Unstable Intermediates. Part 165.[1] Radicals in Irradiated Organolead Compounds: an Electron Spin Resonance Study

By **Robert J. Booth, Stephen A. Fieldhouse, Haydn C. Starkie, and Martyn C. R. Symons,*** Department of Chemistry, The University, Leicester LE1 7RH

Exposure of $PbPh_3Cl$ and $PbBrPh_3$ to ^{60}Co γ-rays at 77 K gives centres having ^{207}Pb and ^{35}Cl or ^{81}Br hyperfine coupling constants consistent with expectation for the parent radical anions. The electron-loss centres are thought to be the corresponding cations, with the hole largely confined to the halogen atoms. Irradiated $PbMe_3Cl$ gives a similar anionic centre in methanolic solution, but the pure material gives largely $Me^{\bullet}$ and $PbMe_2(\dot{C}H_2)Cl$ radicals. Irradiated $PbMe_4$ and $PbEt_4$, pure or in toluene at 77 K, give centres thought to be $PbR_3^{\bullet}$ radicals having $g_{\perp} \approx 2.1$ and $g_{\parallel} \approx 1.9$, and abnormally large anisotropic ^{207}Pb hyperfine coupling constants. In addition, $PbMe_4$ gives a centre thought to be $[PbMe_4]^{-\bullet}$, and both give $R^{\bullet}$ and $PbMe_3(\dot{C}H_2)$ or $PbEt_3(\dot{C}HMe)$. Irradiated Pb_2Ph_6 gives only one clearly defined paramagnetic centre, tentatively identified as the parent anion.

EXPOSURE of ionic solids containing lead(II) ions has been shown, by e.s.r. spectroscopy, to give lead(III) centres having very large hyperfine coupling constants to ^{207}Pb, in the 10 000—13 000 G region.[2-7] † Lead-207 has $I = \frac{1}{2}$ and is 21.6% abundant. The high-field component is found at *ca.* 5 400 G at *X*-band frequencies and corresponds to the $(F = 1, m_F = -1) \longleftrightarrow (F = 1, m_F = 0)$ transition, where $F = S + I$. Isoya *et al.*[8] showed that Pb^{IV} in lead tetra-acetate also gives a similar lead(III) centre on exposure to γ-rays.

Formation of lead(III) centres represents one limit of behaviour for Pb. The other is a weak ' charge-transfer ' interaction between radicals and one or more neighbouring lead ions.[9,10] Thus, for example, $[NO_3]^{2-}$ radicals in irradiated lead(II) nitrate interacted with lead(II) cations by weak electron donation, whilst NO_3 and NO_2 radicals interacted by weakly accepting electrons from nearest-neighbour lead(II) cations.[10] Covalent lead radicals, such as $PbMe_3^{\bullet}$, first detected by Bennett and Howard,[11] fall between these limits, with ^{207}Pb coupling constants in the 2 000 G region. These radicals were prepared by reaction (1) on a rotating cryostat at 77 K,[11] and are almost certainly correctly identified. The e.s.r. data,

$$PbMe_3Cl + Na \longrightarrow PbMe_3^{\bullet} + NaCl \qquad (1)$$

discussed below, are, however, somewhat unexpected for this species. In contrast, electron addition to $PbPh_3Cl$ gave a centre containing both lead and chlorine atoms that we have tentatively described as the primary electron adduct, $[PbPh_3Cl]^-$.[12]

There have been several recent e.s.r. studies of organotin radicals in irradiated solids.[13-15] Also, $SnMe_3^{\bullet}$ has been detected in the liquid phase,[16] as has $Sn[CH(SiMe_3)_2]^{\bullet}$ for which ^{117}Sn and ^{119}Sn isotropic hyperfine coupling were measured.[17] Our irradiation studies showed that $SnMe_3^{\bullet}$ radicals are formed from $SnMe_4$, but evidence was also found for the parent anions, $[SnMe_4]^-$, and for the methyl radical adduct $SnMe_5$.[15] The dimer Sn_2Me_6 gave $Me_2\dot{S}nSnMe_3$, but Sn_2Ph_6 gave a centre thought to be the parent anion, $[Sn_2Ph_6]^-$, with the extra electron primarily in the Sn–Sn σ^* orbital.

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† 1 G = 10^{-4} T.

[1] Part 164, S. P. Mishra, M. C. R. Symons, K. O. Christe, R. D. Wilson, and R. I. Wagner, *Inorg. Chem.*, 1975, **14**, 1103.

[2] G. Born, A. Hofstätter, and A. Scharmann, *Z. Physik.*, 1970, **240**, 163.

[3] D. Schoemaker and J. L. Kolpus, *Solid State Comm.*, 1970, **8**, 435.

[4] V. F. Koryagin and B. N. Grechushnikov, *Kristallografiya*, 1970, **15**, 985.

[5] G. Born, A. Hofstätter, and A. Scharmann, *Phys. Stat. Solidi*, 1970, **37**, 255.

[6] J. L. Kolopus, C. B. Finch, and M. M. Abraham, *Phys. Rev.*, 1970, **B2**, 2040.

[7] R. J. Booth, H. C. Starkie, and M. C. R. Symons, *J. Phys. Chem.*, 1972, **76**, 141.

[8] J-I. Isoya, H. Ishizuka, A. Yamasaki, and S. Fujiwara, *Chem. Letters*, 1972, 397.

[9] H. C. Starkie and M. C. R. Symons, *J.C.S. Dalton*, 1974, 731.

[10] M. C. R. Symons, D. X. West, and J. G. Wilkinson, *J.C.S. Dalton*, 1974, 2247.

[11] J. E. Bennett and J. A. Howard, *Chem. Phys. Letters*, 1972, **15**, 322.

[12] O. P. Anderson, S. A. Fieldhouse, H. C. Starkie, and M. C. R. Symons, *Mol. Phys.*, 1973, **26**, 1561.

[13] K. Höppner and G. Lassman, *Z. Naturforsch.*, 1968, **A23**, 1758.

[14] R. V. Lloyd and M. T. Rogers, *J. Amer. Chem. Soc.*, 1973, **95**, 2459.

[15] S. A. Fieldhouse, A. R. Lyons, H. C. Starkie, and M. C. R. Symons, *J.C.S. Dalton*, 1974, 1966.

[16] G. B. Watts and K. V. Ingold, *J. Amer. Chem. Soc.*, 1972, **94**, 491.

[17] P. J. Davidson, A. Hudson, M. F. Lappert, and P. W. Lednor, *J.C.S. Chem. Comm.*, 1973, 829.

In the present work, we describe similar studies of lead compounds exposed to high-energy radiation.

EXPERIMENTAL

Materials.—Triphenyl-lead bromide, triphenyl-lead chloride, and hexaphenyldilead were from Strem Chemicals Inc. The halides were purified by recrystallisation from ethanol, and hexaphenyldilead by recrystallisation from diethyl ether. Other materials were the highest grades available and were not further purified. The sample of pure trimethyl-lead chloride was kindly donated by Dr. J. E. Bennett.

Irradiations.—Samples in the form of fine powders or small droplets were cooled to 77 K and exposed to ^{60}Co γ-rays in a Vickrad cell at a dose rate of 1.7 Mrad h^{-1} for up to 2 h. In selected cases, samples were deoxygenated immediately prior to cooling, but this had no affect on the results.

E.S.R. Spectra.—These were recorded on a Varian E3 spectrometer at 77 K. Samples were annealed using a variable-temperature Dewar tube or by allowing them to warm in the empty insert Dewar, with addition of liquid nitrogen whenever significant changes in the e.s.r. spectra were observed.

TABLE 1

E.s.r. parameters for various organolead radicals

			^{207}Pb Hyperfine coupling [a] (MHz)			Other hyperfine coupling [a] (MHz)				
Substrate	Radical		$A_{\parallel}$	$A_{\perp}$	A_{iso}	$A_{\parallel}$	$A_{\perp}$	A_{iso}	$g_{\parallel}$ [a]	$g_{\perp}$ [a]
$PbPh_3Cl$	$[PbPh_3Cl]^-$				*ca.* 5 901 [b]	(^{35}Cl) 104	36	21	1.96	2.00
	$[PbPh_3Cl]^+$ [c]		372	346	355	(^{35}Cl) 140	(−) 42	19	2.000	2.024
$PbBrPh_3$	$[PbBrPh_3]^-$		6 651	6 460	6 524	(^{81}Br) 549	319	396	1.95	1.98
	$[PbBrPh_3]^+$ [c]				*ca.* 347	(^{81}Br) 901	*ca.* 0	300	1.99	*ca.* 2.1
$PbMe_3Cl$	$[PbMe_3Cl]^-$				*ca.* 6 046 [d]		*d*		*ca.* 2.00	
Pb_2Ph_6	$[Pb_2Ph_6]^-$ [c]	(*i*)	10 186	8 303	8 931				1 936	1.954
		(*ii*)	10 909	8 989	9 629					
$PbMe_4$	$[PbMe_4]^-$ [c]		10 062	6 354	7 590				1 926	2 087
(+ toluene)	$PbMe_3^{\bullet}$		8 518	5 024	6 189				1 917	2.113
$PbEt_4$	$PbEt_3^{\bullet}$		7 359	3 924	5 069				1.904	2.091
$PbMe_3Cl$ [e] (+Na)	$PbMe_3^{\bullet}$		8 671	5 169	6 336				1.9139	2.1055

[a] Estimated using the full Briet–Rabi equation when necessary. [b] Only one set of features defined, giving $A(^{35}Cl) = 23$ G (see text). [c] Identification tentative. [d] Chlorine hyperfine splitting was not resolved on the high-field ^{207}Pb feature and the central features were obscured by those from $CH_3^{\bullet}$ and $Me_3(\dot{C}H_2)$ radicals. [e] J. E. Bennett, personal communication.

RESULTS AND DISCUSSION

Interpretation of Spectra.—Results are summarised in Table 1. The spectra fall into two classes. One comprises signals in the free-spin (g 2) region from species containing non-magnetic isotopes and those showing only small hyperfine coupling to ^{207}Pb, and the other comprises signals in the high-field region from centres exhibiting a large hyperfine interaction with ^{207}Pb. (The corresponding low-field features, when detected, were generally less well defined than the high-field ones.)

The best defined spectra were obtained from $PbPh_3Cl$ and $PbBrPh_3$ (Figures 1 and 2). Spectra from the former showed features from two paramagnetic species, A and B, of which A was lost rapidly on annealing. A quartet of lines in the high-field region was lost simultaneously [Figure 1(*b*)]. Centre A contains one lead atom and one chlorine atom. However, the ^{35}Cl hyperfine tensor components derived from the central region [Figure 1(*a*)] do not agree with those derived from the high-field region. In fact, the well defined features, having the appearance of asymmetric derivative curves rather than parallel and perpendicular features, give a coupling of 23 G which is close to $A_{\text{iso}}(^{35}Cl)$ derived from the central lines. This effect is probably a consequence of low molecular symmetry, such that $A_{\parallel}(^{35}Cl)$ and $A_{\parallel}(^{207}Pb)$ are non-coincident. Thus, in the central region the highly asymmetric ^{35}Cl components probably dominate the powder pattern, and the values obtained are thought to be the true components. However, for the ^{207}Pb features, the turning points detected in the powder spectra will result from a fortuitous combination of the two asymmetric tensors and neither set of values will correspond to the true components. In the limit that the asymmetry for ^{207}Pb is much greater (in field) than that for ^{35}Cl, the ^{207}Pb data will approach the true values and the ^{35}Cl data will be correct for those directions. In the present case, no well defined parallel features were obtained, suggesting that the turning points are poorly defined. We can conclude only that the directions of the ^{207}Pb and ^{35}Cl hyperfine tensors differ considerably.

Centre B again apparently contains one chlorine and one lead atom but, in this case, the ^{207}Pb hyperfine coupling is small. The main features are poorly defined in Figure 1(*b*) because of overlap, but are clear after annealing.

Very similar results were obtained from $PbBrPh_3$. The central features clearly relate to two centres, C and D in Figure 2(*a*). In this case, centre D was lost on annealing, leaving C together with the high-field quartet in Figure 2(*b*). Both centres appear to contain one lead and one bromine atom.

Results for $PbMe_3Cl$ were less well defined. For the pure material, the central region was dominated by features from $CH_3^{\bullet}$ and $PbMe_2(\dot{C}_2H_2)Cl$ radicals. No well defined high- or low-field features from radicals containing ^{207}Pb were detected. On slight annealing the

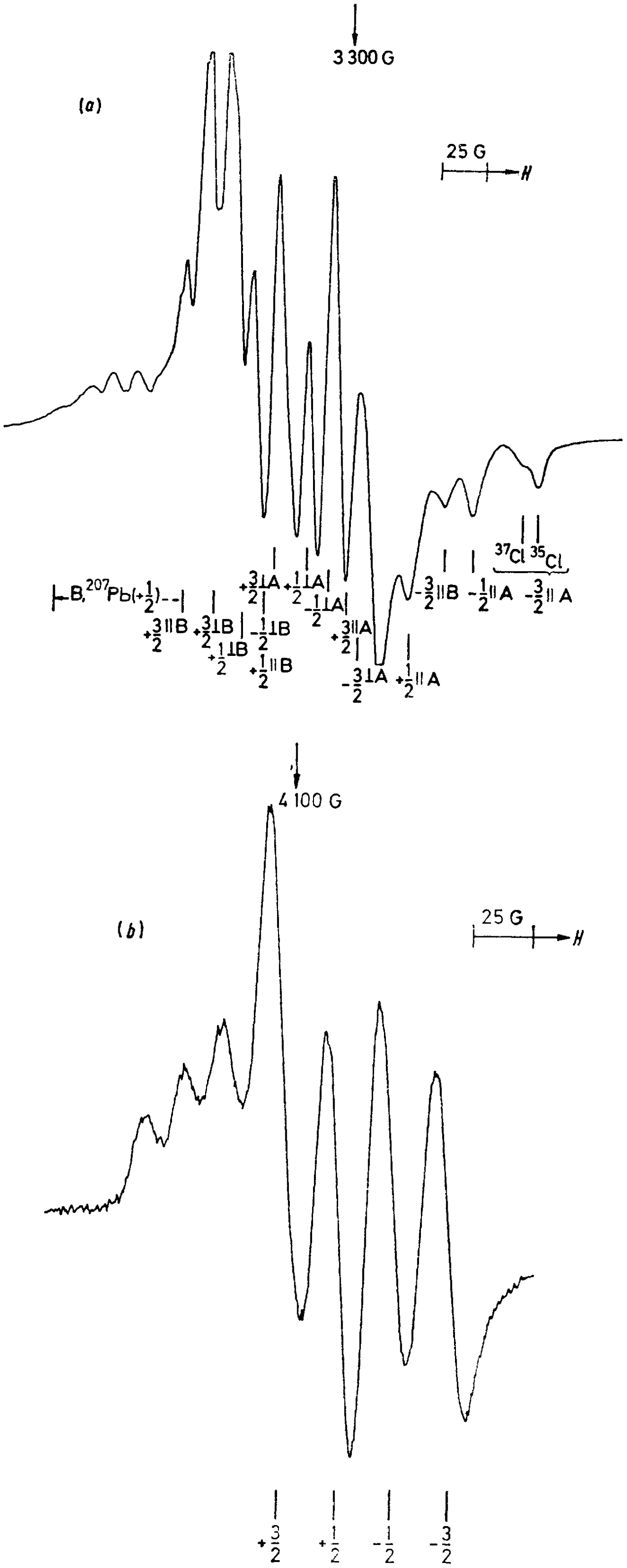

FIGURE 1 First-derivative X-band e.s.r. spectra for $PbPh_3Cl$ after exposure to ^{60}Co γ-rays at 77 K: (*a*) in the free-spin region, showing features assigned to $[PbPh_3Cl]^-$ (A) and $[PbPh_3Cl]^+$ (B); and (*b*) showing the high-field ^{207}Pb features for $[PbPh_3Cl]^-$

$CH_3^{\bullet}$ quartet was lost, revealing well defined features for $PbMe_2(\dot{C}H_2)Cl$ radicals, including those from radicals containing ^{207}Pb. These spectra closely resembled those previously assigned to $PbMe_3(\dot{C}H_2)$ radicals.[18,19] New high-field features including one with a ' parallel ' shape (E in Figure 3) were apparent in these spectra. Solutions in methanol (or CD_3OD), prepared at low temperature to inhibit solvolysis, gave, after irradiation at 77 K, a high-field, poorly resolved, quartet similar to that shown in Figure 1(*b*) (species F). The central features resembled those for the pure material but features E were absent.

Spectra obtained from pure $PbMe_4$ and $PbEt_4$ were comparable. Strong features for $CH_3^{\bullet}$ and $CH_3CH_2^{\bullet}$ overlapped broader features for $PbMe_3(\dot{C}H_2)$ and $PbEt_3(\dot{C}HMe)$ (Figure 4). The former radicals were lost on slight annealing, leading to an enhancement of the feature for the latter, which showed well defined ^{207}Pb satellite lines. In addition, broad intense perpendicular (low-field) and parallel (high-field) features were obtained, closely resembling those assigned to $PbMe_3^{\bullet}$ radicals.[11] These were accompanied by well defined high- and low-field features from radicals containing ^{207}Pb (Figure 4). Toluene glasses of these tetra-alkyl-lead compounds gave broadly comparable spectra except that alkyl radicals were not detected at 77 K. However, for $PbMe_4$ only, the features assigned to $PbMe_3^{\bullet}$ radicals were much narrower and appeared as two strong lines (J and K) with two weak lines in between these. The spectra were simplified on annealing (Figure 5), centres J and K being retained whilst the two intermediate centres were lost.

Results for Pb_2Ph_6 were not clear cut. As shown in Figure 6(*a*), two intense features L and M appeared in the central region, together with a complex set of features in the high-field region [Figure (6*b*)]. In addition, a weaker absorption (O) having defined perpendicular and parallel components appeared between these, but no features were detected in the region expected for a corresponding $M_I = +\frac{1}{2}$ line from ^{207}Pb hyperfine coupling.

Identification.—Centre A obtained from $PbPh_3Cl$ is thought to be the primary anion, $[PbPh_3Cl]^-$. This could have one of three limiting structures: (*a*) that of a substituted benzene anion, $^-Ph{-}PbPh_2Cl$; (*b*) a trigonal-bipyramidal structure, (I), comparable with those postulated for phosphoranyl radicals;[20,21] and (*c*) a σ^* structure, (II), of the type envisaged for radicals derived from N-halogenoamides[22,23] and $[BrCN]^-$,[24] for example.

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[18] A. R. Lyons, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 1063.

[19] J. H. Mackey and D. E. Wood, *Mol. Phys.*, 1970, **18**, 783.

[20] T. Gillbro and F. Williams, *J. Amer. Chem. Soc.*, 1974, **96**, 5032.

[21] D. J. Nelson and M. C. R. Symons, *J.C.S. Dalton*, 1975, 1164.

[22] G. W. Neilson and M. C. R. Symons, *J.C.S. Faraday II*, 1972, 1582.

[23] G. W. Neilson and M. C. R. Symons, *Mol. Phys.*, 1974, **27**, 1613.

[24] S. P. Mishra, G. W. Neilson, and M. C. R. Symons, *J.C.S. Faraday II*, 1974, 1280.

Possibility (*a*) is clearly incorrect for species A in view of the high spin densities on lead and chlorine. Structures (*b*) and (*c*) are both possible, but the fact that the high-field ^{207}Pb component gives different ^{35}Cl hyperfine coupling data from the central components strongly suggests a structure intermediate between (I) and (II), in which at least two of the principle directions of the ^{207}Pb and ^{35}Cl hyperfine tensors are well separated. If we assume that the ^{35}Cl hyperfine tensor components derived from the central features are correct, then, if all the signs are positive, $A_{\text{iso.}} = 59$ MHz and $2B = 45$ MHz ($2B$ is the parallel component of the dipolar coupling). These give, by the usual approximate procedure of dividing by calculated atomic parameters,[25] *ca.* 1.25% 3*s* and 16% 3*p* character on chlorine. The remaining spin

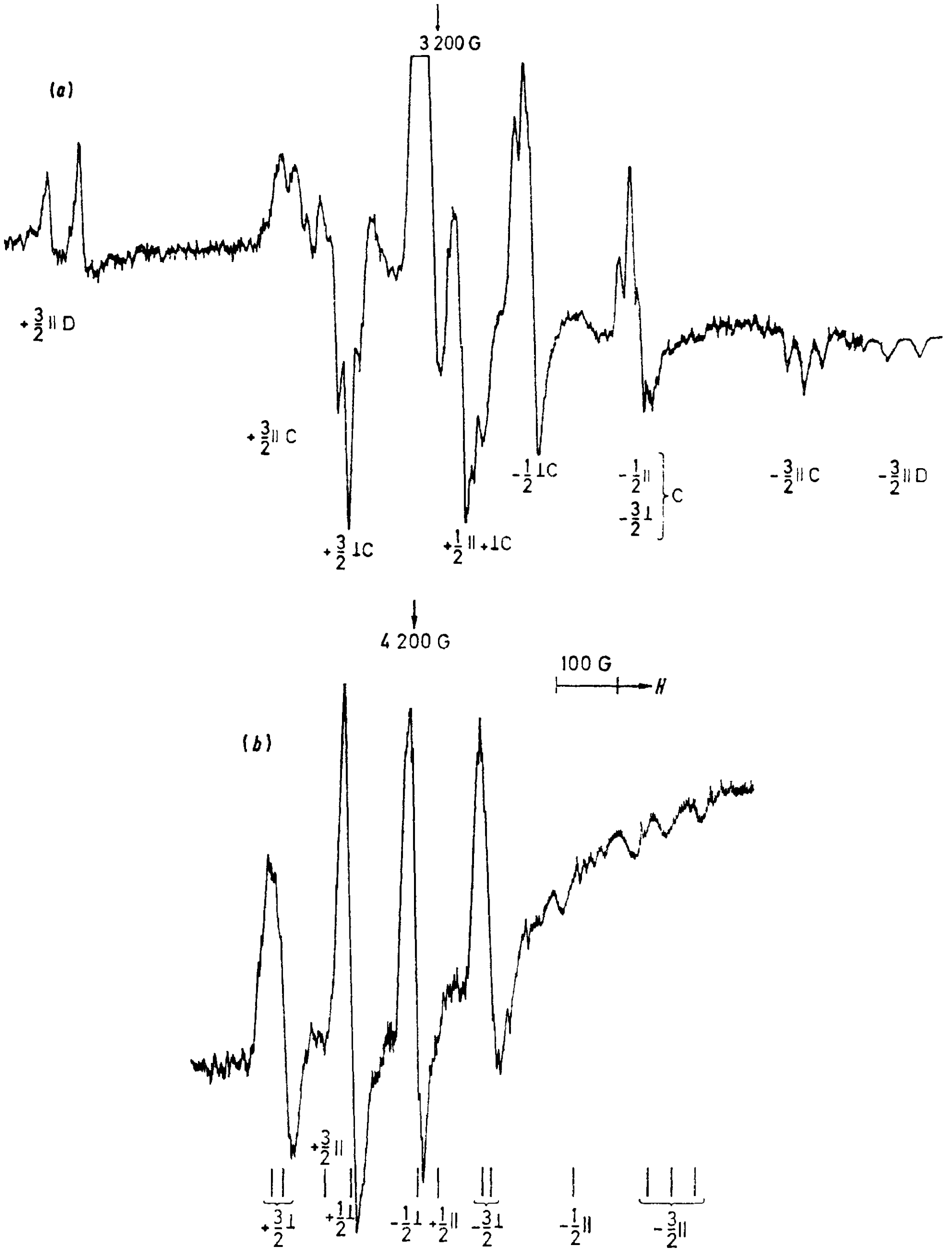
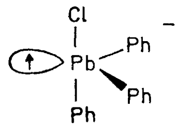
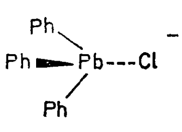


FIGURE 2 First-derivative X-band e.s.r. spectra for $PbBrPh_3$ after exposure to ^{60}Co γ-rays at 77 K: (*a*) in the free-spin region, showing features assigned to $[PbBrPh_3]^-$ (C) and $[PbBrPh_3]^+$ (D); and (*b*) showing the high-field ^{207}Pb feature for $[PbBrPh_3]^-$



(I)



(II)

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[25] P. W. Atkins and M. C. R. Symons, 'The Structure of Inorganic Radicals,' Elsevier, Amsterdam, 1967.

density is probably largely on lead. The isotropic coupling of *ca.* 5 900 MHz corresponds to *ca.* 21% 6*s* character on lead if one uses the isotropic coupling of *ca.* 28 000 MHz found for Pb^{3+} as a rough gauge.[26]

Centre B, in contrast, has a low or even zero direct spin density on lead. The nearly isotropic ^{207}Pb hyperfine coupling is comparable with that for $PbMe_3(\dot{C}H_2)$ radicals (*ca.* 163 G), and we have previously argued that this derives entirely from a spin polarisation of the carbon–lead σ-bonding electrons.[18] We tentatively propose the radical cation $[PbPh_3\dot{C}l]^+$ as the species responsible for these features. The difficulty with such cations is that the two $3p_\pi$ orbitals on chlorine are formally degenerate and, hence, a large positive *g* shift is expected for field along the Pb–Cl bond (*z*). In order to give results comparable with those obtained, we need to postulate a relatively large splitting of these levels. This should give a centre with a large hyperfine coupling along the $3p_x$ orbital with a g_x value of *ca.* 2.00 and small, probably negative, hyperfine coupling constants along *y* and *z*, with $g_z \gg 2.00$ and g_y between g_x and g_z. Our results are satisfactory for A_x and g_x, but g_y and g_z are surprisingly close together (*ca.* 2.024) for the structure envisaged. We favour $[PbPh_3Cl]^+$ because it must be the primary cationic product and because we are unable to formulate reasonable alternatives (see below). In this case, we calculate a $3p_\pi$ spin density of *ca.* 47% on chlorine if $A_\perp$ is negative. This is low for the structure proposed, but some averaging of the anisotropic coupling is expected at 77 K.

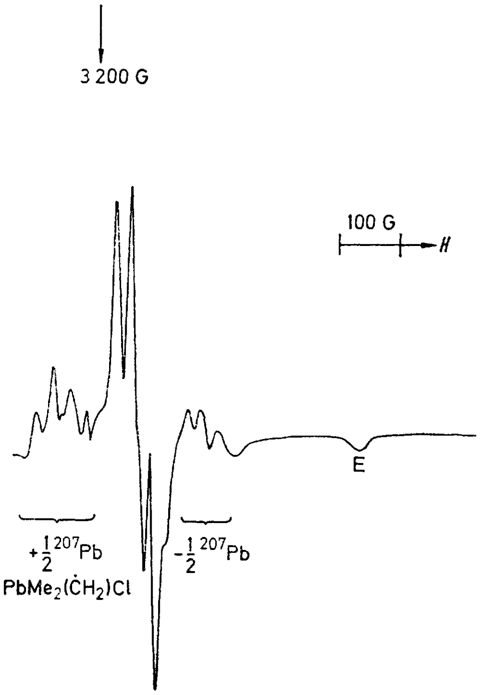

FIGURE 3 First-derivative *X*-band e.s.r. spectrum for $PbMe_3Cl$ after exposure to ^{60}Co γ-rays at 77 K, showing features assigned to $PbMe_2(\dot{C}H_2)Cl$, together with ^{207}Pb satellite lines, and a high-field feature, E, discussed in the text

Centre C in irradiated $PbBrPh_3$ resembles A and is identified as the radical anion $[PbBrPh_3]^-$. The ^{207}Pb hyperfine coupling is again large and, in this case, very poorly defined parallel features on the high- and low-field features enable us to calculate the parallel and perpendicular components (Table 1). If these are close to the principal values, we calculate approximate spin densities of *ca.* 24 and 20% in the 6*s* and 6*p* orbitals on lead. These values must be considered as very approximate. The well defined central features give bromine hyperfine components that correspond to *ca.* 12% 4*p* character if $A_\perp$ is positive. (A negative value for $A_\perp$ gives $A_{iso.} = -5$ G which is most improbable for the species envisaged.) This value is comparable with that deduced for chlorine in $[PbPh_3Cl]^-$. In this case, since the bromine coupling constants obtained from the ^{207}Pb features do not differ greatly from those deduced from the central features, we favour the concept that the structure more closely resembles (II) than (I). The relatively large value of the isotropic coupling to bromine also favours this formulation.

TABLE 2

Hyperfine parameters (MHz) for $PbR_3^\bullet$ radicals after subtracting orbital magnetic contributions

Radical	$2B_{corr.}$	$A_{corr.}$
$PbMe_3^\bullet$	2 169	6 244
$[PbMe_4]^{-\bullet}$	2 341	7 628
$PbEt_3^\bullet$	2 138	5 101
$PbMe_3^\bullet$ *	2 283	6 280

* From ref. 11.

The electron loss centre for $PbMe_3Cl$ is clearly $PbMe_2(\dot{C}H_2)Cl$, possibly formed by loss of a proton from the primary cation. Methyl radicals were also detected, however, so the sequence of events could well be as in (2) and (3). The detection of $CH_3^\bullet$ is evidence for (2),

$$[PbMe_3Cl]^+ \longrightarrow CH_3^\bullet + [PbMe_2Cl]^+ \quad (2)$$

$$CH_3^\bullet + PbMe_3Cl \longrightarrow CH_4 + Pb(\dot{C}H_2)Cl \quad (3)$$

and the increase in $[PbMe_2(\dot{C}H_2)Cl]$ on annealing, when $CH_3^\bullet$ radicals were lost, is evidence for (3).

We were not able to detect the parent anions, $[PbMe_3Cl]^-$, in the pure material irradiation, although they were detected in irradiated methanolic solution. This is surprising since we had expected that methanol would facilitate the process (4) by solvating the chloride ion.

$$PbMe_3Cl + e^- \longrightarrow PbMe_3^\bullet + Cl^- \quad (4)$$

We are unable to explain the apparent absence of an electron-gain centre in the pure material. An extra feature (E in Figure 3) was obtained, but this does not have a low-field counterpart nor does it occur in the regions expected for $[PbMe_3Cl]^-$ or $PbMe_3^\bullet$. We are unable to offer a reasonable interpretation.

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[26] R. J. Booth, H. C. Starkie, and M. C. R. Symons, *J.C.S. Dalton*, 1973, 2233.

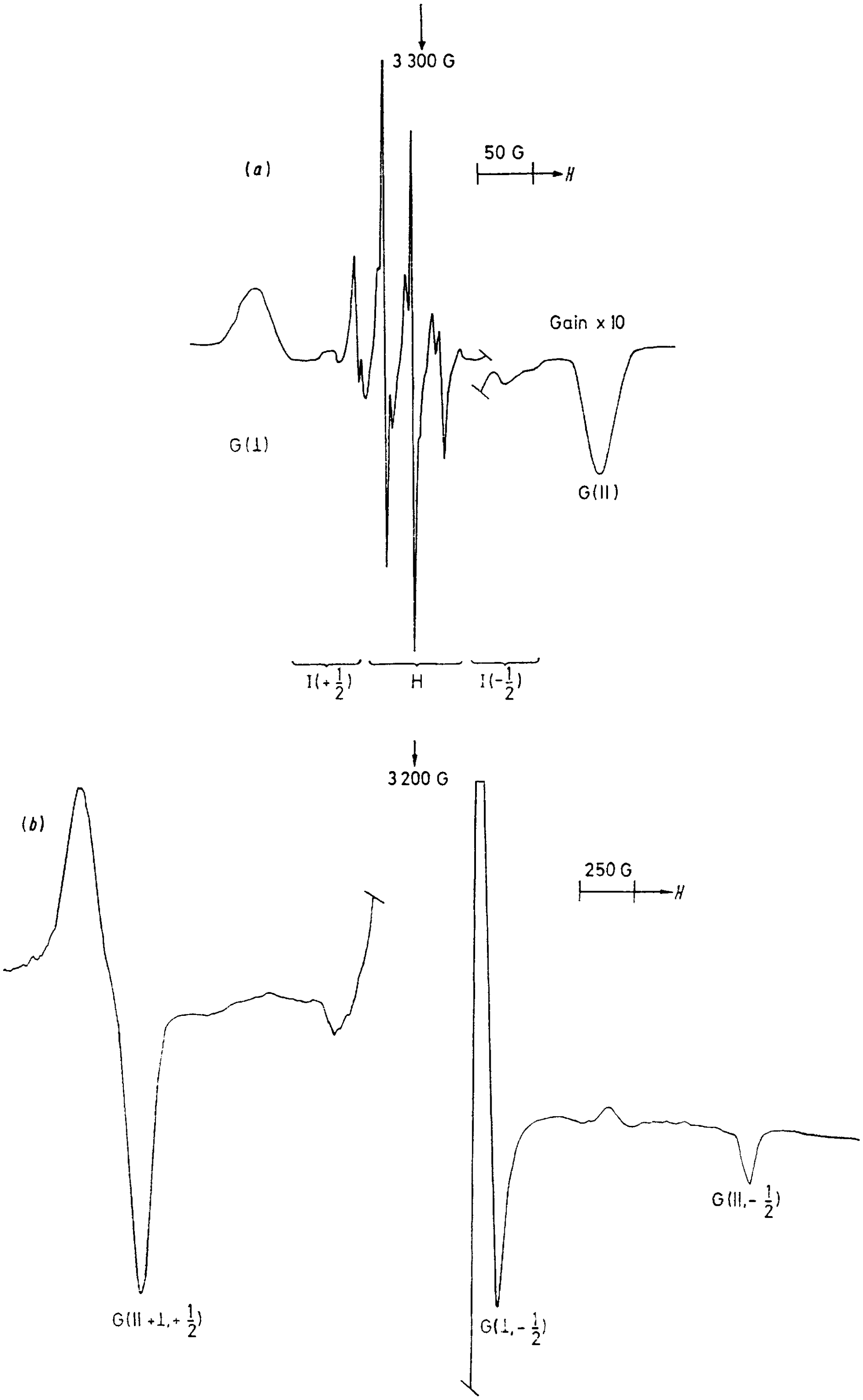


FIGURE 4 First-derivative X-band e.s.r. spectra for $PbEt_4$ after exposure to ^{60}Co γ-rays at 77 K, showing (*a*) parallel and perpendicular features assigned to $PbEt_3^{\bullet}$ (G) together with those assigned to $Et^{\bullet}$ (H) and $^{207}PbEt_3(\dot{C}HMe)$ (I), and (*b*) outer features assigned to $^{207}PbEt_3^{\bullet}$ (G)

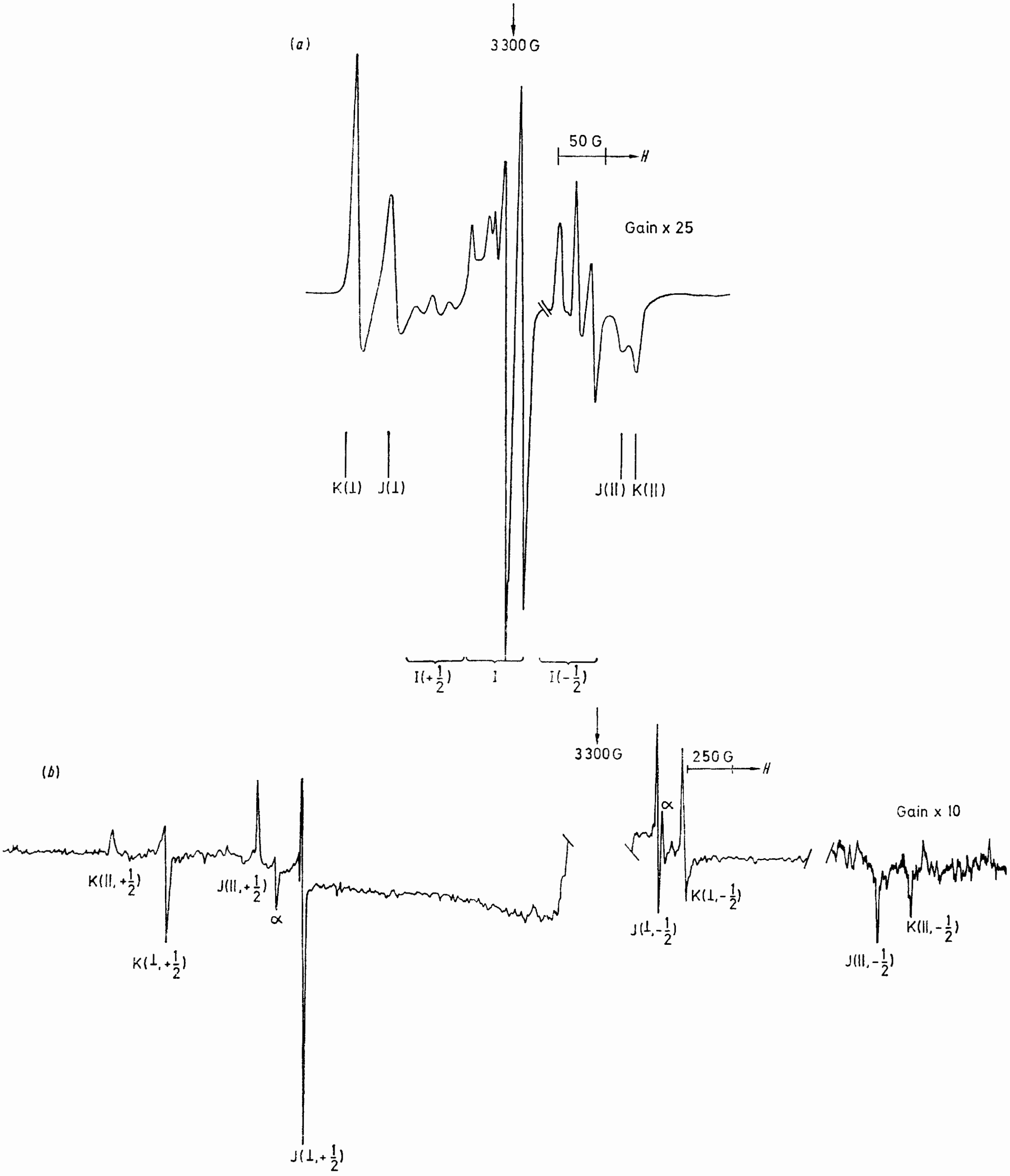


FIGURE 5 First-derivative *X*-band e.s.r. spectra for $PbMe_4$ in toluene after exposure to ^{60}Co γ-rays at 77 K and slight annealing, showing (*a*) features assigned to $PbMe_3^{\bullet}$ (J) and, possibly, $[PbMe_4]^{-\bullet}$ (K), together with those assigned to $PbMe_3(\dot{C}H_2)$ and $^{207}PbMe_3(\dot{C}H_2)$ (I), and (*b*) features assigned to $^{207}PbMe_3^{\bullet}$ (J) and, possibly, $[^{207}PbMe_4]^{-\bullet}$ (K) (the α features are discussed in the text)

Thus, none of these lead halides gave the $PbR_3^•$ radicals obtained by Bennett and Howard[11] on treatment with sodium [equation (1)]. In marked contrast, $PbMe_4$ and $PbEt_4$ gave high yields of these radicals (Figure 4). These species have most unusual magnetic properties and, indeed, we were quite unsure about identification before the publication of Bennett and Howard's results.[11] Their experiment is so direct that we must accept their identification. If these radicals have the expected symmetrical pyramidal structure (III), then, whilst the perpendicular g value of *ca.* 2.1 is reasonable, especially in view of the large spin–orbit coupling constant for lead, the equally large shift to $g_{\parallel} \approx 1.9$ is most difficult to explain. A small negative shift could be expected because of the large positive value for $g_{\perp}$, but a value of 1.9 suggests considerable admixture of vacant orbitals. One naturally turns to the empty outer *d* or *f* orbitals or to the σ* Pb–C orbitals. However, in first order, these

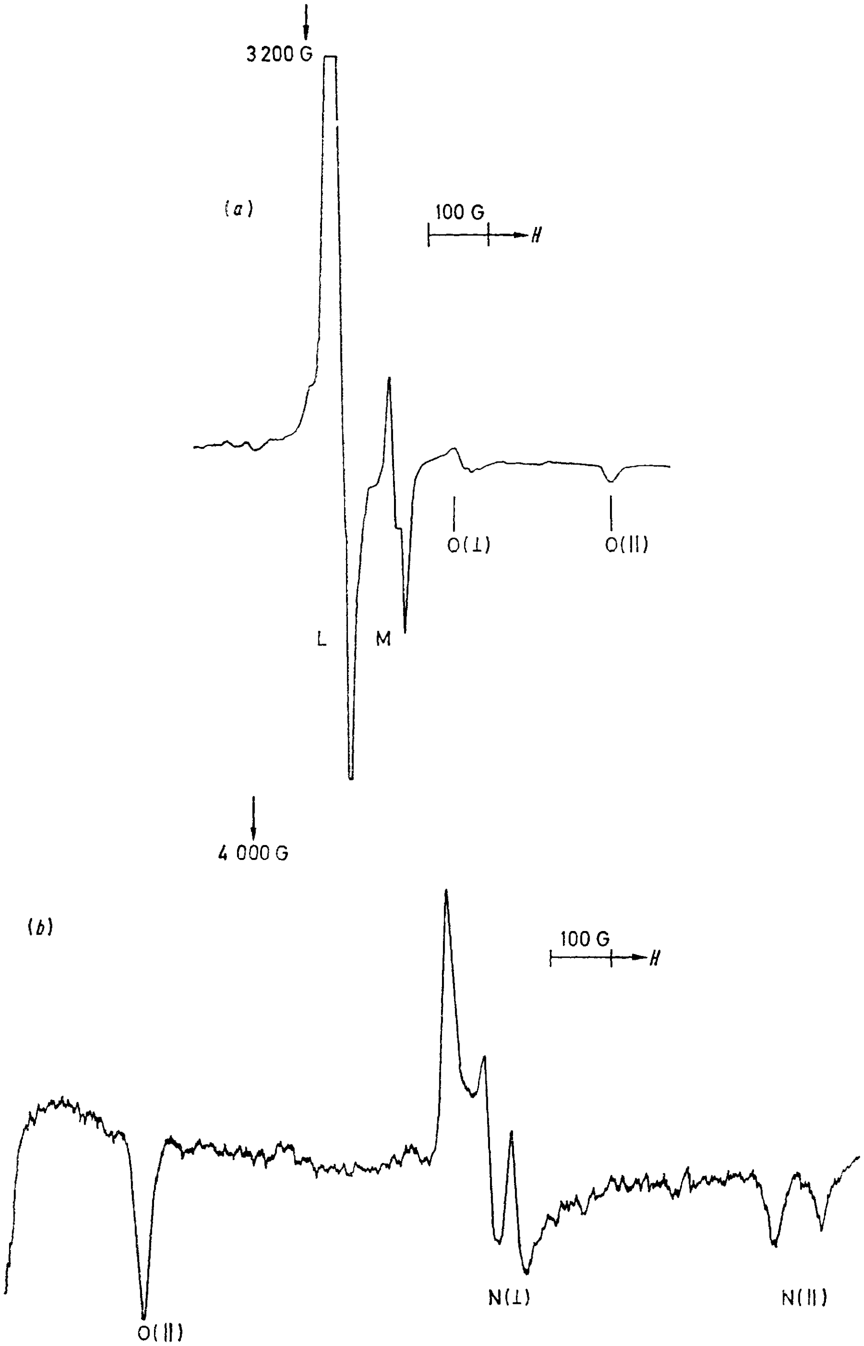
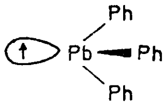


FIGURE 6 First-derivative *X*-band e.s.r. spectra for Pb_2Ph_6 after exposure to ^{60}Co γ-rays at 77 K, showing (*a*) central features L and M and the parallel and perpendicular O features, and (*b*) the very high-field N set of lines discussed in the text

are not expected to mix with the $5s + 5p_z$ hybrid orbital of the unpaired electron in such a way as to contribute orbital angular momentum. Some distortion from structure (III) seems to be indicated.



(III)

Another interpretative problem arises from the ^{207}Pb hyperfine coupling. The computed isotropic coupling is reasonable but the anisotropic coupling is exceptionally large. Using the calculated $2B^0$ value of *ca.* 350 G (estimated from the wavefunctions of Froese[27]) an apparent spin density of *ca.* 218% is estimated. This high value is reminiscent of our earlier results for Pb^{3+} centres,[7] but we have since shown that the high anisotropies reported were the result of using a simplified version of the Briet–Rabi equation, the revised values being quite reasonable.[26] We are satisfied that the present high value does not stem from incorrect calculations.

These derivations of $6p$ character are, however, incorrect in that contributions from orbital paramagnetism have been neglected. For g values of *ca.* 2.1 and 1.9 some correction should be made. Using equations (8) given by Knight and Weltner,[28] we have converted

$$A_{\parallel} = A_{\text{iso.}} + 2A_{\text{dip.}} - a(\Delta g_{\parallel}) \quad (5)$$

$$A_{\perp} = A_{\text{iso.}} - A_{\text{dip.}} + a(\Delta g_{\perp}) \quad (6)$$

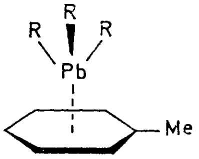
$$a = g_e g_n \beta_e \beta_n \langle r^{-3} \rangle \quad (7)$$

$$A_{\text{dip.}} = g_e g_n \beta_e \beta_n \langle (3\cos^2\theta - 1)\, 2r^{-3} \rangle \quad (8)$$

the data given in Table 2 into ' free-spin ' values and, hence, obtain $2B$ values of *ca.* 2 000 MHz (714 G). This is still far too large. Bennett and Howard[11] suggested that the calculated $2B^0$ value needs to be modified because of relativistic corrections. Mackey and Wood[29] showed that such corrections are needed for $A_{\text{iso.}}$ values reported for the heavier atoms. However, it is by no means clear that the calculated $2B^0$ values should be similarly corrected. When experimental $2B^0$ values are available, there is good agreement with theory and corrections are not required. The sudden change from normal values for the corresponding tin radicals such as $SnMe_3^{\cdot}$ (refs. 11 and 15) is surely significant, and does suggest that the high atomic number for lead is in some way responsible. The fact that the parent anions, such as $[PbBrPh_3]^-$, appear to have normal values for $2B$ and for $g_{\parallel}$ seems to contradict this, but, as stressed above, this might be because the values derived from the powder spectra are not the principal values. Thus, the low value for $g_{\parallel}$ and the large $2B$ value for $PbR_3^{\cdot}$ radicals remain unexplained.

The appearance of multiple lines for $PbR_3^{\cdot}$ radicals in toluene glasses is also difficult to explain. However, after slight annealing, only two strong sets remained [Figure 5(*b*)]. We suggest that the centre exhibiting the largest coupling to ^{207}Pb is $[PbR_4]^{-\cdot}$ rather than $PbR_3^{\cdot}$. The anion $[SnMe_4]^{-\cdot}$ was postulated to explain a set of features obtained from irradiated $SnMe_4$.[15,30] In that case, the ^{119}Sn coupling constants were only slightly greater than those for the $SnR_3^{\cdot}$ radicals and the g values were similar. This is, in our view, the best explanation of the results for the species with broader lines (B) shown in Figure 5(*b*). If this is correct, then the large negative shift for $g_{\parallel}$ and the large anisotropy again need to be explained. It is unfortunate that ^{1}H hyperfine coupling cannot be detected. By analogy with the isostructural phosphoranyl radicals, an isotropic coupling of *ca.* 4—5 G is expected.[31] This is about twice the value expected for the proton coupling in $PbMe_3^{\cdot}$ radicals.[16] Our linewidths fix upper limits of *ca.* 5 G for both radicals. The other weak features (α) may possibly be due to K centres such as (IV).

We had hoped to detect the parent cations and anions in irradiated Pb_2Ph_6. Both these ions are expected to have an unpaired electron in the Pb–Pb bond and, hence, to show hyperfine coupling to two equivalent ^{207}Pb nuclei. However, the probability of radicals containing two ^{207}Pb nuclei is low and such features would have had intensities close to the noise level, if present.



(IV)

The most interesting features are the high-field lines shown in Figure 6(*b*). We interpret these in terms of two very similar lead centres having slightly non-axial parameters. The two groups of features have equal intensities, so one reasonable possibility is that they are due to the parent cations or anions in slightly asymmetric crystal sites such that one lead atom differs slightly from the other. This is supported by the absence of such splitting on the central feature with which these are associated. Since the g values are all less than 2.0023, we suggest that the centre is the parent anion, having the extra electron in the Pb–Pb σ^* orbital. The isotropic ^{207}Pb hyperfine coupling constants (3 277 and 3 533 G) correspond approximately to $6s$-orbital populations of *ca.* 32 and 35%. The anisotropic coupling constants (482 and 492 G) are again greater than the

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[27] C. Froese, *J. Chem. Phys.*, 1966, **45**, 1417.

[28] L. B. Knight and W. Weltner, *J. Chem. Phys.*, 1971, **55**, 2061.

[29] J. H. Mackey and D. E. Wood, *J. Chem. Phys.*, 1970, **52**, 4914.

[30] S. A. Fieldhouse, H. C. Starkie, and M. C. R. Symons, *Chem. Phys. Letters*, 1973, **23**, 508.

[31] P. J. Krusic, W. Mahler, and J. K. Kochi, *J. Amer. Chem. Soc.*, 1972, **94**, 6033.

calculated $2B^0$ value, and can only be used to establish that there is considerable population of the $6p_z$ orbitals.

No other centre was firmly identifiable. The second intense central feature having $g = 2.002$ does not seem to have any associated satellite lines from ^{207}Pb nuclei. The high-field set (H) could have been the M_I (^{207}Pb) $= -\frac{1}{2}$ lines, but there was no sign of the corresponding $+\frac{1}{2}$ features. Thus, we are unable to make further identifications. It is curious that well defined features from the parent radical cation or $PbPh_3^{\bullet}$ were not detected. However, the overall yields were low and, since $PbPh_3^{\bullet}$ is expected to have an e.s.r. spectrum closely resembling those for the trialkyl derivatives, the spectrum would be spread over a wide field range and, hence, the parallel and perpendicular features would be of low intensity.

Aspects of Mechanism.—One of the most interesting results is that $PbR_3^{\bullet}$ radicals are extensively formed from PbR_4 molecules but not, under our conditions, from PbR_3X (X = halogen) molecules. This is the inverse of expectation. A reasonable reaction for PbR_4 is a ' photolysis ' (9), and certainly $R^{\bullet}$ radicals were formed

$$PbR_4 \longrightarrow PbR_3^{\bullet} + R^{\bullet} \qquad (9)$$

concurrently. This homolysis may, of course, occur by the two-step mechanism (10) and (11). However,

$$PbR_4 \longrightarrow [PbR_4]^{+\bullet} + e^- \qquad (10)$$

$$[PbR_4]^{+\bullet} + e^- \longrightarrow PbR_3^{\bullet} + R^{\bullet} \qquad (11)$$

Gardner and Kochi [32] showed that the parent cations readily release alkyl radicals [equation (12)] so the

$$[PbR_4]^+ \longrightarrow R^{\bullet} + [PbR_3]^+ \qquad (12)$$

presence of alkyl radicals in our studies does not confirm processes (9) or (10) and (11).

We conclude that the radiation properties of these organolead compounds are very similar to those of the corresponding tin derivatives.[15] The e.s.r. spectra for the $PbR_3^{\bullet}$ centres, however, differ markedly because of the curious, but characteristic, positive and negative g shifts, and the very large anisotropic coupling to ^{207}Pb.

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[32] H. C. Gardner and J. K. Kochi, *J. Amer. Chem. Soc.*, 1974, **96**, 1982.