# An Electron Spin Resonance Study of the Photolysis of Some Cyclopentadienyl-lead Compounds: the Comparison with Tin

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Photolysis of a hydrocarbon solution of cyclopentadienyltrimethyl-lead, cyclopentadienyltriphenyl-lead, or dicyclopentadienyldiphenyl-lead with u.v. light shows the e.s.r. spectrum of the cyclopentadienyl radical. Under the same conditions, cyclopentadienyltriethyl-lead shows the spectrum of only the cyclopentadienyl radical above −50 °C, and of only the ethyl radical below −100 °C. These reactions provide a convenient source of the corresponding organolead radicals. The lead radicals have properties parallel to those of the corresponding tin

$$CpPbR_3 \xrightarrow{h\nu} Cp^{\bullet} + {}^{\bullet}PbR_3$$
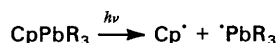
radicals, though they are less reactive towards alkyl bromides and alkenes. The radicals $Me_3Pb^{\bullet}$, $Et_3Pb^{\bullet}$, and $Ph_3Pb^{\bullet}$ add to biacetyl to give pairs of radicals which are identified as the fluxional cis- and trans-monodentate adducts; $CpPh_2Pb^{\bullet}$ gives what is believed to be the cis-adduct which is non-fluxional on the e.s.r. time scale. Similarly $Me_3Pb^{\bullet}$ and $Ph_3Pb^{\bullet}$ form an adduct with 3,6-di-t-butyl-1,2-benzoquinone which is rapidly fluxional, whereas $CpPh_2Pb^{\bullet}$ gives an adduct which is slowly fluxional. All four lead radicals are trapped by 2-methyl-2-nitropropane to give the persistent nitroxyl radicals $Me_3C(R_3PbO)NO^{\bullet}$.

WE have recently shown that cyclopentadienyltin compounds, $C_5H_5SnX_3$, unlike alkyltin compounds, are very photosensitive, and when they are irradiated with u.v. light, they show strong e.s.r. spectra of the cyclopentadienyl radical [equation (1; $Cp = C_5H_5$)].[1-3]

$$CpSnX_3 \xrightarrow{h\nu} Cp^{\bullet} + {}^{\bullet}SnX_3 \qquad (1)$$
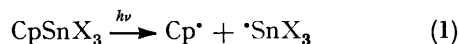
These reactions provide a route to tin-centred radicals carrying a variety of ligands X, and enabled the ligand effect on the reactions of these radicals with reagents such as alkyl halides, alkenes, and 1,2-diones to be investigated.[2,3]

The corresponding cyclopentadienyl compounds of silicon and germanium do not show this photosensitivity. We describe here an e.s.r. study of the photolysis of some cyclopentadienyl-lead compounds; we show that their photosensitivity is similar to that of the corresponding tin compounds, and that these systems provide a route to a variety of lead-centred radicals, which, in a number of processes, are less reactive than the corresponding tin species.

There have been very few previous studies of organolead radicals, but Hudson and Jackson investigated by e.s.r. the reaction of trialkyl-lead radicals with alkyl halides, alkenes, and 1,2-diones, and found that they were less reactive than trialkyltin radicals.[4,5]

Our results on the photolysis of cyclopentadienyltrimethyl-lead, cyclopentadienyltriethyl-lead, cyclopentadienyltriphenyl-lead, and dicyclopentadienyldiphenyl-lead are generalised in the Scheme. The e.s.r. spectra of the new radicals are listed in the Table.

Homolysis of the Lead–Carbon Bond.—Photolysis of all four compounds in toluene in the absence of any co-reagent showed the spectrum of the cyclopentadienyl radical. The compounds $CpPbPh_3$ and Cp_2PbPh_2 gave spectra similar in intensity to those obtained from cyclo-

pentadienyltin compounds, and provide a useful alternative source of cyclopentadienyl radicals.

Above −50 °C, the compound $CpPbEt_3$ showed a relatively weak spectrum of the $Cp^{\bullet}$ radical; as the temperature was reduced, the spectrum of the ethyl radical became apparent, until at −73 °C the intensity of the spectra of $Et^{\bullet}$ and $Cp^{\bullet}$ were approximately equal, and below −100 °C (in cyclopropane solvent) only a weak spectrum of the ethyl radical could be observed. This is in contrast to the behaviour of cyclopentadienyltrimethyl-lead and cyclopentadienyltributyltin, which, over the same range of temperature, show a very clean spectrum of the cyclopentadienyl radical, with no sign of the appropriate alkyl radical.[1]

The behaviour of the compound $CpPbEt_3$ might be taken to imply either that photolysis of both the $Cp–Pb^{IV}$ and $Et–Pb^{IV}$ bonds are involved as a primary photolytic process, or that a lead(III) radical is formed which then breaks down to diethyl-lead(II) and an ethyl radical [equation (2)].

$$CpPbEt_3 \xrightarrow{h\nu} Cp^{\bullet} + {}^{\bullet}PbEt_3 \longrightarrow {:}PbEt_2 + Et^{\bullet} \qquad (2)$$
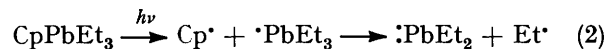
We failed to find any evidence for the equivalent conversion of Sn^{III} into Sn^{II} compounds.[3] To probe the possibility of the photolysis of an alkyl-lead(IV) bond, we have briefly investigated the photolysis of triethyl-lead chloride; this should provide a reasonable model for cyclopentadienyltriethyl-lead, because of the similar ligand effect of the chloro and cyclopentadienyl groups.[3]

Photolysis of triethyl-lead chloride in toluene gave a weak spectrum of the ethyl radical from −75 to −12 °C, and a solid was deposited on the walls of the tube. It seems possible then, that the ethyl radical may likewise be a primary product of the photolysis of cyclopentadienyltriethyl-lead, and that it need not necessarily be formed by the stepwise process of equation (2). When

SCHEME
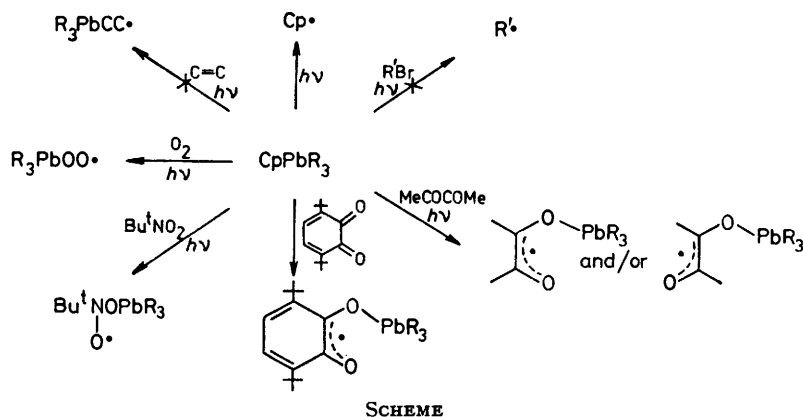
di-t-butyl peroxide was added to the solution of triethyl-lead chloride, the intensity of the spectrum of the ethyl radical was enhanced, but it was still much weaker than that which is observed under the same conditions with triethyltin chloride.[6] The S_H2 reaction at lead [equation (3)] thus appears to be slower than that at tin.

$$Bu^tO^{\bullet} + Et_3PbCl \longrightarrow Bu^tOPbEt_2Cl + Et^{\bullet} \quad (3)$$
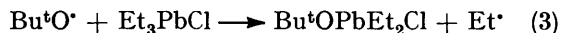
In contrast, Howard and Furimsky [7] showed that the reaction of t-butylperoxyl radicals with hexaphenyldi-lead, presumably by reaction (4; M = Pb), was 10^3

the relative reactivities reflect the relative activation energies.

If dicyclopentadienyltin(II) is photolysed, a strong spectrum of the cyclopentadienyl radical can be observed though some yellow solid is precipitated.[1] On the other hand, photolysis of dicyclopentadienyl-lead(II) produces no recognisable spectrum of the cyclopent-adienyl radical unless di-t-butyl peroxide or biacetyl is added to the solution, when the reaction probably involves an S_H2 reaction at the lead centre by t-butoxyl radicals or carbonyl triplets respectively.

E.s.r. spectra of new adducts of organotin and organolead radicals [a]

	R_3M	$T/°C$	a/G	g
	Ph_3Sn	−68	8.9 (6 H), 9.0 (Sn)	2.003 9
	Me_3Pb	−15	8.0 (6 H)	2.003 8
	Et_3Pb	+20	8.2 (6 H)	2.004 5
	Ph_3Pb	−5	8.3 (6 H), 6.0 (Pb) [b]	2.003 6
	$CpPh_2Pb$	−10	9.25 (3 H), 8.0 (3 H)	2.003 0
	Ph_3Sn	−68	ca. 8.0 (6 H)	2.005 0
	Me_3Pb	−34	6.0 (6 H) [c]	2.004 4
	Et_3Pb	−33	6.7 (6 H) [c]	2.005 3
	Ph_3Pb	−20	7.1 (6 H) [c]	2.004 2
	Ph_3Sn	−10	3.7 (2 H), 11.3/12.0 (Sn)	2.003 0
	Me_3Pb	−15	3.4 (2 H), 6.3 (Pb)	2.004 4
	Ph_3Pb	−40	3.0 (2 H)	2.003 8
	$CpPh_2Pb$	−42	2.7 (1 H), 4.3 (1 H),[c] 2.5 (Pb)[d]	2.003 5
	Ph_3Sn	−46	29.0 (N), 3.0 (Sn)	2.004 8
	Me_3Pb	−60	28.0 (N), 6.0 (Pb)	2.005 2
	Et_3Pb	−6	28.3 (N), 4.8 (Pb) [e]	2.005 1
	Ph_3Pb	+15	28.75 (N), 7.25 (Pb) [f]	2.003 7
	$CpPh_2Pb$	0	28.25 (N)	2.004 9

[a] In toluene solution. [b] $da(^{207}Pb)/dT = +27.5$ mG deg^{-1}. [c] With alternating linewidth effect. [d] 3.0 G at +64 °C. [e] 6.0 G at −63 °C. [f] $da(^{207}Pb)/dT = +49.4$ mG deg^{-1}.

times faster than the equivalent reaction with hexa-phenylditin (M = Sn).

$$Bu^tOO^{\bullet} + Ph_3MMPh_3 \longrightarrow$$
$$Bu^tOOMPh_3 + Ph_3M^{\bullet} \quad (4)$$
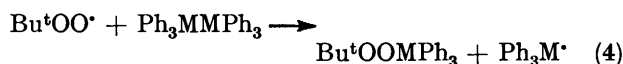
The reaction of the ditin, however, had the lower activation energy and the lower pre-exponential factor, and its reduced reactivity was ascribed to steric conges-tion about the tin. This steric effect is probably un-important in the tri-n-alkyl-tin and -lead chlorides, and

Reaction of Lead Radicals with Oxygen.—If the organo-lead(IV) compounds are photolysed under air or oxygen, the lead(III) radicals react to form the lead peroxyl radicals (see Scheme), which show a persistent broad singlet spectrum at low field. Thus cyclopentadienyl-triphenyl-lead at 0 to −70 °C showed the spectrum of the radical $Ph_3PbOO^{\bullet}$, g 2.0280, ΔH_{pp} 15 G, $t_{\frac{1}{2}}$ ca. 30 min at −70 °C. Bennett and Howard [8] have reported the formation of the persistent radical $Me_3PbOO^{\bullet}$, g 2.034, from the photolysis of a solution of di-t-butyl peroxide

and trimethyl-lead hydride in cyclopropane in the presence of oxygen.

Reaction of Lead Radicals with Alkyl Halides.—One of the most characteristic reactions of trialkyltin radicals is their S_H2 reaction at halogen in an alkyl halide to displace an alkyl radical.[9] This is the basis of one of the methods for generating alkyl radicals for e.s.r. studies,[4] and it is the key step in the preparative reduction of an alkyl halide to an alkane by an alkyltin hydride.

Cooper *et al.*[4] reported that photolysis of hexamethyldilead alone in cyclopropane gave a weak spectrum of the methyl radical, but, in the presence of ethyl, isopropyl, or t-butyl bromide this spectrum was replaced by that of the alkyl radical derived from the alkyl bromide. When carbon tetrachloride was present, the spectra of both the radicals $CH_3^{\bullet}$ and $^{\bullet}CCl_3$ were observed.

Our cyclopentadienyl-lead compounds behaved differently. When they were photolysed in the presence of ethyl bromide or t-butyl bromide, the lines of the cyclopentadienyl radicals were broadened, as has been reported previously,[1] but there was no evidence for the formation of the alkyl radical from the alkyl bromide. Under the same conditions, cyclopentadienyltributyltin or cyclopentadienyltriphenyltin show a strong spectrum of the alkyl radical derived from the bromide. Photolysis of allyl bromide alone in cyclopropane shows a spectrum of the allyl radical, but this is quenched when cyclopentadienyltriphenyl-lead is added; presumably, all the light is now being absorbed by the organolead compound, and the spectrum of the cyclopentadienyl radical is not being observed because it is broadened by the bromide.

This apparent difference in the behaviour of $Me_3Pb^{\bullet}$ radicals derived from $Me_3PbPbMe_3$ or from $CpPbMe_3$ might be accounted for in two ways. First, it might be that, under our conditions, the trimethyl-lead or alkyl radicals are scavenged by rapid addition to the diene group of the cyclopentadienyl-lead compound; against this, we could observe no adduct radical when the $Me_3Pb^{\bullet}$ radical was generated in the presence of cyclopentadiene. Alternatively, the halogen-abstracting species formed from hexamethyldilead might be $Me_3PbMe_2Pb^{\bullet}$ rather than $Me_3Pb^{\bullet}$.

Reaction of Lead Radicals with Alkenes.—The second most characteristic reaction of trialkyltin radicals is their addition to alkenes, and again this is useful in both e.s.r. studies and preparative chemistry.[9] Again, the organolead radicals are less reactive in this respect. Photolysis of cyclopentadienyltriethyl-lead in ethylene as solvent showed the spectra of the cyclopentadienyl and ethyl radicals, but not of the adduct $Et_3PbCH_2CH_2^{\bullet}$; under the same conditions, cyclopentadienyltributyltin shows the spectrum of the cyclopentadienyl radical and of the radical $Bu_3SnCH_2CH_2^{\bullet}$.[1] Similarly, cyclopentadienyltriphenyl-lead and dicyclopentadienyldiphenyl-lead showed no sign of giving any radical adduct with cyclohexene, and the photolysis of cyclopentadienyl-trimethyl-lead, -triethyl-lead, or -triphenyl-lead in the presence of cyclopentadiene showed the spectrum of only

the cyclopentadienyl radical and none of any allyl radical resulting from addition of $Ph_3Pb^{\bullet}$ to the diene system. On the other hand, photolysis of cyclopentadienyltriphenyltin in the presence of cyclopentadiene showed the spectrum of the cyclopentadienyl radical and of the triphenylstannylcyclopentenyl radical formed by addition of the triphenylstannyl radical to cyclopentadiene.

Reaction of Lead Radicals with 1,2-Diones.—Hudson *et al.*[5] showed that the tricyclohexyl-lead radical was less reactive than the tributyltin radical towards carbonyl compounds in that it could not be observed to form adducts with acetone or diethyl oxalate, but photolysis of hexacyclohexyldilead in the presence of biacetyl showed a weak e.s.r. spectrum, $a(3H)$ 8.6, $a(3H)$ 2.8 G. From the reaction of tributyltin radicals with biacetyl, we have observed the formation of two adducts, one showing a spectrum consisting of a regular binomial septet, $a(6H)$ 8.5 G, g 2.0040, and the other, at lower temperature, consisting of a septet with a strong alternating linewidth effect, $a(6H)$ 7.5 G, g 2.0045. From evidence based in part on a comparison with the corresponding butylchlorotin derivatives Bu_nCl_{3-n}-SnOCMeCMeO$^{\bullet}$ $(n = 0—2)$, these radicals were assigned the fluxional *cis*- and *trans*-structures (I) and (II) respectively $(MR_3 = SnBu_3)$.[2]


(I)   (II)
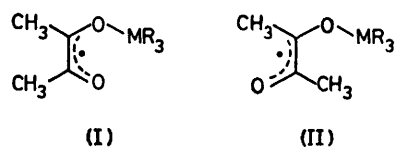
Photolysis of cyclopentadienyltriethyl-lead in the presence of biacetyl at 20 °C (at which temperature only Cp–Pb cleavage occurs), showed a spectrum consisting of a regular septet, $a(6H)$ 8.2 G, g 2.0045. At and below 0 °C, this and a second radical, $a(6H)$ 6.7 G, g 2.0053, with a strong alternating linewidth effect, were apparent. Cyclopentadienyltrimethyl-lead behaved similarly.

In view of the similarity in temperature dependence, hyperfine coupling constants, alternating line-width effects, and g-values, with the trialkyltin derivatives, we assign to these two radicals the rapidly fluxional *cis*-structure (I), and the more slowly fluxional *trans*-structure (II), respectively $(M = R_3Pb)$.* It seems likely that the tricyclohexyl-lead derivatives which was observed at -20 °C[5] was the *trans*-derivative [II; $MR_3 = (C_6H_{11})_3Pb$] which is rendered non-fluxional on the e.s.r. time scale by more bulky ligands around lead.

The behaviour of cyclopentadienyltriphenyl-lead was similar to that of the trialkyl analogues. Above -20 °C, the only spectrum which was observed was a regular septet, a 8.3 G, g 2.0036, with a strongly temperature-dependent lead hyperfine coupling, $a(^{207}Pb)$ 6.0 G at

* Prolonged photolysis of a mixture of triethylcyclopentadienyl-lead and biacetyl above 30 °C gave a very strong and persistent spectrum, with, apparently, $a(8\ H)$ 2.2 G, ΔH_{pp} 1.25 G, g 2.0048; we have not been able to identify the radical which gives rise to this spectrum.

—5 °C, $da(^{207}Pb)/dT$ +27.5m G deg^{-1} (Figure). We assign this spectrum to the cis-radical (I; MR$_3$ = PbPh$_3$), but it is interesting that, when MR$_3$ = SnBu$_3$, radical (I) shows a negative, rather than positive, temperature coefficient of the $^{117/119}$Sn hyperfine coupling.[2]
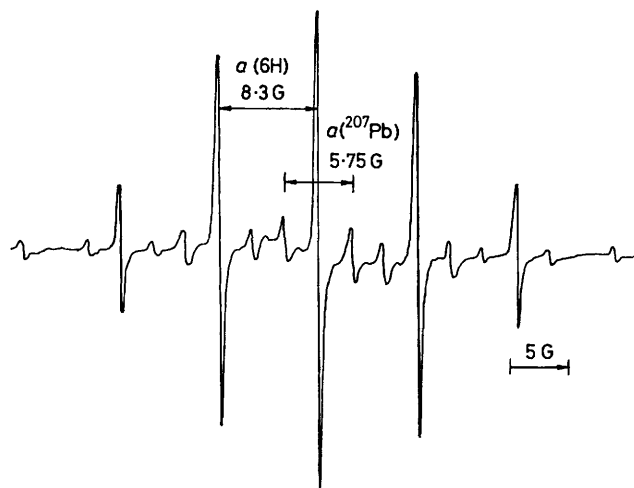
E.s.r. spectrum, showing ^{207}Pb hyperfine coupling, of the radical cis-Ph$_3$PbOCMeCMeO·, obtained from the photolysis of a solution of CpPbPh$_3$ and biacetyl in toluene at −8 °C; ethyl bromide has been added to quench the spectrum of the Cp· radical (^{207}Pb, 21.1% abundance, $I = \frac{1}{2}$)

Below −20 °C, a second spectrum was apparent with a higher g value (2.0042) and smaller proton hyperfine coupling constant (7.1 G), with a strong alternating line-width effect, and we identify this with the trans-derivative (II; MR$_3$ = PbPh$_3$). Under the same conditions, triphenylcyclopentadienyltin showed from −75 to +50 °C a spectrum consisting of a regular septet, a(6H) 8.88, $a(^{119}$Sn) 9.0 G, g 2.0039, which we assign to the cis-radical (I; MR$_3$ = SnPh$_3$). Below ca. −50 °C,

the spectrum of a second, more persistent, radical could be observed, with much broader lines (ΔH_{pp} ca. 4 G rather than 0.5 G), a(6H) ca. 8.0 G, g 2.0050, which we assign to the trans-isomer (II; MR$_3$ = SnPh$_3$).

Photolysis of dicyclopentadienyldiphenyl-lead in the presence of biacetyl gave the relatively weak spectrum of an adduct, which at −10 °C could be analysed in terms of a quartet of quartets, a(3H) 9.25, a(3H) 8.0 G,

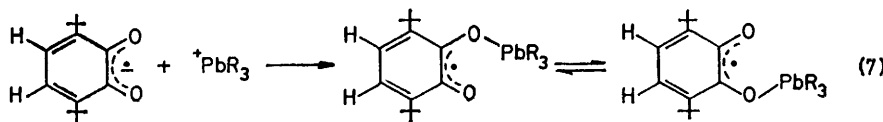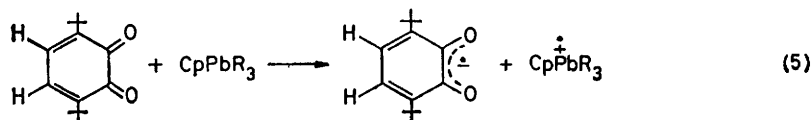g 2.0030. A similar quartet of quartets was observed from the reaction of biacetyl with the radicals CpṠnBu$_2$ [a(3H) 11.2, a(3H) 7.0 G] [3] and ClṠnBu$_2$ [a(3H) 10.6, a(3H) 7.5 G],[2] and it seems likely that all three radicals have the cis-structure (I), in which the electronegative cyclopentadienyl or chloro-ligands reduce the fluxionality of the metallic group.

3,6-Di-t-butyl-1,2-benzoquinone is a useful trap for metallic radicals because the semidione radicals which are formed have simple e.s.r. spectra, and are often persistent. The quinone reacted with cyclopentadienyl-triphenyl-lead without photolysis to show over the range −63 to 0 °C a spectrum consisting of a triplet, a(2H) 3.5, $a(^{207}$Pb) 4.0 G, g 2.0038. At low temperatures, the spectrum showed an alternating line width effect, and at −63 °C the ratio between the amplitude of the central line and the sum of the outer lines was 1 : 1.28 rather than 1 : 1. Under the same conditions, cyclopentadienyltriphenyltin formed a semidione (see Table) which showed a less pronounced alternating line width effect, with, at −63 °C, the ratio 1 : 1.86. In this situation, therefore, the Ph$_3$Pb group is slightly less mobile than the Ph$_3$Sn group.

Cyclopentadienyltrimethyl-lead reacted similarly to show a triplet spectrum.

Dicyclopentadienyldiphenyl-lead reacted with the quinone to show a spectrum consisting at −42 °C of a doublet of doublets, a(H) 2.7, a(H) 4.3, $a(^{207}$Pb) 2.5 G. As the solution was warmed to 64 °C, the proton hyperfine coupling stayed constant, but the central pair of peaks broadened and the hyperfine coupling to lead increased to 3.0 G; above +64 °C, the solution decomposed. The intensity of the spectrum was enhanced by brief photolysis.

Presumably the reactions proceed by electron transfer followed by fragmentation of the organometallic radical cation [equations (5)—(7)]. When R$_3$ = Ph$_3$, the

(5)

(6)

(7)

degenerate exchange of the radical is rapid and hyperfine coupling of the two protons is equivalent on the e.s.r. time scale. The introduction of one cyclopentadienyl ligand (R$_3$ = CpPh$_2$) reduces the mobility of the metallic group, as it does in the adducts with biacetyl (see above), and the two coupling protons appear non-equivalent at all accessible temperatures.
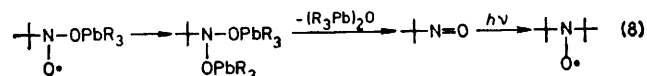
Reactions of Lead Radicals with 2-Methyl-2-nitro-

propane.—Reuter and Neumann [10] have shown that aromatic and aliphatic nitro-compounds can serve as useful traps for metallic radicals, giving persistent nitroxyl radicals, and we have used these compounds for trapping the radicals derived from cyclopentadienyl-tin compounds.[3] Photolysis of a mixture of cyclo-pentadienyltriphenyl-lead and 2-methyl-2-nitropropane in toluene gave a strong spectrum of the t-butyl(tri-phenylplumbyloxy)nitroxyl radical (see Scheme) $a(N)$, 28.75 G, in which the hyperfine coupling to ^{207}Pb showed a strong positive temperature coefficient. Under the

it was heated under reflux for 1.5 h, then cooled and filtered. The filtrate was evaporated yielding dicyclopentadienyl-diphenyl-lead as a yellow solid (Found: C, 53.6; H, 4.1. Calc. for $C_{22}H_{20}Pb$: C, 53.7; H, 4.1%).

Cyclopentadienyltriphenyl-lead.—A similar reaction be-tween cyclopentadienyl-lithium and triphenyl-lead chloride gave a deep yellow solution. Water was added to destroy any remaining butyl-lithium. The product was then extracted into ether, dried ($MgSO_4$), and recrystallised from benzene (Found: C, 54.2; H, 4.0. Calc. for $C_{23}H_{20}Pb$: C, 54.85; H, 3.95%).

Cyclopentadienyltrimethyl-lead.[13]—Cyclopentadienyl-

$$\underset{\underset{O\bullet}{|}}{+}N-OPbR_3 \longrightarrow \underset{\underset{OPbR_3}{|}}{+}N-OPbR_3 \xrightarrow{-(R_3Pb)_2O} +N=O \xrightarrow{h\nu} \underset{\underset{O\bullet}{|}}{+}N+ \quad (8)$$

same conditions, cyclopentadienyltriphenyltin gave the stannyloxynitroxyl radical, $a(N)$ 29.0 G, but the hyper-fine coupling to ^{119}Sn was now independent of temper-ature.

Photolysis of $CpPbMe_3$ or $CpPbEt_3$ in the presence of 2-methyl-2-nitropropane gave the t-butyl(trialkyl-plumbyloxy)nitroxyls: these were less stable than the corresponding triphenyl-lead derivative, decomposing rapidly to the di-t-butylnitroxyl radical, perhaps by the mechanism suggested by Neumann [equation (8)], but over the range −63 to −26 °C the temperature co-

sodium and trimethyl-lead chloride were stirred together in tetrahydrofuran for 90 min at 0 °C. The solvent was removed under reduced pressure and the residue was dis-solved in toluene, δ_H(PhMe) 0.65 [9 H, s, Me_3Pb, $J(^{207}Pb)$ 66 Hz], 6.15 [5 H, s, Cp, $J(^{207}Pb)$ 30 Hz]. Ref. 13 reports δ_H (C_6H_6) 0.60 (J 58 H_H) and 6.07 (J 25 Hz).

Cyclopentadienyltriethyl-lead.[13]—The reaction between cyclopentadienyl-lithium and triethyl-lead chloride gave, after filtration, a yellow solution. Volatile material was removed, under reduced pressure, from the solution which was kept at −20 °C, leaving cyclopentadienyltriethyl-lead as a yellow oil, which was very sensitive to light, heat, and