Organolead Chemistry. Part IV.[1] Cleavage Reactions of Bis(η-cyclopentadienyl)lead(II) and the Preparation of η-Cyclopentadienyl-lead(II) Halides

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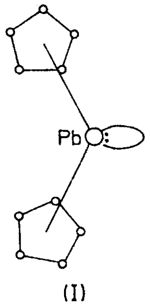
Bis(η-cyclopentadienyl)lead(II) reacts with HX to give $Pb(\eta\text{-}C_5H_5)X$ when X = Cl, Br, I, or $MeCO_2$ and PbX_2 when X = Bu^tCO_2, RCOCHCOR(R = Me, CF_3, or Bu^t), and RO (R = Me or Bu^t), with iodine and methyl iodide to give $Pb(\eta\text{-}C_5H_5)I$, and with acetyl chloride to give $Pb(\eta\text{-}C_5H_5)Cl$. The compounds $Pb(\eta\text{-}C_5H_5)X$ are thought to have polymeric structures with bridging X groups.

BIS(η-CYCLOPENTADIENYL)LEAD(II) was first prepared by Fischer and his co-workers, who found it to be a yellow solid which could be purified by vacuum sublimation.[2-5] From its high dipole moment[4,6,7] and by analysis of its infrared spectrum,[6,8-10] the bent-sandwich structure, (I), for the compound was soon proposed. This structure was confirmed for the compound in the gas phase by an electron-diffraction study,[11] but in the solid state a different structure was found by *X*-ray diffraction studies.[12,13] Here, each lead atom is bound to one terminal η-C_5H_5 group and to two bridging η-C_5H_5 groups, giving rise to a polymeric chain structure in which each lead atom has trigonal-planar co-ordination. Solutions of $Pb(\eta\text{-}C_5H_5)_2$ in diethyl ether or tetrahydrofuran were found to behave as 1 : 1 electrolytes, suggesting that ionisation to $[Pb(\eta\text{-}C_5H_5)]^+$ and $C_5H_5^-$ occurs.[14]



(I)

Although there has been considerable interest in the structure and spectroscopic properties[15] of $Pb(\eta\text{-}C_5H_5)_2$, until our preliminary communication was published[16] none of the chemical properties of the compound had been investigated except for reports that it was air and water sensitive.[6] In contrast the chemistry of $Sn(\eta\text{-}C_5H_5)_2$ has been very closely studied in recent years;[17] thus it can act as a Lewis base using the lone pair of electrons on Sn^{II},[18-20] it will undergo oxidative-addition reactions,[21-23] and cleavage of the cyclopentadienyltin bonds can give a wide range of tin(II) compounds.[24-27] We now report in detail some of our investigations on the chemical properties of $Pb(\eta\text{-}C_5H_5)_2$ and compare them with those of the analogous $Sn(\eta\text{-}C_5H_5)_2$ where relevant.

RESULTS AND DISCUSSION

Solutions of $Pb(\eta\text{-}C_5H_5)_2$ in benzene reacted rapidly with dry oxygen and with water, yielding in each case lead(II) oxide, so that stringent precautions were taken to exclude both oxygen and water in all experiments.

Reactions with Hydrogen Halides.—Reactions of $Pb(\eta\text{-}C_5H_5)_2$ in benzene or diethyl ether solution with an equimolar quantity of anhydrous HX (X = Cl, Br, or I) led to precipitation of the corresponding compound $Pb(C_5H_5)X$. The compounds are white (X = Cl or Br) or pale yellow solids (X = I); they possess high thermal stability, decomposing without melting in the range 330—360 °C, and are insoluble in most common

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organic solvents. They decompose considerably more slowly than the parent $Pb(\eta\text{-}C_5H_5)_2$ in moist air.

The low solubility made full characterisation of the compounds difficult, but the cyclopentadienyl group was easily shown to be in the $\eta\text{-}C_5H_5$ bonded form by the characteristic i.r. spectra (Table 1). Thus each compound gave only one C–H stretching band in the 3 000—3 100 cm^{-1} region and only a single C–H stretching overtone at *ca.* 6 000 cm^{-1}, typical of compounds with $\eta\text{-}C_5H_5$ groups; $\sigma\text{-}C_5H_5$ groups give more complex bands in both regions.[28-31] The chief peaks in the mass spectra of the compounds $Pb(\eta\text{-}C_5H_5)X$ are given in Table 2 together with the relative abundances. Only $Pb(\eta\text{-}C_5H_5)Br$ gave a parent ion in the mass spectrum, and for this compound there was also evidence that disproportionation to $Pb(\eta\text{-}C_5H_5)_2$ and $PbBr_2$ took place in the mass spectrometer. All the compounds gave major peaks corresponding to the ions $[Pb(C_5H_5)]^+$ and Pb^+.

TABLE 1

Infrared spectra (650—4 000 cm^{-1}) of the compounds $Pb(\eta\text{-}C_5H_5)X$ *

Cl	Br	I	$MeCO_2$
3 580vw	3 584vw	3 584vw	3 580w
3 040s	3 045m	3 050m	
2 960s	2 959m	2 930m	
2 920s (sh)	2 910m		
			1 520vs
			1 455vs
			1 400s
			1 384s
			1 370s
			1 333s
1 257m	1 255m	1 259s	1 255m
1 085m	1 100m	1 100m	1 040w
			1 012m
			1 002m
			930m
788m	790s	795m	
746s	742s	775s	762vs
735m		720m	670s
			662s

* Recorded as Nujol or Hostaflon mulls.

TABLE 2

Mass spectra of $Pb(\eta\text{-}C_5H_5)_2$ and $Pb(\eta\text{-}C_5H_5)X$ *

Fragment	$Pb(\eta\text{-}C_5H_5)_2$	$Pb(\eta\text{-}C_5H_5)Cl$	$Pb(\eta\text{-}C_5H_5)Br$	$Pb(\eta\text{-}C_5H_5)I$
PbX_2		0	4	0
$Pb(C_5H_5)X$		0	2.3	0
$Pb(C_{10}H_{10})$	1.6	1	64	
PbX		64	0.0	1.5
$Pb(C_5H_5)$	100.0	100	64.0	12
Pb	36.6	62	39	5
HX		2.8	33.04	0.7
X		19.6	51.30	0.0
C_6H_7	29.6	0.0	0.0	0.0
C_6H_6	29.6	17.4	0.0	0.0
C_6H_5	5.6	17.6	0.0	0.0
C_5H_7	2.0	12.9	13.91	4.8
C_5H_6	29.0	14.2	56.2	100.0
C_5H_5X		0.0	100.0	1.0
C_5H_5	13.5	14.3	16.5	41.7
C_5H_4	0.0	17.7	16.5	0.0
C_5H_3X		11.1	55.6	0.0
C_4H_5	0.0	0.0	47.8	0.0
C_3H_4	7.2	10.2	0.0	17.3
C_3H_3	11.2	10.2	0.0	22.9
C_2H_4	40.5			
C_2H_3	72.5			
C_2H_2	8.9			

* Relative abundances of the fragments given are total values corrected for natural abundancies of lead, chlorine, and bromine.

The physical properties of the compounds are quite different from those of the corresponding tin compounds, which have been shown to be monomeric with the angular structure (II).[32] Thus $Sn(\eta\text{-}C_5H_5)Cl$ melts at 130—133 °C while $Pb(\eta\text{-}C_5H_5)Cl$ decomposes without melting at 330 °C. The high melting point and low solubility suggest that the compounds have a polymeric structure with bridging halide groups as shown in structure (III). The only solvent we have found to dissolve these compounds is dimethyl sulphoxide (dmso), which may break down the polymeric structure by co-ordinating to lead. The ^1H n.m.r. spectra in $[^2H_6]$dmso contained a singlet for the C_5H_5 protons for each compound, with no coupling to ^{207}Pb being observed. This suggests that rapid exchange of cyclopentadienyl groups occurs in solution. The chemical shift of the C_5H_5 protons was dependent on the halogen so that ionisation to $[Pb(\eta\text{-}C_5H_5)]^+$ and X^- apparently does not occur and a pyramidal structure (IV) is likely in solution.

A similar exchange process to the above also took place in solutions of $Pb(\eta\text{-}C_5H_5)_2$ where no coupling of ^{207}Pb to the C_5H_5 protons was observed in the ^1H n.m.r. spectrum at temperatures as low as −70 °C in $[^2H_8]$-toluene (below this temperature the compound was

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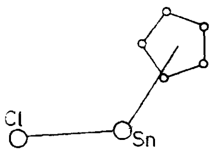
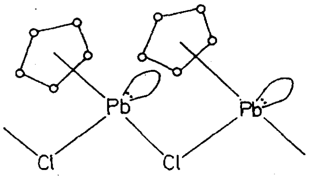
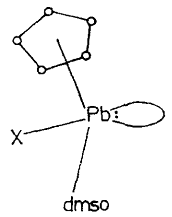
insufficiently soluble to allow the n.m.r. spectrum to be recorded), although coupling of ^{119}Sn to the C_5H_5 protons of $Sn(\eta\text{-}C_5H_5)_2$ is observed at room temperature.[17,18] We also recorded the ^{13}C n.m.r. spectrum of $Pb(\eta\text{-}C_5H_5)_2$ in $CDCl_3$ solution [$\delta(C_5H_5)$ 81.6 p.p.m. upfield from CS_2, $^1J(^{13}CH)$ 167.0 Hz] and similarly find no $^1J(^{207}Pb^{13}C)$ coupling. Thus the exchange process, which could occur by ionisation to $[Pb(\eta\text{-}C_5H_5)]^+$ and $C_5H_5^-$ or through an intermediate with bridging η-C_5H_5 groups such as is found in the structure of solid $Pb(\eta\text{-}C_5H_5)_2$, takes place considerably faster in the lead compounds than in the tin analogues. It is also worth noting that the ^{13}C data are exceptional to the rule that η-C_5H_5 groups have ^{13}C chemical shifts in the region above 100 p.p.m. to high field of CS_2 and with $^1J(^{13}CH)$ in the 175—180 Hz region. This rule, which has been suggested as a means of distinguishing between η-C_5H_5 and σ-C_5H_5 groups,[33] should therefore be used with caution.



(II)



(III)



(IV)

Reaction of $Pb(\eta\text{-}C_5H_5)_2$ with excess of hydrogen halide in diethyl ether or benzene solution caused cleavage of both cyclopentadienyl groups and gave the corresponding lead(II) halide in quantitative yield.

Reactions with Other Protic Reagents.—Equimolar quantities of acetic acid and $Pb(\eta\text{-}C_5H_5)_2$ in diethyl ether reacted to give $Pb(\eta\text{-}C_5H_5)(O_2CMe)$ as a sparingly-soluble white solid. The cyclopentadienyl group was shown to be η-bonded by the i.r. spectrum, as for the cyclopentadienyl-lead halides described above. The asymmetric $\nu(CO_2)$ vibration of the acetate group was at 1 520 cm^{-1} (lower than the value of 1 556 cm^{-1} for the acetate ion) and together with the low solubility in non-donor solvents strongly suggests that the compound has structure (III) with bridging acetate groups.

In an attempt to obtain a more soluble derivative $Pb(\eta\text{-}C_5H_5)_2$ was treated with pivalic acid, but it was only possible to isolate lead(II) pivalate and unchanged $Pb(\eta\text{-}C_5H_5)_2$ from the system. It seems likely that there is a rapid equilibrium between $Pb(\eta\text{-}C_5H_5)_2$ and lead(II) pivalate, and η-cyclopentadienyl-lead(II) pivalate, and that the least soluble product, lead(II) pivalate, crystallises from solution. A similar effect was observed in reactions with β-diketones, when only the lead(II) diketonates could be isolated rather that the expected cyclopentadienyl-lead(II) diketonate. These reactions with protic reagents are useful for preparing some lead(II) compounds. Thus the reactions with methanol and t-butyl alcohol to give lead(II) methoxide or t-butoxide respectively provide the most convenient preparative route to these compounds yet known. The reactions do not proceed with very weakly protic reagents however. It had been hoped that alk-1-ynes would react to give alkynyl-lead(II) species, but phenylacetylene did not react with $Pb(\eta\text{-}C_5H_5)_2$ even under forcing conditions.

Reactions with Methyl Iodide, Acetyl Chloride, and Iodine.—Heating $Pb(\eta\text{-}C_5H_5)_2$ under reflux in methyl iodide led to formation of a precipitate of $Pb(\eta\text{-}C_5H_5)I$, and methylcyclopentadiene was also formed. This may be compared with the similar reaction of $Sn(\eta\text{-}C_5H_5)_2$ which gives the product of oxidative addition $SnMe(\sigma\text{-}C_5H_5)_2I$, although by a rather complex series of reactions.[22,23] It may well be that the analogous product $PbMe(\sigma\text{-}C_5H_5)_2I$ is formed as an intermediate in the reaction with $Pb(\eta\text{-}C_5H_5)_2$ but, since the oxidation state II is relatively more favourable for lead than for tin, the initial adduct undergoes reductive elimination of methylcyclopentadiene to give the final product $Pb(\eta\text{-}C_5H_5)I$. The compound $PbMe_2(\sigma\text{-}C_5H_5)_2$ is known to decompose in solution to $Pb(\eta\text{-}C_5H_5)_2$, a reaction which provides a precedent for that proposed above.[34]

According to this reaction mechanism one would expect 5-methylcyclopenta-1,3-diene to be the organic product of reaction, but examination by gas–liquid chromatography and mass spectroscopy showed that a mixture of isomers of methylcyclopentadiene was formed. This is not surprising since the isomers are readily interconverted under basic conditions. The reaction of $Pb(\eta\text{-}C_5H_5)_2$ with methyl iodide was therefore carried out in the presence of *N*-phenylmaleimide, in order to trap the initially formed isomer of methylcyclopentadiene as its Diels–Alder adduct with the *N*-phenylmaleimide.[35] The product was shown to be very largely the adduct of 5-methylcyclopentadiene with *N*-phenylmaleimide by its m.p. and by comparison of its ^{1}H n.m.r. spectrum with that of an authentic sample,[35] thus giving some support to the mechanism proposed. Under more forcing conditions, methyl iodide reacted with $Pb(\eta\text{-}C_5H_5)_2$ to cleave both cyclopentadienyl groups and give lead(II) iodide.

Iodine reacts with $Sn(\eta\text{-}C_5H_5)_2$ to give the product of oxidative addition $Sn(\sigma\text{-}C_5H_5)_2I_2$,[22] but with $Pb(\eta\text{-}C_5H_5)_2$

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only $Pb(\eta\text{-}C_5H_5)I$ was formed. This again illustrates the relatively lower stability of the oxidation state IV for lead compared with tin, and again the reaction with $Pb(\eta\text{-}C_5H_5)_2$ may well proceed *via* $Pb(\sigma\text{-}C_5H_5)_2I_2$ as a short-lived intermediate. Acetyl chloride reacted with $Pb(\eta\text{-}C_5H_5)_2$ to give $Pb(\eta\text{-}C_5H_5)Cl$ and presumably acetylcyclopentadiene.

The reactions of the bis(η-cyclopentadienyl) derivatives of tin [24-27] and lead with protic reagents are very similar, but the different reactions with methyl iodide and iodine are due to the lower stability of the oxidation state IV for lead than for tin.

EXPERIMENTAL

Bis(η-cyclopentadienyl)lead(II) was prepared by the method of Dave *et al.*[6] and was purified as required by vacuum sublimation. All operations involving reactions of this compound were made in an atmosphere of dry nitrogen or *in vacuo*.

Infrared spectra were recorded using a Perkin-Elmer 577 spectrophotometer, n.m.r. spectra using a Perkin-Elmer R12B spectrometer, and mass spectra using a Mikromass 12 spectrometer.

η-Cyclopentadienyl-lead(II) *Chloride*.—Anhydrous hydrogen chloride (6.0 mmol) was condensed on to a solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6.0 mmol) in benzene (15 cm^3) at −196 °C. The *product* precipitated as a white solid on allowing the mixture to warm to room temperature. It was filtered off, washed with dry diethyl ether, and dried *in vacuo*, yield 87%. The product decomposes without melting at 330 °C (Found: C, 19.35; H, 1.80. Calc. for C_5H_5ClPb: C, 19.5; H, 1.65%); n.m.r. in [$^2H_6$]dimethyl sulphoxide, $\delta(C_5H_5)$ 5.91 p.p.m. The same product was precipitated by adding a solution of dry hydrogen chloride in diethyl ether to an equimolar quantity of $Pb(\eta\text{-}C_5H_5)_2$ in diethyl ether. Addition of excess of hydrogen chloride gave lead(II) chloride in quantitative yield.

η-Cyclopentadienyl-lead(II) *Bromide*.—This was obtained as a white solid by reaction of gaseous hydrogen bromide with $Pb(\eta\text{-}C_5H_5)_2$ as described above, yield 82%. It decomposes without melting at 360 °C (Found: C, 17.1; H, 1.45. Calc. for C_5H_5BrPb: C, 17.0; H, 1.45%); n.m.r. in [$^2H_6$]dimethyl sulphoxide, $\delta(C_5H_5)$ 6.01 p.p.m.

η-Cyclopentadienyl-lead(II) *Iodide*.—This was obtained similarly as a pale yellow solid, yield 60%. It does not melt or decompose below 360 °C (Found: C, 14.7; H, 0.95. Calc. for C_5H_5IPb: C, 15.0; H, 1.25%); n.m.r. in [$^2H_6$]-dimethyl sulphoxide, $\delta(C_5H_5)$ 6.11 p.p.m.

η-Cyclopentadienyl-lead(II) *Acetate*.—Glacial acetic acid (0.355 g, 6.0 mmol) in diethyl ether (5 cm^3) was added to a solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6.0 mmol) in diethyl ether (15 cm^3). The yellow solution of $Pb(\eta\text{-}C_5H_5)_2$ was immediately decolourised. On partial evaporation of the solvent *in vacuo*, the *product* precipitated as a white solid, yield 77%. It decomposes without melting at 180 °C (Found: C, 25.15; H, 2.20. Calc. for $C_7H_8O_2Pb$: C, 25.3; H, 2.40%); n.m.r. in $CDCl_3$, $\delta(CH_3)$ 1.71 and $\delta(C_5H_5)$ 5.83 p.p.m. Addition of excess of acetic acid to $Pb(\eta\text{-}C_5H_5)_2$ in diethyl ether gave lead(II) acetate in quantitative yield.

Lead(II) 2,2-*Dimethylpropionate*.—A solution of 2,2-dimethylpropionic acid (1.224 g, 12.0 mmol) in benzene (5 cm^3) was added to $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6.0 mmol) in benzene (15 cm^3). On partial evaporation of the solvent *in vacuo*, the *product* precipitated as a white solid, yield 70% (Found: C, 29.6; H, 4.50. Calc. for $C_{10}H_{18}O_4Pb$: C, 29.3; H, 4.40%). The same product together with unchanged $Pb(\eta\text{-}C_5H_5)_2$ was obtained from a similar reaction using a 1 : 1 mol ratio of reactants.

Lead(II) *Methoxide*.—A solution of $Pb(\eta\text{-}C_5H_5)_2$ in dry methanol (15 cm^3) was heated under reflux. A dense white precipitate of the *product* formed rapidly, yield 80%. It was identified by comparison with an authentic sample.

Lead(II) *t-Butoxide*.—This was prepared in a similar way as a pale brown solid, yield 74% (Found: C, 27.35; H, 5.10. Calc. for $C_8H_{18}O_2Pb$: C, 27.1; H, 5.10%).

Lead(II) *Pentane*-2,4-*dionate*.—Pentane-2,4-dione (1.0 cm^3) was added to a solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6.0 mmol) in benzene (15 cm^3). The *product* was precipitated by reducing the volume and then adding light petroleum. It was identified by comparison of its i.r. spectrum with that of an authentic sample and by its n.m.r. spectrum in $CDCl_3$: $\delta(CH_3)$ 2.35 and $\delta(CH)$ 6.26 p.p.m., relative areas 6 : 1.

Lead(II) 1,3-*Bis*(*trifluoromethyl*)*propane*-1,3-*dionate*.—1,3-Bis(trifluoromethyl)propane-1,3-dione (2.46 g, 12 mmol) was added to a solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6.0 mmol) in dry benzene (15 cm^3). A pale yellow precipitate of the *product* slowly formed, yield 88%. It decomposes without melting at 200 °C (Found: C, 19.3; H, 0.40; F, 36.4. Calc. for $C_{10}H_2F_{12}O_4Pb$: C, 19.55; H, 0.35; F, 37.1%); n.m.r. in $CDCl_3$, $\delta(CF_3)$ 4.75 p.p.m. downfield from CF_3CCl_3 (broad singlet).

Reactions of $Pb(\eta\text{-}C_5H_5)_2$.—*With methyl iodide*. A solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6.0 mmol) in methyl iodide (15 cm^3) was heated under reflux for 3 h. The resulting pale yellow precipitate was filtered off and identified as $Pb(C_5H_5)I$ by its i.r., n.m.r., and mass spectra. The filtrate was shown by gas–liquid chromatography and mass spectroscopy to contain a mixture of isomers of 5-methylcyclopenta-1,3-diene. In another experiment the above reagents with *N*-phenylmaleimide (6 mmol) were heated in a sealed Carius tube at 100 °C for 2 d. The resulting yellow precipitate was shown to be lead(II) iodide with occluded methyl iodide. The soluble products were chromatographed over silica gel using dichloromethane as eluant, giving the Diels–Alder adduct of 5-methylcyclopentadiene with *N*-phenylmaleimide, identified by its m.p. and n.m.r. spectrum.

With acetyl chloride. Acetyl chloride (0.46 g, 6.0 mmol) was added to a solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6.0 mmol) in anhydrous diethyl ether at −80 °C. On allowing to warm to room temperature a white precipitate of $Pb(\eta\text{-}C_5H_5)Cl$ was formed in high yield.

With iodine. A solution of iodine (1.5 g, 6.0 mmol) in benzene was added dropwise to a solution of $Pb(\eta\text{-}C_5H_5)_2$ (2.0 g, 6.0 mmol) in benzene. A pale yellow precipitate of $Pb(\eta\text{-}C_5H_5)I$ was formed almost immediately, identical with samples prepared by the alternative methods above.

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