. These products were separated by g.l.c. and identified using i.r., n.m.r., and mass spectrometry and elemental analysis. The fact that the same e.s.r. spectrum was obtained independent of whether *cis*- or *trans*-bis(diphenylphosphinyl)ethylene was used, shows that the radical anion produced from both the *cis*- and the *trans*-compound has the same configuration and structure. This is confirmed by the fact that it is only the *trans*-bis(phenylphosphinyl)ethylene which is obtained whether the starting material is *cis* or *trans*. (It was established that the *cis*-compound was not converted into the *trans*- in the g.l.c. separation.)

This product analysis also shows that, as in the formation of the dianion, two phenyl groups have been removed from the starting compound. Thus cleavage does not occur between the phosphorous atom and the ethylenic carbon atom, as found by Aguir¹⁶ using lithium in boiling tetrahydrofuran. The removal of the phenyl groups is further confirmed by the fact that diphenyl-

¹⁶ A. M. Aguir, J. J. Aguir, T. G. Archibald, and D. Diagle, *J. Organometallic Chem.*, 1966, **5**, 205.

phosphide radicals ($\text{Ph}_2\text{PM}^{\cdot-}$), whose e.s.r. spectra are well documented,³ are not observed in the system.

E.s.r. Spectra.—The splitting constants are given in Table 2. The spectra show the presence of a septet, two

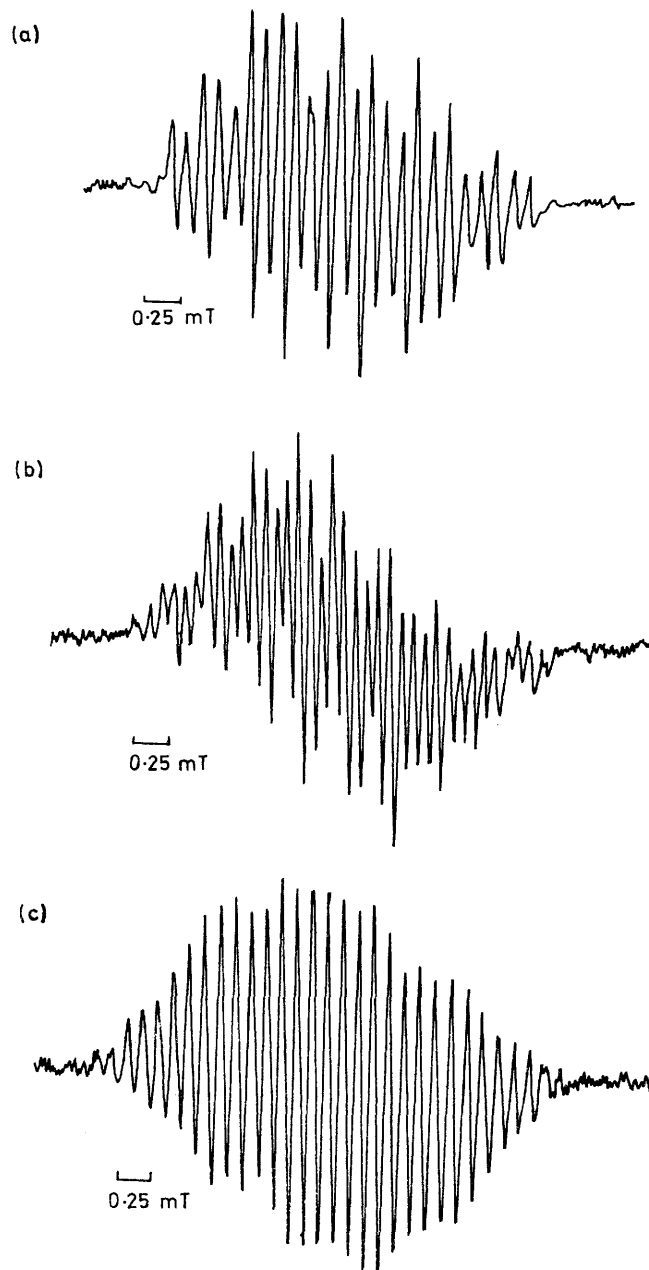


FIGURE 1 E.s.r. spectra at -80° of the radical anion formed by the passage of a THF solution of *trans*-1,2-bis(diphenylphosphinyl)ethylene over films of (a) potassium, (b) rubidium, and (c) caesium

triplets, and a quintet. This is in agreement with a radical species containing two phenyl groups; the septet arises because the *ortho*- and *para*-hydrogens of both rings are equivalent, the quintet is due to the equivalence of the four *meta*-hydrogens, the two equivalent phosphorus atoms give one triplet, and the two equivalent

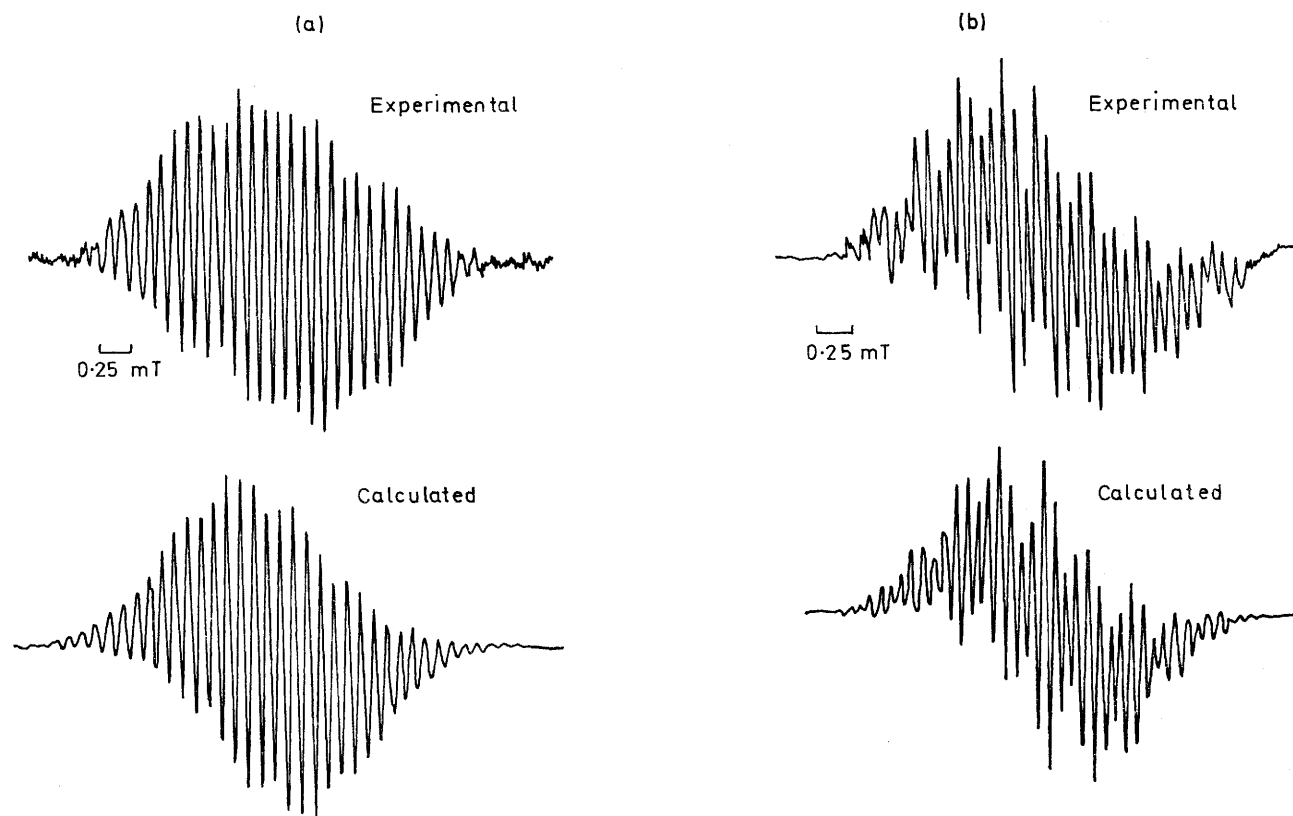
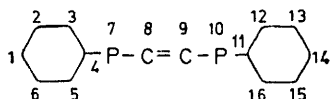


FIGURE 2 Experimental and calculated e.s.r. spectra for the radical anion formed by the passage of a THF solution of *trans*-1,2-bis(diphenylphosphinyl)ethylene over a film of (a) caesium or (b) rubidium

TABLE 2

Analysis of the e.s.r. spectra obtained by passing *trans*- or *cis*-1,2-bis(diphenylphosphinyl)ethylene over various alkali metals in THF or 2-methyl-THF at -70°

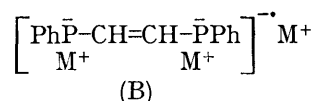


Isomer	Solvent	Metal	Splitting constants/mT				M^+	g Value
			1, 3, 5 12, 14, 16	2, 6 13, 15	8, 9 or P	P or 8, 9		
<i>trans</i>	THF	K ⁺	0.225	0.100	0.355	0.400		2.0111
		Rb ⁺	0.240	0.09	0.355	0.420		2.0115
		Cs ⁺	0.240	0.09	0.355	0.430	0.110 *	2.0119
	2-Methyl-THF	K ⁺	0.230	0.110	0.425	0.425		2.012
		Rb ⁺	0.200	0.110	0.425	0.425		2.0129
		Cs ⁺	0.225	0.110	0.425	0.425	0.110 *	2.012
<i>cis</i>	THF	K ⁺	0.225	0.10	0.355	0.410		2.0111
		Rb ⁺	0.240	0.09	0.355	0.420		2.0115
		Cs ⁺	0.240	0.09	0.355	0.430	0.110 *	2.0119
	2-Methyl-THF	K ⁺	0.230	0.110	0.425	0.425		2.012
		Rb ⁺	0.200	0.110	0.425	0.425		2.0129
		Cs ⁺	0.225	0.110	0.425	0.425	0.110 *	2.012

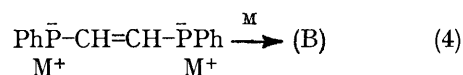
* The spectra show that the hyperfine splitting due to the metal arises from two Cs⁺ ions associated with the radical anion species.

ethylenic protons the other. This analysis was achieved by superimposing over the observed spectrum, a spectrum calculated from assigned splitting constants, and making adjustments in the splitting constants until the best fit was obtained. Figure 2 shows such a simulation with caesium and rubidium as gegenions in THF using the splitting constants given in Table 2. As can be seen, a good fit was obtained, and this was achieved in every case.

Structure of the Radical Anion.—The products from treatment of the radical anion with ethanol together with its e.s.r. spectra and the 4.09 : 1 ratio of metal to anion in the case of the dianion species, unequivocally show that the radical anion has structure (B) and is obtained



from the dianion by reaction (4).



Effect of Metal Ion.—Only when caesium metal was used as gegenion in THF or 2-methyl-THF could a metal hyperfine interaction (0.110 mT) be detected. In the case of potassium as gegenion the spectra obtained have lines wider than when rubidium and caesium were used, and this suggests that potassium is interacting to a small extent with the negative species, although the potassium splitting constant could not be obtained.

For the case of caesium, the e.s.r. spectrum shows that two metal ions are intimately associated with the radical anion since it was found that the best simulation of the e.s.r. spectrum was obtained when two caesium nuclei were taken into account in the calculation (see Figure 2). Since we know from metal : P ratio determinations that the diamagnetic dianion has two metal atoms associated with it, there must be a third metal atom involved in the radical dianion. The e.s.r. results therefore mean that this third metal atom is not equivalent to the other two. It may be that this third atom has a splitting constant too small to be detected or it may be solvent separated or dissociated. Each of the two metal ions intimately associated with the dianion must be close to a phosphorus atom. This is known to be the case for many alkali metal phosphides (refs. 4 and 5) and the bonding would be even stronger in our case which involves negatively charged radical anions. The fact that addition of a saturated solution of $\text{K}^+(\text{BPh}_4)^-$ to a solution of the

caesium radical anion at -78° has no effect on the e.s.r. spectrum means that the two equivalent metal atoms are very strongly bonded to the phosphorus atoms of the radical anion, whereas the third metal atom is present as a solvent separated gegenion or even as a dissociated ion. This is represented by structure (B).

The magnitude of the caesium interaction can be used to estimate the amount of unpaired electron spin density at the Cs^+ nucleus. The isotropic splitting constant for an electron which exists solely in the 6s orbital of a caesium atom has been estimated to be¹⁷ $Q = 82.008$ mT. Consequently a splitting constant of 0.110 mT indicates a spin density of $0.110/82.008 = 1.2 \times 10^{-3}$ on each Cs^+ nucleus. Such a small value would be expected in the case of an ionic P-metal bond. The ionic nature of such bonds has been indicated by Issleib^{5c} who has observed the red shift of λ_{max} in the visible spectrum of Ph_2PM as M is changed from Li to K. Such shifts are typical of ionic species.¹⁸

Effect of Solvent.—Only two noticeable changes are found in changing from THF to 2-methyl-THF. (1) The formation of the anion and consequently the radical anion is much slower in 2-methyl-THF. This is probably due to the poorer solvating power of the solvent. (2) The splitting constant of the triplets in the e.s.r. spectra are larger in 2-methyl-THF, one being significantly so, *i.e.* 0.355 mT in THF and 0.425 mT in 2-methyl-THF. These splitting constants which are either from the phosphorus atom or the ethylenic protons show that the unpaired electron density at these positions has been increased from THF to 2-methyl-THF by *ca.* 20%. These changes in spin density could occur by changes in localised complexes between the solvent and the polar phosphorus atoms in the radical anion. This solvation would be significantly different in THF from that in 2-methyl-THF since the latter has a smaller solvating power than THF.

Transmission of the Electron through Phosphorus.—The e.s.r. spectra show that the unpaired electron exists in an orbital which extends over the whole molecule, giving two equivalent phenyl groups, two equivalent ethylenic protons, and two equivalent phosphorus atoms, *i.e.* complete delocalisation has occurred.

Our thanks are due to University College, Cardiff, for a Tutorial Fellowship (to D. S.).

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¹⁷ P. Kusch and H. Taub, *Phys. Rev.*, 1949, **75**, 1477.

¹⁸ H. V. Carter, B. J. McClelland, and E. Warhurst, *Trans. Faraday Soc.*, 1960, **56**, 455.