The Chemistry of (Cyclopentadienyl)phenyl-lead(IV) Compounds

By **Christine Gaffney** and **Philip G. Harrison,*** Department of Chemistry, University of Nottingham, University Park, Nottingham NG7 2RD

The yellow air-stable (cyclopentadienyl)phenyl-lead(IV) compounds, $PbPh_{4-n}(cp)_n$ [n = 1 or 2, cp = C_5H_5], have been synthesised by the reaction of the corresponding phenyl-lead(IV) chloride and lithium cyclopentadienide in diethyl ether. Crystals of $PbPh_3(cp)$ are monoclinic, space group $P2_1/c$, with a = 9.5426, b = 12.3843, c = 16.1714 Å, β = 102.3358°, and Z = 4, and comprise discrete non-interacting molecules with a distorted tetrahedral geometry. The Pb–C(cp) bond distance [2.30(2) Å] is significantly longer than the Pb–C(Ph) distances [mean 2.22(2) Å], indicating a substantial weakening of this bond. The endocyclic C–C bonds of the cyclopentadienyl ring (which is planar) are consistent with a concentration of π-electron density over the carbon atoms remote from the lead. Reaction of $PbPh_3(cp)$ with acetic acid, thiophenol, and imidazole proceeds with exclusive Pb–C(cp) bond cleavage affording $PbPh_3(O_2CMe)$, $PbPh_3(SPh)$, and $PbPh_3(N_2C_3H_3)$, respectively. Only $PbPh_4$ was isolated from the reaction with 4-chlorophenol. The compound $PbPh_2(cp)_2$ decomposes on attempted sublimation at 60—70 °C and 0.01 mmHg giving $Pb(cp)_2$, whilst reaction with hydrogen chloride, carboxylic acids, and imidazole yields the corresponding diphenyl-lead(IV) derivative. Cleavage of all four Pb–C bonds occurs on reaction with thiols, when lead(II) thiolates are the products. Reaction with phenols yields products of composition $[PbPh_2(O_2CMe)]_n$ which presumably contain metal–metal bonds. The mechanisms of the reactions are discussed.

THE chemical, structural, and spectroscopic properties of cyclopentadienyl derivatives of silicon(IV), germanium(IV), and tin(IV) have been widely studied. In contrast, the analogous compounds of lead(IV) have been restricted to one report,[1] which describes the synthesis and spectroscopic characterisation of the methyl- and ethyl-(cyclopentadienyl)lead(IV) derivatives, $PbR_{4-n}(C_5H_4R')_n$ (R = Me or Et; R' = H or Me; n = 1 or 2). These compounds are yellow oils, sensitive to oxygen and moisture, and unstable at ambient or even lower temperatures. In this paper, we describe the preparation and some reactions of the phenyl-lead(IV) analogues, $PbPh_{4-n}(cp)_n$ (n = 1 or 2), and, in addition, the crystal and molecular structure of $PbPh_3(cp)$.

RESULTS

Synthesis and Properties.—Both $PbPh_3(cp)$ and $PbPh_2(cp)_2$ were prepared by the reaction of the appropriate phenyl-lead(IV) chloride with lithium cyclopentadienide in diethyl ether [equation (1)]. Both compounds are yellow solids which

$$PbPh_{4-n}Cl_n + nLi(cp) \longrightarrow PbPh_{4-n}(cp)_n + nLiCl \quad (n = 1 \text{ or } 2) \qquad (1)$$

appear to be reasonably stable in air [*cf.* the alkyl-lead(IV) analogues].[1] The triphenyl-lead derivative melts quite sharply at 89—91 °C but the diphenyl-lead compound darkens slowly above 100 °C and becomes dark brown by 167 °C. Even at room temperature, this material slowly darkens, but may be stored in the dark in the refrigerator for several weeks with only minor decomposition. Both compounds are freely soluble in aprotic organic solvents such as benzene and chloroform; however, such solutions are photosensitive and darken quite rapidly when exposed to light. All reactions were, therefore, carried out in the dark and under an atmosphere of dry argon.

The ^1H n.m.r. spectra of the derivatives exhibited (besides the phenyl-group proton resonances) a single sharp resonance at *ca.* τ 3.8 showing that the cyclopentadienyl group is fluxional, in common with the cyclopentadienyl derivatives of other Group 4 elements. Collapse of the signal could not be achieved by cooling to −60 °C, when serious crystallisation problems were encountered.

The Crystal and Molecular Structure of (*Cyclopentadienyl*)-*triphenyl-lead*(IV).—Crystals of $PbPh_3(cp)$ comprise discrete non-interacting molecules with a distorted tetrahedral geometry at lead (Figure 1), the valence angles varying between 101.6(9) and 113.4(9)°. The Pb–C bond distances to the phenyl groups [mean 2.22(2) Å] are close to those found in $PbPh_4$ [2.19(3) Å], but Pb–C to the cyclopentadienyl group is substantially longer [2.30(2) Å], indicating a substantial weakening of this bond. The cyclopentadienyl group is planar (Table 1), and bent over towards the lead atom [Pb(1)–C(19)–C(20/21) 104(1)°].

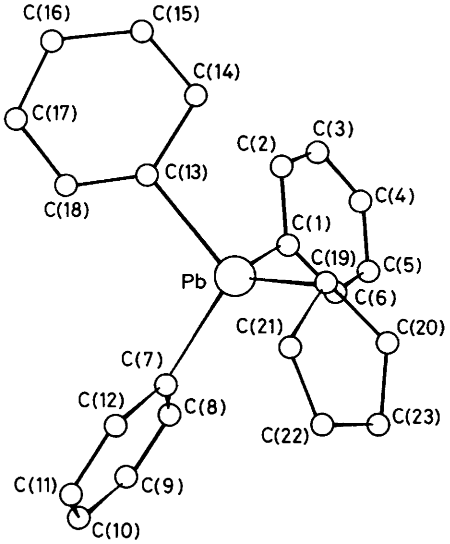
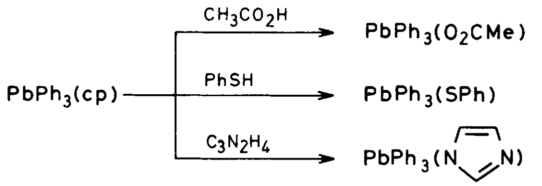


FIGURE 1 The molecular structure of $PbPh_3(cp)$ showing the atomic numbering

Interestingly, the bond distances within the cyclopentadienyl ring differ (Figure 2). Those involving the carbon atom bonded directly to lead are substantially longer [1.47(3) and 1.51(4) Å] and are characteristic single-bond distances, whereas the other three endocyclic bond distances have values typically found in aromatic compounds.

Reactions of (Cyclopentadienyl)triphenyl-lead(IV).—(Cyclopentadienyl)triphenyl-lead(IV) reacts smoothly with acetic acid, thiophenol, and imidazole in benzene according to equation (2). The reaction of 4-chlorophenol with $PbPh_3(cp)$ in benzene yields, after the usual work-up procedure, only tetraphenyl-lead, presumably *via* disproportionation of the (aryloxo)triphenyl-lead(IV) intermediate [equation (3)].



(2)

TABLE 1

Perpendicular distances (Å) of the carbon atoms in the cyclopentadienyl group from the mean plane

Atom	Distance
C(19)	0.048(4)
C(20)	−0.084(6)
C(21)	0.023(2)
C(22)	0.021(2)
C(23)	−0.009(2)

$$\mathrm{PbPh_3(cp)} + 4\text{-}\mathrm{ClC_6H_4OH} \longrightarrow \mathrm{PbPh_3(OC_6H_4Cl\text{-}4)} \longrightarrow \mathrm{PbPh_4} \quad (3)$$

Reactions of Bis(cyclopentadienyl)diphenyl-lead(IV).—Since $PbPh_2(cp)_2$ is photosensitive, particularly in solution when an unidentified brown solid is eventually deposited, all reactions of this compound were carried out with the rigorous exclusion of light.

Attempted sublimation of $PbPh_2(cp)_2$ at 60—70 °C at 0.01 mmHg * yields bis(cyclopentadienyl)lead(II), identified by comparison of its i.r. spectrum with that of an authentic sample [obtained from the reaction of anhydrous lead(II) acetate with lithium cyclopentadienide in tetrahydrofuran]. Exposure of a benzene solution of the compound to air yields diphenyl-lead oxide, due to hydrolytic cleavage of the cyclopentadienyl groups from lead. Similar protolytic cleavage of the cyclopentadienyl groups also occurs with hydrogen chloride, carboxylic acids, and imidazole at room temperature affording the corresponding diphenyl-lead(IV) derivative in quantitative yield. That the reaction with (undried) glacial acetic acid produces diphenyl-lead(IV) diacetate as a binuclear molecule solvated by both water and benzene was corroborated by an *X*-ray diffraction study.[2]

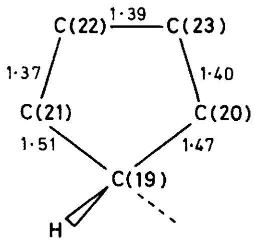
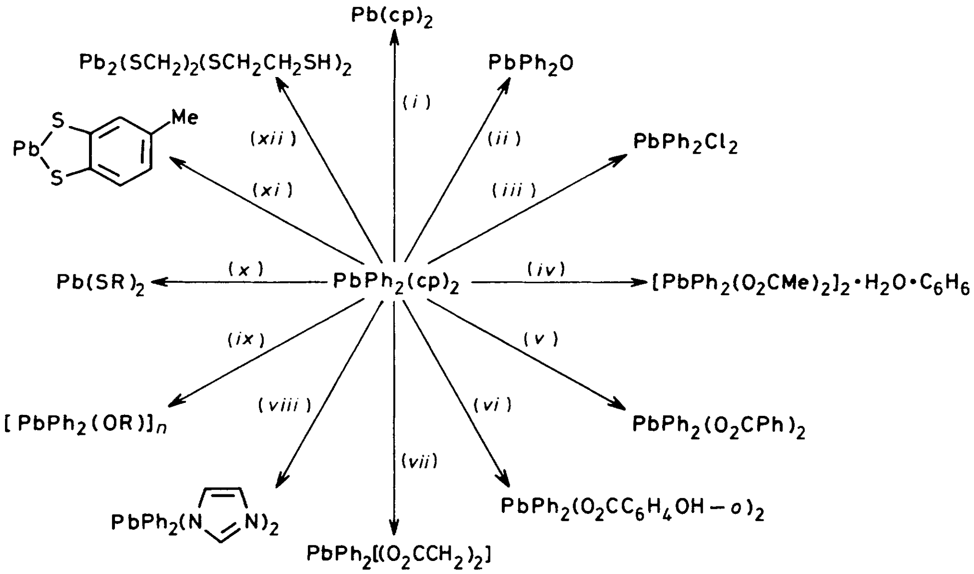


FIGURE 2 Endocyclic carbon–carbon bond distance (Å) data for the cyclopentadienyl ring



SCHEME Reactions of bis(cyclopentadienyl)diphenyl lead (IV)

(*i*) Heat; (*ii*) moist air; (*iii*) hydrogen chloride; (*iv*) glacial $MeCO_2H$, (*v*) $PhCO_2H$; (*vi*) salicylic acid; (*vii*) succinic acid; (*viii*) imidazole; (*ix*) ROH (R = Ph, C_6H_4Cl-4, or C_6H_4Me-4); (*x*) RSH (R = Ph or $PhCH_2$); (*xi*) toluene-3,4-dithiol; (*xii*) $HSCH_2CH_2SH$

Reaction with phenols in benzene at room temperature over 24—48 h gave amorphous solid products of composition $[PbPh_2(OR)]_n$ (R = Ph, C_6H_4Cl-4, or C_6H_4Me-4), which could not be redissolved or recrystallised without decomposition. Reaction with thiols under similar conditions produces, rather surprisingly, lead(II) thiolates.

Reactions of $PbPh_2(cp)_2$ are summarised in the Scheme.

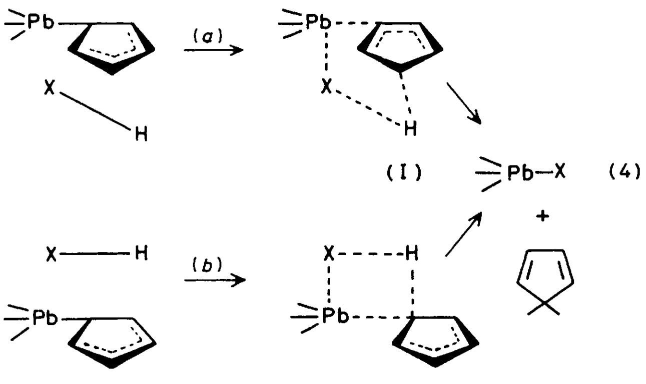
DISCUSSION

The structural data for (cyclopentadienyl)triphenyl-lead(IV) offer some rationalisation for the observed

---

* Throughout this paper: 1 mmHg ≈ 13.6 × 9.8 Pa.

increased reactivity of the Pb–C(cp) bond over that of Pb–C bonds involving alkyl, aryl, or alkenyl groups. First, the increased bond distance, the longest Pb–C distance yet recorded, is indicative of a substantially weaker bond, which will facilitate both homolytic and heterolytic fission. Secondly, examination of the endocyclic C–C bond distances of the cyclopentadienyl ring indicates a concentration of π-electron density at the carbon atoms more remote from the lead atom. These atoms, therefore, might be expected to be the preferred sites for electrophilic substitution. In the light of these observations, we propose a mechanism for the protolytic cleavage of cyclopentadienyl groups from lead involving protonation of the ring at one of the carbon atoms most remote from lead and a transition state such as (I) [equation 4(*a*)], rather than a simple four-centre process involving the carbon atom bonded directly to lead, (II) [equation 4(*b*)].

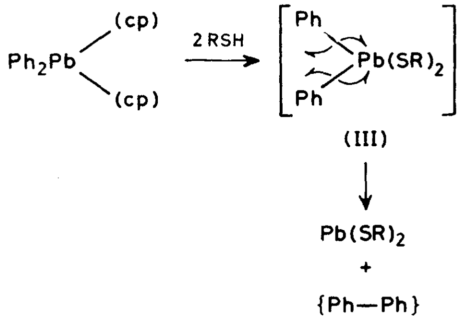


(I)

(II)

The reactions of $PbPh_2(cp)_2$ with hydrogen chloride, carboxylic acids, and imidazole proceed with exclusive cleavage of both cyclopentadienyl groups and the formation of the corresponding diphenyl-lead(IV) derivatives, which are thermally quite stable. Reactions involving thiols and phenols, however, yield unexpected products and, therefore, require further discussion. With the former, the only lead-containing products isolated were the lead(II) thiolates, and no evidence for organolead(IV) thiolates was apparent. In this case, therefore, we propose that, by analogy of the reaction of (cyclopentadienyl)triphenyl-lead(IV) with thiophenol, the initial products of the reaction are the diphenyl-lead(IV) bis(thiolates) (III), which subsequently rapidly decompose by a concerted reductive-elimination step with loss of both phenyl groups [equation (5); RSH = PhSH, $PhCH_2SH$, or ½(toluene-3,4-dithiol.)

Although diorganolead(IV) bis(thiolates) are notoriously difficult to prepare, diphenyl-lead(IV) bis(benzenethiolate) has been isolated and is quite stable in the solid state. However, it decomposes in boiling benzene–ethanol over 8 h to yield $PbPh_3(SPh)$, $Pb(SPh)_2$, and PhSSPh.[3] Examples of this mode of thermal decomposition are not uncommon in the literature; dimethyllead(IV) dihalides[4] and diethyl-lead(IV) dicarboxylates[5,6] and dinitrate[7] follow the same pathway, which is considered to proceed *via* an initial bimolecular disproportionation reaction followed by a unimolecular reductive elimination from the unstable mono-organolead(IV) derivative [equation (6); R = alkyl, X = halogen or NO_3].

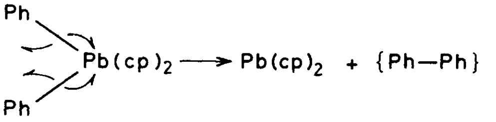


(5)

$$2\,PbR_2X_2 \longrightarrow PbR_3X + \{PbRX_3\} \longrightarrow PbX_2 + RX \quad (6)$$

In the present case, the reaction of $PbPh_2(cp)_2$ with thiols does not afford mixtures of products arising from the decomposition of the intermediate diphenyl-lead(IV) bis(thiolates) (III) along this route. This suggests that they are formed in some excited state from which the unimolecular elimination of the two organic groups [equation (5)] is more facile.

An identical reductive-elimination mechanism can also be proposed for the thermolysis of $PbPh_2(cp)_2$, where bis(cyclopentadienyl)lead(II) was the only lead-containing product isolated [equation (7)]. The organic product, presumed to be biphenyl, was not characterised. An alternative mechanistic pathway would be the stepwise loss of phenyl radicals *via* the lead-centred radical (IV) [equation (8)], although in the present case there are insufficient data for an unequivocal choice.



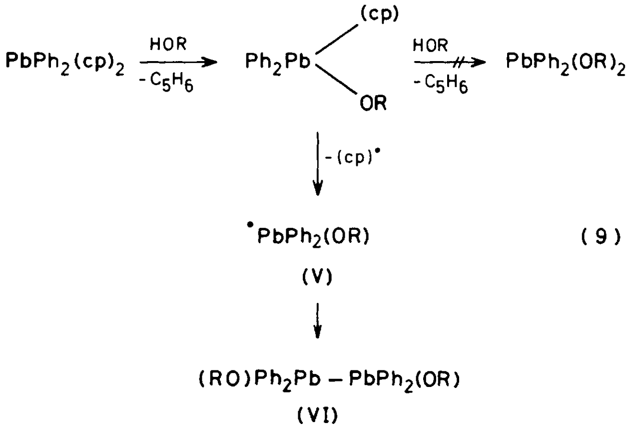
$$Ph_2Pb(cp)_2 \longrightarrow Pb(cp)_2 + \{Ph{-}Ph\} \quad (7)$$

$$\underset{}{PbPh_2(cp)_2} \xrightarrow{-Ph^{\bullet}} \underset{(IV)}{{}^{\bullet}PbPh(cp)_2} \xrightarrow{-Ph^{\bullet}} Pb(cp)_2 \quad (8)$$

Phenyl radicals are involved in the thermal decomposition of $PbPh_4$, where the major product of the decomposition *in vacuo* at 300 °C is biphenyl, but become benzene when the decomposition is carried out in the presence of a hydrogen-atom donor, such as ethylene glycol or diethylamine.[8] The dimethyl- and diethyl-bis(cyclopentadienyl)lead(IV) homologues $PbR_2(C_5H_4R')_2$ (R = Me or Et, R′ = H or Me) are much less stable, and decompose in a similar fashion even at low temperatures to afford the corresponding bis(cyclopentadienyl)lead(II) derivatives, $Pb(C_5H_4R')_2$.[1] It is interesting here to note the contrasting course of reaction in the photolysis of $PbPh_2$-

$(cp)_2$. Thermolysis appears to proceed with rupture of the Pb–C(Ph) bonds only, whilst on photolysis exclusive homolytic Pb–C(cp) bond fission occurs.*

Protolytic cleavage of one cyclopentadienyl group from lead is also considered to be the initial step of the reaction of $PbPh_2(cp)_2$ with phenols. Since the products isolated contain only one aryloxy-group bound to lead, it seems clear that protolysis of the second cyclopentadienyl group does not take place. Rather, it would appear that protolytic cleavage of the second group is too slow,† and homolysis of the second Pb–C(cp) bond occurs generating the aryloxy-substituted lead-centred radicals (V), which can subsequently associate to afford the 1,2-bis(aryloxo)-1,1,2,2-tetraphenyldiplumbane derivatives (VI) isolated [equation (9); R = Ph, C_6H_4Me-4, or C_6H_4Cl-4]. The only other examples of functionally substituted diplumbanes appear to be the tris(acetato)-triaryldiplumbanes, $Pb_2R_3(O_2CMe)_3$ (R = Ph or *p*-tolyl), obtained by cleavage of Pb_2Ph_6 by acetic acid–acetic anhydride, for which an unsymmetrical structure was favoured. The corresponding 1-acetato- and 1,2-bis(acetato)-diplumbanes have been proposed as unstable intermediates in the cleavage of Pb_2Ph_6 by acetic acid in dioxan.[9] Insolubility of the 1,2-bis(aryloxo)diplumbanes obtained in the present case precluded molecular-weight measurements and attempted recrystallisation yielded only $PbPh_4$, hence the structural identity of these derivatives is unknown. However, it would seem likely from their physical properties that they are associated, with the aryloxy-groups functioning as bridging ligands.



(9)

EXPERIMENTAL

All manipulations were carried out under an atmosphere of rigorously dried oxygen-free argon and in the dark. All solvents were also rigorously dried by standard methods and redistilled prior to use. Glacial acetic acid was not dried.

Preparation of (Cyclopentadienyl)triphenyl-lead(IV) *and Bis(cyclopentadienyl)diphenyl-lead*(IV).—Freshly distilled cyclopentadiene (0.42 g, 6.3 mmol) in dry diethyl ether (25 cm^3) was added to a solution of butyl-lithium (6.4 mmol, 1 mol dm^{-3}) in hexane at −78 °C. White lithium cyclopentadienide precipitated out immediately. Solid triphenyl-lead chloride (6.3 mmol) was added and the reaction mixture allowed to warm to room temperature. After 2 h, the reaction mixture was deep yellow. Ice was added to destroy any unreacted butyl-lithium, and the product extracted with diethyl ether. After drying the ethereal solution with magnesium sulphate, the ether was removed *in vacuo* affording *(cyclopentadienyl)triphenyl-lead*(IV) as a yellow solid, which was recrystallised from benzene (Found: C, 54.2; H, 4.00; Cl, 0. Calc. for $C_{23}H_{20}Pb$: C, 54.85; H, 3.95%).

The preparation of *bis(cyclopentadienyl)diphenyl-lead*(IV) was similar, except that the reaction mixture was refluxed for 1.5 h before work-up, and the final product was not recrystallised (Found: C, 53.6; H, 4.10. Calc. for $C_{22}H_{20}Pb$: C, 53.7; H, 4.20%).

Reactions of (Cyclopentadienyl)triphenyl-lead(IV) *and Bis(cyclopentadienyl)diphenyl-lead*(IV).—Experimental and analytical details for these reactions are summarised in Tables 2 and 3, respectively.

TABLE 2

Experimental details of the reactions of (cyclopentadienyl)-triphenyl-lead(IV)

			Microanalysis data (%) [b]		
Reagent [a]	Product	M.p. (°C)	C	H	N
PhSH	$PbPh_3(SH)$	98—99 [c]	52.8 (52.65)	3.70 (3.65)	
$MeCO_2H$	$PbPh_3(O_2CMe)$	192—193 [d]	48.9 (48.25)	3.65 (3.60)	
Imidazole	$PbPh_3(N_2C_3H_3)$	273 (decomp.) [e]	49.95 (49.9)	3.60 (3.55)	5.00 (5.55)
$4-ClC_6H_4OH$	$PbPh_4$	213—216 [f]	55.9 (55.9)	4.10 (3.80)	

[a] Conditions for all reactions are benzene, room temperature, and 18 h. [b] Calculated values in parentheses. [c] Lit.,[9] 106.7 °C. [d] Lit.,[9] 204.6 °C. [e] Lit.,[9] 283 °C (decomp). [f] Lit.,[9] 223—225 °C.

Crystal Structure of (Cyclopentadienyl)triphenyl-lead(IV).—A crystalline sample of $PbPh_3(cp)$ was obtained on recrystallisation from a cold benzene solution in the dark. A suitable crystal (0.4 × 0.3 × 0.3 mm) was loaded into a Lindemann tube and used for the initial photography and to collect the intensity data.

Crystal data. $C_{23}H_{20}Pb$, $M = 503.42$, Monoclinic, space group $P2_1/c$ with $a = 9.5426$, $b = 12.3843$, $c = 16.1714$ Å, $\beta = 102.3358°$, $U = 1\,867.0$ Å^3, $Z = 4$, $D_c = 1.790$ g cm^{-3}, $F(000) = 960$, $\mu = 88.88$ cm^{-1}, and $\lambda(\text{Mo-}K_\alpha) = 0.7107$ Å.

Structure determination and refinement was carried out by the usual Patterson and Fourier techniques using the intensity data of 2 331 independent reflections with $I > 3\sigma I$ collected on a Hilger and Watts four-circle diffractometer employing Mo-K_α radiation. Corrections were applied for Lorentz and polarisation effects, but not for absorption. Data reduction and subsequent calculations were performed using the CRYSTALS programs,[10] and the molecular structures were drawn using the PLUTO programs.[11] The atomic scattering factors used were those for neutral atoms.[12] The final *R* value was 0.0864.

Final fractional atomic co-ordinates are listed in Table 4,

---

* Reactions involving homolytic fission of the Pb–C(cp) bond will be reported in a separate paper.

† Some support for this hypothesis is available from tin chemistry, where the stability of the Sn–(cp) bond towards cleavage by carboxylic acids increases in the order $SnR_3(cp) > SnR_2(cp)_2 > SnR(cp)_3 > Sn(cp)_4$ (see N. D. Kolosova, N. N. Zemlyanski, Y. A. Ustynyuk, and K. A. Kocheskov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1976, 625).

TABLE 3

Experimental details for the reactions of bis(cyclopentadienyl)diphenyl-lead

Reagent	Molar ratio [a]	Reaction conditions	Product	M.p. (°C)	Microanalysis data [b] (%) C	H	N,Cl,S
Thermolysis		60—70 °C, 10^{-2} mmHg	$Pb(cp)_2$				
Moist air		benzene, r.t.	$PbPh_2O$				
HCl gas		benzene, r.t.	$PbPh_2Cl_2$	273 (decomp.)	32.3 (33.3)	2.4 (2.3)	
Glacial $MeCO_2H$	1 : 2	benzene, r.t., 48 h	$PbPh_2(O_2CMe)_2$ [c]	204—206 [d]	43.3 (43.3)	3.7 (3.8)	
o-$(HO)(HO_2C)C_6H_4$	1 : 2	benzene, r.t., 8 h	$PbPh_2(O_2CC_6H_4$-o$)_2$	150 (decomp.)	49.2 (49.1)	3.0 (3.1)	
$PhCO_2H$	1 : 2	benzene, r.t., 24 h	$PbPh_2(O_2CPh)_2$	200 (decomp.)	52.1 (51.7)	3.1 (3.3)	
$(HO_2CCH_2)_2$	1 : 1	benzene, r.t.	$PbPh_2[(O_2CCH_2)_2]$	200 (decomp.)	42.9 (40.3)	3.4 (2.9)	
Imidazole	1 : 2	diethyl ether + benzene, r.t.	$PbPh_2(N_2C_3H_3)_2$	274—275 (decomp.)	44.5 (43.6)	2.9 (3.2)	10.2 (11.3)
PhOH	1 : 2	benzene, r.t., 24 h	$\{PbPh_2(OPh)\}_2$	220 [e] (decomp.)	47.8 (47.6)	3.2 (3.3)	
$4-MeC_6H_4OH$	1 : 2	benzene, r.t., 48 h	$\{PbPh_2(OC_6H_4Me-4)\}_2$	222 [e] (decomp.)	47.9 (48.7)	3.6 (3.6)	
$4-ClC_6H_4OH$	1 : 2	benzene, r.t., 48 h	$\{PbPh_2(OC_6H_4Cl-4)\}_2$	228 [e] (decomp.)	43.9 (44.2)	2.8 (2.9)	7.2 (7.3)
PhSH	1 : 2	benzene, r.t., 48 h	$Pb(SPh)_2$	194—196 [f]	33.3 (33.9)	2.4 (2.4)	12.0 (15.1) [g]
$PhCH_2SH$	1 : 2	benzene, r.t., 48 h	$Pb(SCH_2Ph)_2$	>200 (decomp.)	17.2 (18.5)	1.4 (1.5)	
Toluene-3,4-dithiol	1 : 1	benzene, r.t., 18 h	$Pb(S_2C_6H_3Me)$	301—304 (decomp.)	23.4 (23.3)	1.7 (1.7)	12.6 (17.7) [g]
$HSCH_2CH_2SH$	1 : 1	benzene, r.t., 18 h	$Pb_2(SCH_2)_2(SCH_2CH_2SH)_2$ [h]	>155 (decomp.)	10.3 (10.1)	2.1 (2.4)	20.2 (27.0) [g]

[a] Ratio $PbPh_2(cp)_2$: reagent. [b] Calculated values in parentheses. [c] As the hemihydrate hemi(benzene) solvate (from X-ray crystallographic studies).[2] The water presumably arises from the glacial acetic acid. [d] Lit. values: 286.6 °C (decomp.) ($PbPh_2Cl_2$) and 200—201 °C [anhydrous $PbPh_2(O_2CCH_3)_2$] from L. C. Willemsens and G. J. M. Van der Kerk, ' Investigations in the Field of Organolead Chemistry,' Schotanus and Jens, Utrecht, 1965. [e] *Decomposition with effervescence to leave an orange-brown oil.* [f] Lit.: 195—196 °C from R. A. Shaw and M. Woods, *J. Chem. Soc. A*, 1971, 1569. [g] Sulphur analyses were invariably low, as also found by Shaw and Woods (see footnote *f*). [h] Calc. for $Pb(SCH_2CH_2S)$: C, 8.0; H, 1.3; S, 21.4. Calc. for $Pb(SCH_2CH_2SH)_2$: C, 12.2; H, 2.5; S, 32.5%.

TABLE 4

Final fractional atomic co-ordinates of (cyclopentadienyl)triphenyl-lead

Atom	X/a	Y/b	Z/c
Pb(1)	0.265 85(8)	−0.009 83(5)	0.116 06(5)
C(1)	0.761(3)	0.350(2)	0.473(2)
C(2)	0.775(3)	0.131(2)	0.059(1)
C(3)	0.790(3)	0.221(2)	0.113(1)
C(4)	0.788(3)	0.324(2)	0.082(2)
C(5)	0.770(2)	0.340(2)	−0.008(2)
C(6)	0.757(3)	0.248(1)	0.441(2)
C(7)	0.894(2)	0.479(1)	0.305(1)
C(8)	−0.007(2)	0.395(2)	0.321(1)
C(9)	0.106(3)	0.392(2)	0.276(2)
C(10)	0.121(3)	0.469(2)	0.222(2)
C(11)	−0.016(3)	0.056(2)	0.299(2)
C(12)	0.094(2)	0.061(2)	0.253(1)
C(13)	0.262(2)	0.148(1)	0.049(1)
C(14)	0.159(2)	0.223(2)	0.054(1)
C(15)	0.164(3)	0.177(2)	0.511(2)
C(16)	0.262(3)	0.156(2)	0.469(1)
C(17)	0.373(3)	0.235(2)	0.464(1)
C(18)	0.371(3)	0.166(2)	0.003(1)
C(19)	0.501(2)	0.484(2)	0.308(2)
C(20)	0.487(2)	0.375(2)	0.271(1)
C(21)	0.497(3)	0.051(2)	0.270(2)
C(22)	0.500(3)	0.486(2)	0.161(2)
C(23)	0.497(3)	0.379(2)	0.186(2)

TABLE 5

Intramolecular bond distances (Å) and angles (°) for (cyclopentadienyl)triphenyl-lead with estimated standard deviations in parentheses

(*a*) Bond distances

Pb(1)–C(1)	2.23(2)	C(19)–C(20)	1.47(3)
Pb(1)–C(7)	2.20(2)	C(19)–C(21)	1.51(4)
Pb(1)–C(13)	$2.22_5(2)$	C(20)–C(23)	1.40(3)
Pb(1)–C(19)	2.30(2)	C(21)–C(22)	1.37(4)
		C(22)–C(23)	1.39(4)

Phenyl ring 1 [C(1)—C(6)] 1.36(3)—1.44(4)
Phenyl ring 2 [C(7)—C(12)] 1.32(4)—1.46(4)
Phenyl ring 3 [C(13)—C(18)] 1.30(3)—1.46(4)

(*b*) Bond angles *

C(1)–Pb(1)–C(7)	109.3(9)	Pb(1)–C(13)–C(14)	$120_5(1)$
C(1)–Pb(1)–C(13)	112.3(9)	Pb(1)–C(13)–C(18)	177(1)
C(1)–Pb(1)–C(19)	106.6(9)	Pb(1)–C(19)–C(20)	104(1)
C(7)–Pb(1)–C(13)	113.3(6)	Pb(1)–C(19)–C(21)	104(1)
C(7)–Pb(1)–C(19)	113.4(9)	C(20)–C(19)–C(21)	101(2)
C(13)–Pb(1)–C(19)	101.6(7)	C(19)–C(20)–C(23)	110(2)
Pb(1)–C(1)–C(2)	119(2)	C(19)–C(21)–C(22)	111(2)
Pb(1)–C(1)–C(6)	119(2)	C(21)–C(22)–C(23)	109(2)
Pb(1)–C(7)–C(8)	117(2)	C(20)–C(23)–C(22)	110(2)
Pb(1)–C(7)–C(12)	$120_5(1)$		

* Internal angles of the three phenyl rings all lie in range 118(2)—122(2)°.

intramolecular bond distances and angles are collected in Table 5, and the atomic numbering is shown in Figure 1.

The final anisotropic thermal parameters and observed and calculated structure factors are available as Supplementary Publication No. SUP 23262 (25 pp.).*

---

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

We thank the S.R.C. for a Research Studentship (to (C. G.), the Esso Petroleum Company Ltd. for financial assistance, and Professor T. J. King for collecting the intensity data.

[1/1638 *Received*, 22nd *October*, 1981]

REFERENCES

[1] H. P. Fritz and K. E. Schwarzhaus, *Chem. Ber.*, 1964, **97**, 1390.

[2] C. Gaffney, P. G. Harrison, and T. J. King, following paper.

[3] W. E. Davidsohn, K. Hills, and M. C. Henry, *J. Organomet. Chem.*, 1965, **3**, 285.

[4] H. J. Haupt, F. Huber, and J. Gmehling, *Z. Anorg. Allg. Chem.*, 1972, **390**, 31.

[5] B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 1949, 919.

[6] R. Heap, B. C. Saunders, and G. J. Stacey, *J. Chem. Soc.*, 1951, 658.

[7] D. Potts and A. Walker, *Can. J. Chem.*, 1969, **47**, 1621.

[8] K. G. Kochetikhina, G. A. Domrachev, and G. A. Razuvaev, *Zh. Obshch. Khim.*, 1969, **39**, 2048.

[9] V. G. K. Das and P. R. Wells, *J. Organomet. Chem.*, 1970, **23**, 143.

[10] J. R. Carruthers, The Oxford Crystallographic Package CRYSTALS.

[11] W. D. S. Motherwell, ORTEP Program for Plotting Molecular and Crystal Structures, Cambridge, 1977.

[12] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974, vol. 4.