Journal of Organometallic Chemistry, 172 (1979) 427–444

Organolead Chemistry Part VI. Removal of Methyllead Compounds from Aqueous Solution by Reaction with Zinc

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(Received March 5th, 1979)

Summary

Trimethyllead chloride or dimethyllead dichloride in aqueous solution reacts with zinc to give ultimately methane, lead and zinc oxide and zinc chloride The reactions proceed in two distinct stages, the first involving rapid removal of the organolead species from solution and the second leading to the final products The intermediacy of organometallic compounds with lead-zinc bonds, which undergo 1,2-shift of methyl groups from lead to zinc followed by hydrolysis of the resulting methylzinc species, is suggested The reactions have application in the treatment of effluents from the manufacture of tetramethyllead

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Introduction

Effluents from the manufacture of tetramethyllead or tetraethyllead contain considerable quantities of lead as the corresponding trialkyllead(IV) and dialkylead(IV) species, which are soluble in water, as well as lead(II) species. Using conventional treatment methods, the overall concentration of lead in effluent can be reduced to 10 - 100 p.p m. with most of the lead being in the form of organoleads A further reduction to less than 2 p p m lead concentration is obtained by passing the treated effluent through a column of zinc, or by stirring the effluent with zinc[1]. We have begun an investigation into the nature and mechanism of this reaction, which has obvious application in reducing organolead pollution. In this paper we present some results on reactions of methyllead(IV) compounds with zinc.

Results

The Stoichiometry of the Reaction

In preliminary experiments, the volatile products of reaction of Me_3PbCl with zinc in aqueous solution were shown to be tetramethyllead and methane. After long reaction times (⩾ 6 days) methane was the only volatile product. Quantitative studies were made using a gas burette to measure the volume of methane evolved. This work showed that methane was eventually formed in 100% yield according to the stoichiometry

$$Me_3PbCl \longrightarrow 3\ CH_4$$

Tetramethyllead was formed in the early stages of reaction in a maximum yield of ∿10% (based on the stoichiometry 4 $Me_3PbCl \longrightarrow 3\ Me_4Pb$) but then its concentration decreased and it clearly formed methane eventually

The reactions occurred more rapidly in 5% sodium chloride solution than in aqueous solution alone and the rate increased with temperature However, the overall stoichiometry did not depend on the reaction conditions. The results are summarised in Table 1

Very similar results were obtained in analogous reactions of dimethyllead dichloride with zinc. Typically at 40°C in 5% aqueous sodium chloride

Table 1

Products formed on reaction of Me_3PbCl with Zn in 5% aqueous NaCl solution and in salt-free aqueous solution

Time (hours)	Results in 5% aqueous NaCl						Results in aqueous solution[a]			
	% Me_4Pb formed[b]			% CH_4 formed[c]			% Me_4Pb formed[b]		% CH_4 formed[c]	
	21°C	25°C	50.5°C	21°C	25°C	50.5°C	21°C	50.5°C	21°C	50.5°C
1	6.3	4.3	6.5	17	16	37	5.1	5.3	13	29
2	7.7		7.7	32		56	6.5	6.4	24	42
3		9.1			35					
5	10.6	9.3	10.2	42	39	77	10.1	10.0	34	61
6		9.3			40					
7		9.2			41					
10		9.1			42					
12										
24	8.7	5.2	8.6	58	56	85	7.4	5.6	50	71
48		1.1		71	76	93			63	82
72		0.3		81	88	100			71	90
120		0.1			98					
144		0			99					
168		0			99					

[a] Initial concentration of Me_3PbCl was 3.3×10^{-3} M in each case

$$b = \frac{\text{moles } Me_4Pb \text{ formed}}{\text{moles } Me_3PbCl \text{ added}} \times \frac{400}{3} \qquad c = \frac{\text{moles } CH_4 \text{ formed}}{\text{moles } Me_3PbCl \text{ added}} \times \frac{100}{3}$$

solution, complete conversion to methane occurred in seven days. Again tetramethyllead was formed at intermediate stages (maximum yield 10% after 3 hours) and then reacted further to give methane To check that maximum apparent yields of Me_4Pb were not limited by its volatility, all tetramethyl lead formed was extracted into hexane in some cases and g l c analysis of the hexane extract was carried out. Yields of Me_4Pb determined either by g.l.c. analysis of the gas phase or hexane extract were in good agreement.

During the reactions of Me_3PbCl or Me_2PbCl_2 with zinc, the metal became tarnished and a white solid was formed. The white solid was identified as zinc oxide by its X-ray powder diffraction pattern, but also contained some chloride. The weight of zinc oxide was considerably higher in reactions carried out in an atmosphere of air or oxygen than when conducted under nitrogen or vacuum, and independent experiments showed that oxygen was absorbed by zinc-sodium chloride solutions to give zinc oxide However it is clear that zinc oxide (containing some chloride) is formed in the reaction of Me_3PbCl or Me_2PbCl_2 with zinc for a period of seven days, though the material could not be collected quantitatively and the yield was not determined A solution containing trimethyllead chloride, 5% sodium chloride and zinc under nitrogen had initially pH 5 8 but this rose rapidly to pH 6.8 and then slowly to pH 6.9 as the reaction proceeded. Evidently the zinc oxide - zinc chloride system acts as a buffer maintaining an almost constant pH once reaction begins

Examination of the zinc after extended reaction with organolead halides by scanning electron microscopy has identified the lead as metallic lead in zones on the zinc where considerable etching of the zinc surface occurs[2]. A sample of zinc after reaction with Me_3PbCl for 10 days was filtered off and the lead content was subsequently analysed. The analysis accounted for 95% of the lead initially added as Me_3PbCl presumably in the form of metallic lead.

Overall the stoichiometry of reaction of Me_3PbCl with Zn is therefore given by equation 1

$$2\ Me_3PbCl + 4\ Zn + 3\ H_2O \longrightarrow 6\ CH_4 + 2\ Pb + 3\ ZnO + ZnCl_2 \qquad (1)$$

This is somewhat simplified since the zinc oxide - zinc chloride system is complex, and various hydroxochlorozinc species are probably present in the equilibrium mixture[3] Similarly the reaction with Me_2PbCl_2 can be represented by equation 2

$$Me_2PbCl_2 + 2\ Zn + H_2O \longrightarrow 2\ CH_4 + Pb + ZnO + ZnCl_2 \qquad (2)$$

The rate of removal of methyllead halides from solution

To complement the studies of reaction rate by monitoring the volatile products formed, a spectrophotometric method was developed for analysis of both trimethyllead(IV) and dimethyllead(IV) species in solution so that the rate of removal could be studied directly[4]

Reaction of trimethyllead chloride in 5% sodium chloride solution with zinc occurred rapidly, 50% removal of Me_3PbCl occurred in 4 minutes and 89% removal occurred in 10 minutes. Typical results are given in Table 2 The reaction followed first order kinetics in $[Me_3PbCl]$ to about 90% removal and the rate then decreased sharply The rate of reaction was essentially independent of temperature over the range 21-50°C The rate was independent of sodium chloride concentration in the initial stages, but the rate tailed off after 55% removal of Me_3PbCl in the absence of sodium chloride. This is illustrated by the plots of Figure 1 The rate was dependent on the surface area of zinc, being greater for zinc powder than for granulated zinc but was apparently independent of the purity of the zinc used

It is apparent that the removal of trimethyllead(IV) species from solution is considerably faster ($t_{1/2}$ 4 minutes) than the evolution of methane ($t_{1/2}$ 13-15 hours) and hence the reaction must occur in two distinct stages This phenomenon is illustrated clearly in Figure 2 The nature of this rapid step was then studied in greater detail

In the absence of sodium chloride, it was shown that the concentration of chloride in solution remained constant during reaction of Me_3PbCl with zinc (Table 2). Thus the trimethyllead(IV) species is not removed as the

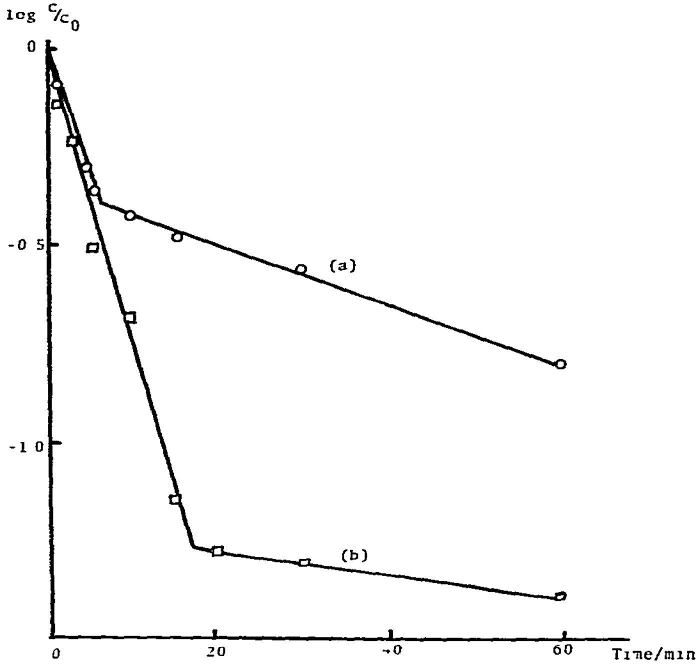


Figure 1 First order plots for the removal of trimethyllead species from solution by reaction with zinc (a) aqueous solution, (b) 5% sodium chloride solution c and c_0 refer to the concentration of trimethyllead(IV) species at time t and 0 respectively.

chloride, but presumably as a solvated ion The quantity removable and rate of removal of trimethyllead chloride from solution was not dependent on the ratio of trimethyllead chloride to zinc used Thus quantities of Me_3PbCl from 3 44 - 27.9 x 10^{-4} mol were treated with zinc (1 gram) in 5% aqueous sodium chloride and the rate of removal and final percentage of trimethyllead chloride removed remained constant for a fixed time period (Table 3). At the higher organolead concentrations there were not nearly enough surface zinc atoms available to chemisorb the trimethyllead(IV) present and hence rapid etching of the zinc must occur at this stage

Similar results were obtained in reactions of dimethyllead dichloride with zinc. Again the removal of dimethyllead dichloride was faster than

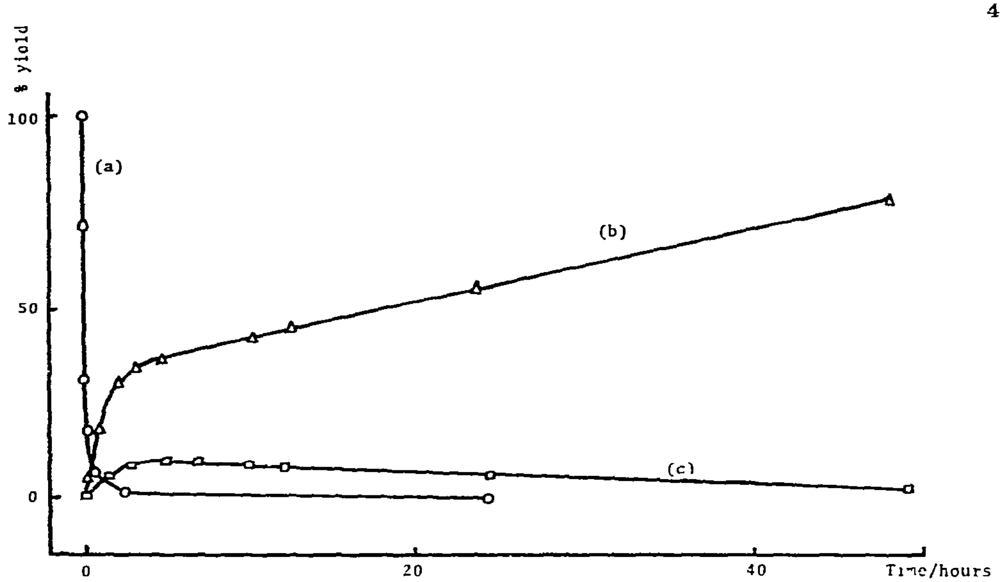


Figure 2 Yields of products in reaction of trimethyllead chloride with zinc in 5% aqueous sodium chloride solution at 25°C (a) % Me_3Pb^+ remaining (b) % CH_4 formed (c) % Me_4Pb formed

methane evolution (Table 4 and Figure 3), and the situation was further complicated by the formation and subsequent further reaction of trimethyllead(IV) species in solution It has already been shown that trimethyllead(IV) species react rapidly with zinc in aqueous solution.

The nature of the adsorbed species

Since the removal of trimethyllead(IV) species from solution occurs more rapidly than methane evolution, it follows that a methyllead species must be formed which adheres strongly to the zinc surface. We have attempted to characterise this species by removing and drying the zinc after exposure to trimethyllead chloride in 5% aqueous sodium chloride for 30 minutes The following experiments were then carried out

(i) The zinc was dissolved in hydrochloric acid and the gaseous products were analysed A considerable quantity of methane was produced (along with the hydrogen) indicating the presence of methyllead or

Table 2

The rate of removal of trimethyllead(IV) species
from solution by reaction with zinc

Time/min	% removal Me_3Pb^+ 5% NaCl solution[a]	% removal Me_3Pb^+ aqueous solution[b]	% removal aqueous solution[c]	
			$[Me_3Pb^+]$[c]	$[Cl^-]$[c]
0	0	0	0	0
1	28	18		
3	42	44	45	0
5	69	51		
10	89	63		
15	93	68		
30	95	72		
60	96	85	99 5	0
1440	100	100		

Initial concentration of Me_3PbCl [a]3.31×10^{-3} M [b]$3\ 26 \times 10^{-3}$ M
[c]4.83×10^{-3} M All reaction carried out at 25°C

methylzinc bonds Quantitative estimation of the methane was not possible

(ii) Attempts were made to react the adsorbed species with benzyl bromide in refluxing tetrahydrofuran. Any Me_3Pb-Zn bonded species would be expected to yield trimethylbenzyllead under these conditions but none could be detected.

(iii) Soxhlet extraction of the zinc was carried out in the hope of extracting soluble organolead compounds. Solvents used were hexane, dichloromethane, tetrahydrofuran and methanol. Traces of tetramethyllead were found in all cases but, if the extraction was carried out under nitrogen, no other methyllead compounds were formed. If the methanol extraction was carried out in air or under an atmosphere of CO_2, trace

Table 3

Removal of Me_3PbCl from solution at various concentrations[a]

Initial concentration of Me_3Pb^+/M	Concentration of Me_3Pb^+ after 30 min/M	% Removal
3.44×10^{-3}	$2\ 47 \times 10^{-4}$	92 7
6.95×10^{-3}	$7\ 13 \times 10^{-4}$	89 7
$1\ 39 \times 10^{-2}$	$1\ 88 \times 10^{-3}$	87 0
$2\ 08 \times 10^{-2}$	$3\ 53 \times 10^{-3}$	83 2
$2\ 79 \times 10^{-2}$	$2\ 78 \times 10^{-3}$	89 9

[a] In each case 100 cm^3 of a solution of Me_3PbCl in 5% NaCl solution was stirred with zinc (1 g) at 25°C

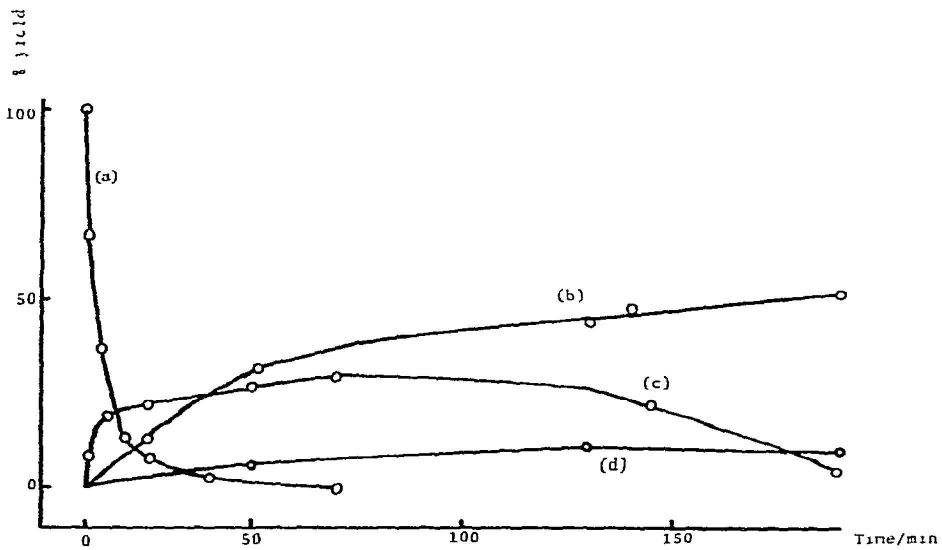


Figure 3 Yields of products with time in reaction of dimethyllead dichloride with zinc in 5% aqueous sodium chloride solution at 40°C (a) % Me_2Pb^{2+} remaining (b) % CH_4 formed (c) % Me_3Pb^+ (d) % Me_4Pb

Table 4

The products of reaction of dimethyllead dichloride with zinc[a]

Time/min	Aqueous solution[b]		5% NaCl solution[c]			
	% Me_2Pb^{2+}	% Me_3Pb^+	% Me_2Pb^{2+}	% Me_3Pb^+	% Me_4Pb	% CH_4
0	100	0	100	0	0	0
1	70	13	66	8		
3	48	21				4
4			36	19		
5	29	27				
10	26	30				
15			7	21		12
30	1.5	40	3	24		
40					6	30
60	0	29	0 3	30		
70						38
120	0	19			11	44
130						48
135			0	22		
147						49
160	0	9				
180			0	4	10	51
1,140						52
1,440	0	0				54
2,580					1	88
4,320						95
10,000						98

[a] at 40°C. [b] initial $[Me_2PbCl_2]$ 3.3 x 10^{-3} M [c] initial $[Me_2PbCl_2]$ 3 4 x 10^{-3} M

quantities of bis(trimethyllead) carbonate were formed presumably by reaction with CO_2

It seems that the organometallic compound is very strongly bound to the zinc and can only be removed under conditions which destroy the compound.

Reactions in other solvents

The reaction of trimethyllead chloride with zinc in D_2O gave CH_3D only as identified by analysis using G.L C -M S This suggests that methane is formed by hydrolysis of a methylmetal compound

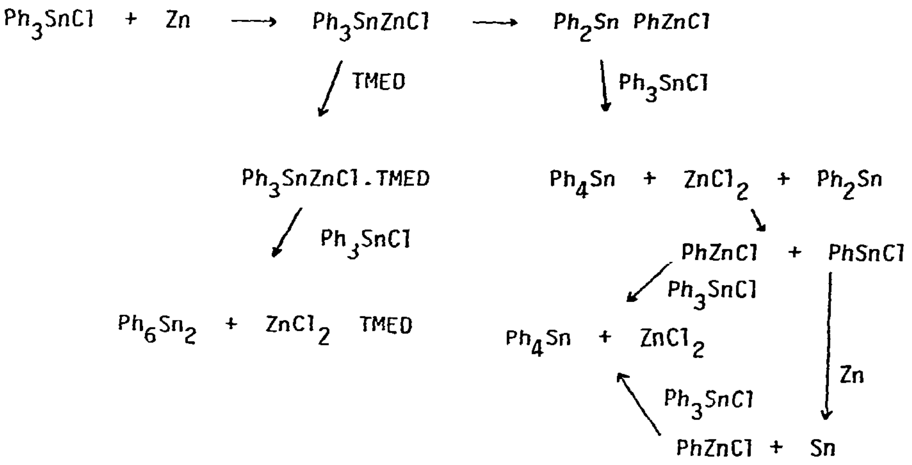
Reaction of trimethyllead chloride with zinc did not occur readily in dry organic solvents Thus essentially no reaction occurred in benzene, tetrahydrofuran or pyridine over a period of 3 days at room temperature A slow reaction occurred in methanol to give methane and tetramethyllead, but the rapid removal of Me_3PbCl observed in aqueous solution did not take place Slow reaction also occurred in moist organic solvents Thus in moist pyridine, methane and tetramethyllead were formed slowly and a white precipitate, presumably of zinc oxide, was formed In pyridine moistened with D_2O the gaseous product was CH_3D In another experiment trimethyllead chloride was treated with zinc in pyridine-toluene-d_8 mixture Very little reaction occurred but the methane formed was identified as CH_4 with no deuterium incorporation Methane is thus formed by hydrolysis of methylmetal bonds by adventitious water If methyl radicals were formed CH_3D would be expected by abstraction of deuterium from toluene-d_8

Discussion

Reactions of organolead halides with zinc have apparently not been studied in the past[5], but reactions with other metals are known Thus reaction of Et_3PbCl with aluminium in aqueous solution is a commonly used method for preparing Et_6Pb_2 in good yield[6] Reaction of Et_3PbCl with sodium at 77°K gives triethyllead radicals initially[7] Reactions of organotin halides with zinc in the form of zinc-copper couple have been studied[8-11] In aprotic media the reactions ultimately lead to formation of tetraalkyltin and metallic tin and the mechanism shown in Scheme 1 was proposed There is good evidence for formation of tin-zinc bonded compounds $R_3SnZnCl$, for 1,2-alkyl shifts to give $R_2SnRZnCl$, and for further alkylation of organotin complexes by organozinc reagents It

Scheme 1

Reactions of Ph_3SnCl with Zn in aprotic media (TMED = $Me_2NCH_2CH_2NMe_2$)

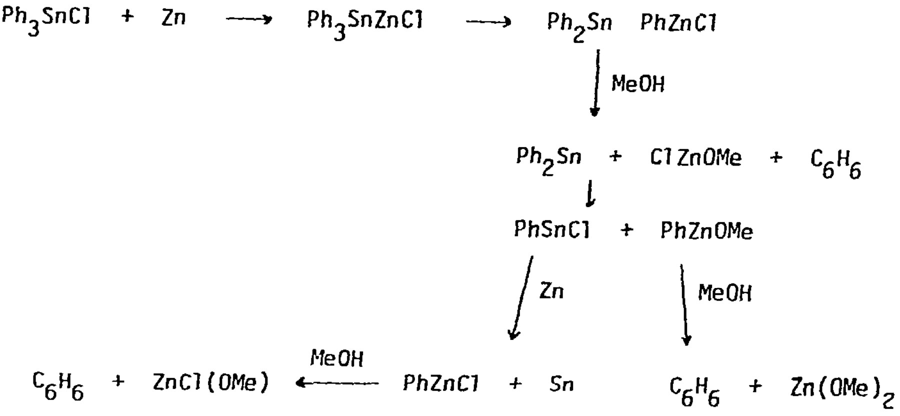


is interesting that strong donors such as N,N,N^1,N^1-tetramethylethylene diamine suppress the 1,2-alkyl shift by co-ordination to zinc and the organotin product is then a hexaalkylditin formed by the reaction (equation 3)

$$R_3SnZnCl + R_3SnCl \longrightarrow R_6Sn_2 + ZnCl_2 \qquad (3)$$

Scheme 2

Reactions of Ph_3SnCl with Zn in protic media



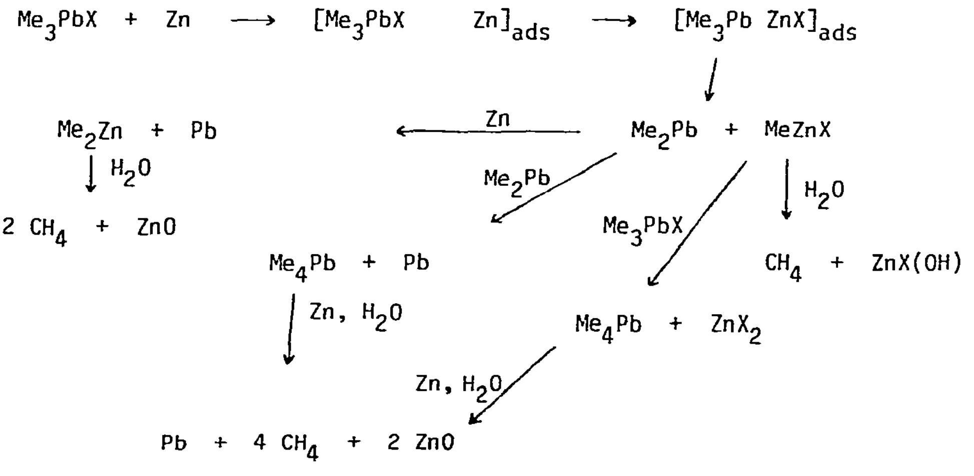
In protic solvents such as methanol reaction gave the alkane RH and tin according to Scheme 2. Now any alkylzinc species formed are rapidly hydrolysed to alkane before alkylation of tin can occur[11]

It is possible to interpret the reactions of trimethyllead chloride with zinc in an analogous way (Scheme 3) The following points should be considered

(i) The nature of the initial product from the rapid removal of trimethyllead chloride from solution is not known It cannot simply be a chemisorbed compound, Me_3PbX, since the reaction is not a simple surface effect If it were a lead-zinc bonded species Me_3PbZnX then it would be expected to decompose or react with water rapidly, whereas methane, the final product, is formed only slowly Our attempts to characterise the species chemically have been unsuccessful and direct spectroscopic studies are required (such as ESCA or reflectance IR studies) to characterise it further. In aqueous solution trimethyllead chloride exists as $[Me_3Pb(OH_2)_2]^+Cl$ and the chloride was shown to remain in solution throughout the reaction However, in the presence of excess chloride a series of equilibria exist (equation 4)[12]

Scheme 3

Reactions of Me_3PbCl with Zn in water



$$[Me_3Pb(OH_2)_2]^+ \overset{Cl^-}{\rightleftharpoons} [Me_3PbCl(OH_2)] \overset{Cl^-}{\rightleftharpoons} [Me_3PbCl_2]^- \quad \ldots \ (4)$$

Since removal of trimethyllead(IV) species occurred more efficiently in the presence of sodium chloride, it is possible that compounds with a PbCl bond are adsorbed more efficiently than the aqua ion but our analytical techniques were not sufficiently accurate to settle this point. Thus, in general, the group X in Scheme 3 could be Cl or OH.

(ii) We have assumed that all Me_4Pb is formed by reaction of methylzinc species with trimethyllead(IV) species However, it is known that trimethyllead chloride disproportionates in aqueous solution according to equation (5)[13].

$$3\ Me_3PbCl \rightleftharpoons 2\ Me_4Pb + MeCl + PbCl_2 \quad \ldots \ (5)$$

Model studies in the absence of zinc suggested that this reaction was far too slow to account for tetramethyllead formation observed, but it could contribute to a minor extent. No dimethyllead(IV) species were detectable during the reaction and methyl chloride was absent or present in only trace amounts. Tetramethyllead could also be formed by decomposition of hexamethyldilead[14], of which trace quantities were detected occasionally, but again this cannot explain the quantities of tetramethyllead formed

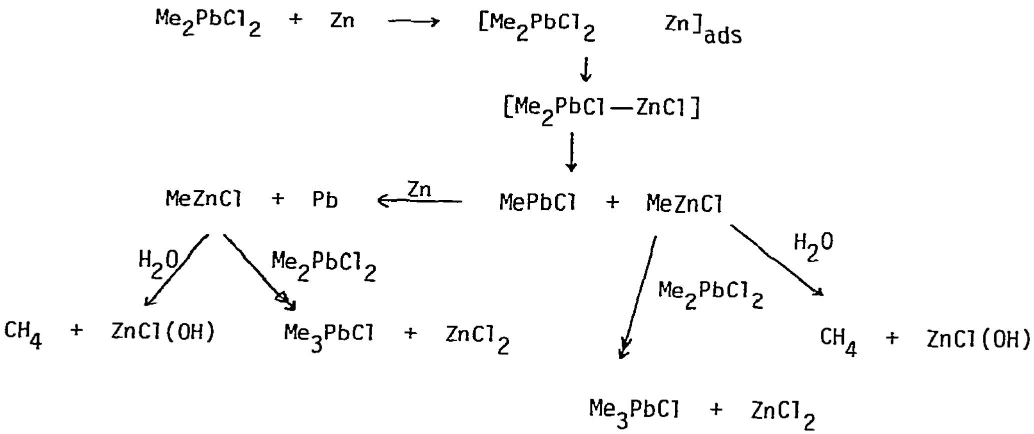
(iii) The mechanism of formation of the proposed intermediate $Me_3Pb\text{-}ZnX$ is not known. There is some evidence that it is formed by a free radical mechanism, as in the formation of Grignard reagents from alkyl halides and magnesium[15] This point will be discussed further in a later publication.

The reaction of dimethyllead dichloride with zinc can be interpreted in a similar way (Scheme 4) The formation of trimethyllead chloride and tetramethyllead follows naturally It is also possible that some trimethyllead chloride arises by the disproportionation reaction (equation 6)[16], though only traces of methyl chloride were found.

$$2\ Me_2PbCl_2 \longrightarrow Me_3PbCl + PbCl_2 + MeCl \quad (6)$$

Scheme 4

Reactions of Me_2PbCl_2 with Zn in water



The reactions of methyllead salts with zinc are clearly very suitable for effluent treatment Thus the highly toxic methyllead species are removed very efficiently to give eventually methane and metallic lead

The lead can potentially be recovered. Since the zinc is etched in the reactions, a fresh zinc surface is continually exposed and the use of zinc is very efficient, indeed the zinc will eventually react completely giving sparingly soluble zinc oxide as the principal product In a stirred system it is also possible to recover the tetramethyllead formed at intermediate stages of reaction.

Experimental Section

NMR spectra were recorded using a Perkin-Elmer R12B spectrometer operating at 60 MHz G.L C and G L.C -M S. experiments were carried out using a Pye 104 Chromatography instrument coupled to a Mikromass 12 spectrometer G L C analysis of tetramethyllead was carried out using a column packed with 8% squalene, 2% silicone oil on chromosorb W, and analysis of alkanes using a squalene column

Analysis of lead-zinc mixture

The lead-zinc mixture was dissolved by warming in 50% hydrochloric aicd Excess sulphuric acid was added, the solution was warmed and diluted with distilled water The precipitated lead sulphate was separated, dried and weighed.

Analysis of trimethyllead(IV) and dimethyllead(IV)

This was carried out by a modification of the dithizone method, by which Me_3Pb^+, Me_2Pb^{2+} and Pb^{2+} can be analysed separately when present as a mixture by extraction into chloroform containing dithizone The dithizonates of each species have distinct UV-visible spectra and can be estimated spectrophotometrically In our experiments, Zn^{2+} was present and interfered. Therefore EDTA was added to each aliquot to be analysed in order to complex both Zn^{2+} and Pb^{2+}, and the Me_3Pb^+ and Me_2Pb^{2+} were then estimated by the literature method[4]. Full calibrations were carried out to check the validity of the procedure

Analysis for chloride was carried out by potentiometric titration with silver nitrate solution

Materials used - Zinc metal and tetramethyllead (as an 80% W/W solution with toluene) were supplied by the Associated Octel Company The zinc was supplied from Biebesheim I.S.C. Alloys Ltd., as air-blown zinc, 7-30 Mesh, 99.95% purity Occasional experiments with zinc powder and granulated zinc were also performed. The particle size of the zinc used was intermediate between granular and powdered zinc. Trimethyllead chloride was prepared by reaction of HCl with Me_4Pb at -70°C and was recrystallized from ethyl acetate Dimethyllead dichloride was freshly prepared by reaction of chlorine with Me_4Pb at -20°C Both compounds were stored at 0°C in the dark.

Rate Studies

(a) Methane and Me_4Pb evolution

In a typical experiment Me_3PbCl (3.33×10^{-4} mol) was added to zinc

(5g) suspended in a solution of sodium chloride (5g) in distilled water (100 cm^3) in a flask held in a thermostatted shaker and connected to a gas burette The atmosphere was thoroughly flushed with nitrogen before addition. Gas evolution was monitored using the gas burette Occasional samples for analysis by G L C were taken through a septum device using a gas syringe

(b) Removal of Me_3Pb^+ and Me_2Pb^{2+} from solution

Typically, Me_3PbCl (3 08 x 10^{-4} mol) in a solution of NaCl (5g) in water (100 cm^3) was added to zinc (5g) contained in a 3-neck flask held in a constant temperature water bath An atmosphere of nitrogen was maintained in the flask, and the contents were stirred using a magnetic stirrer Aliquots of the solution were withdrawn periodically through a septum cap using a syringe, and were subsequently analysed using the dithizone method

Characterisation of bis(trimethyllead)carbonate

The white solid extracted from reacted zinc using methanol was characterised thus Analysis, Found C, 13.35, H, 3 27, Pb, 74 1%, Equivalent weight, 288 Calc. for $C_7H_{18}O_3Pb_2$ C, 14 88, H, 3 19, Pb, 73 4%, Equivalent weight, 283 The equivalent weight was determined by titration with HCl NMR in $CDCl_3$ · δ(MePb) 1 9 ppm, $^2J(^{207}PbH)$ 68 Hz IR $\nu(CO_3)$ 1730, 1280 cm^{-1} The mass spectrum did not give a parent ion but peaks at 297, 296, 295 due to $Me_3PbCO_2^+$, 283, 282, 281 due to $Me_2PbCO_2H^+$, 267, 266, 265 due to $MePbCO_2^+$ were prominent

Acknowledgements

We thank the Associated Octel Company for support through a CASE award (to M H) for gifts of chemicals and for many stimulating discussions.

References

1 D E Lill and D R W Bass to the Associated Octel Company Ltd , Brit Pat 1,417,078 (1975).

2. A.J. Baker, University of Birmingham, in a report to the Associated Octel Company, Reference file RA 6784 (1975).

3 J.W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Longmans, London, 1922.

4. T R. Crompton, Chemical Analysis of Organometallic Compounds, Vol 3, Academic Press, 1974.

5 H Shapiro and F W. Frey, The Organic Compounds of Lead, Interscience, New York, 1968.

6 G.A. Razuvaev, N.S. Vyazankin and N N Vyshinskii, Zh. Obsch Khim , 29, 3662 (1959), 30, 967 (1960)

7. J.E Bennett and J.A. Howard, Chem. Phys Letters, 15, 322 (1972)

8 J G Noltes, F.J A. des Tombe and G.J M. van der Kerk, J Organometal. Chem , 13, P 9 (1968)

9. J G. Noltes, H M J.C. Creemers, F J A. des Tombe and G J M van der Kerk J C.S. Chem. Comm., 914 (1966)

10 H M J.C. Creemers, J.G. Noltes and G J.M van der Kerk, J Organometal Chem , 14, 217 (1968).

11 F J A des Tombe, G J.M van der Kerk and J G Noltes, J Organometal. Chem , 43, 323 (1972), 51, 173 (1973)

12. R Barbieri, M Giustiniani, G. Faraglia and G. Tagliavini, Ric Sci. 33, 975 (1963). K. Hills and M C Henry, J Organometal Chem., 3, 159 (1965). N Bertazzi, G Alonzo, A Silvestri and G Consiglio, J Organometal. Chem., 37, 281 (1972). G D Shier and R.S Drago, J Organometal Chem , 6, 359 (1966)

13 H J Haupt, F Huber and J. Gmehling, Z. Anorg. Allgemeine Chem., 390, 31 (1972)

14. D.P. Arnold and P R Wells, J Organometal. Chem., 111, 269, 285 (1976); 113, 311 (1976).

15 H W.H J Bodewitz, C Blomberg and F. Bickelhaupt, Tetrahedron, 29, 719 (1973).

16 H.J. Haupt and F Huber, Z. Anorg. Allgemeine Chem , 390, 31 (1972); 393, 131 (1972)