

LEAD

ANNUAL SURVEY COVERING THE YEAR 1982

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Contents

I.	Books and Reviews	211
II.	Syntheses	211
III.	Reactions	216
IV.	Physical Chemistry	223
V.	Applications	226
VI.	Analysis	227
VII.	Wastes, Pollution and Industrial Hygiene	228
VIII.	Toxicology	229
IX.	References	232

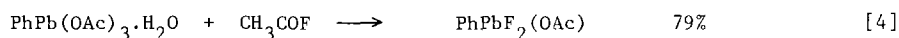
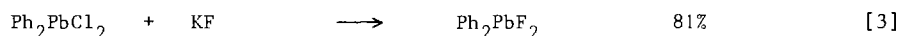
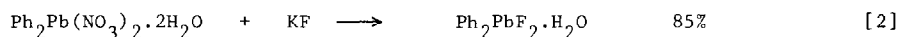
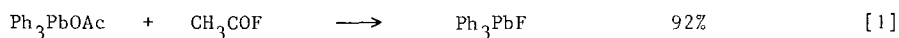
I. Books and Reviews

Several books and reviews dealing with organolead chemistry, have been published: annual survey 1980 (1); a complete overview (2) and a special review on compounds containing transition metal lead bonds (3) in an excellent standard work of 9 volumes on organometallic chemistry; the plenary lectures of the 3rd International Conference on the Organometallic and Coordination Chemistry of Ge, Sn and Pb, Dortmund, 1980 (4); new applications in organic synthesis (5); coordination chemistry of group IV (6); metallatranes including plumbatranes (7); compounds containing a methylene bridge (8); ligand chemistry of tellurium e.g. reactions with organolead compounds (9); electronic effects in thiophene derivatives (10); kinetics and mechanism of ozone oxidation (11); HPLC (12); methods to determine lead alkyls in gasoline (13); a study on environmental lead (14); the biological methylation of metals (15).

II. Syntheses

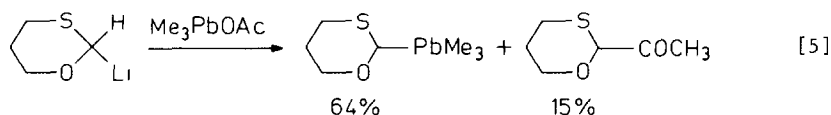
Huber et al. have prepared a range of new organolead derivatives.

Compounds of the type R_3PbDNG ($R=Me, Ph$) and $Ph_2Pb(DNG)_2$ have been synthesized from R_3PbOH or $[Ph_2PbO]_n$ and HDNG ($N-(2,4-dinitrophenyl)glycine$). Me_3PbDNG has also been obtained from Me_3PbBr and TDNG. R_3Pb groups are planar, while bridging occurs through bidentate carboxylate groups. For $Ph_2Pb(DNG)_2$ a chain structure with hexacoordination of Pb has been proposed (16). Triphenyllead derivatives of N -benzoyl-glycine and N -formylglycine have been prepared from Ph_3PbOH and BzGlyH or for GlyH in yields of 75% and 56% respectively. It has been concluded from IR data that bidentate carboxylate groups are present (17). A number of organolead fluorides has been reported. Various synthetical routes have been applied [1-4] (18).

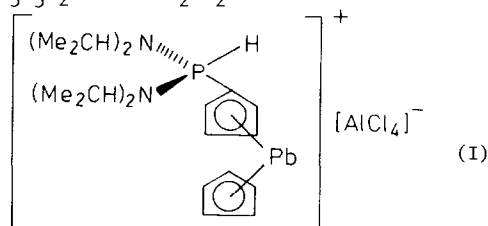


Bis(triphenylplumbyl)chromate has been mentioned in a patent application (19).

Reaction of 1,3-oxathianyllithium with Me_3PbOAc yielded 2- $PbMe_3$ substituted 1,3-oxathiane. Subsequent reaction of the organolead compound with $sec.BuLi$ gave the Li derivative, which was treated with D_2O leading to 95% of the 2-D compound (100% incorporation) (20).

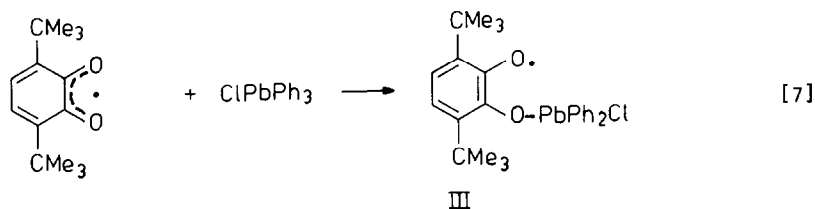
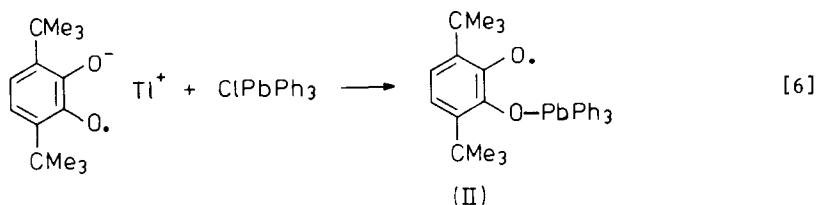


The phosphonium salt $[(i-Pr_2N)_2P]^+ [AlCl_4]^-$ has been reacted with plumbocene, $(\eta^5-C_5H_5)_2Pb$, in CH_2Cl_2 at $-20^\circ C$ to yield (I) (89.6%).

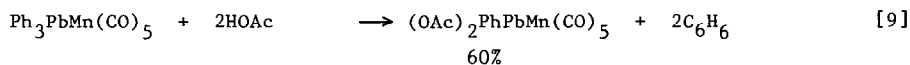
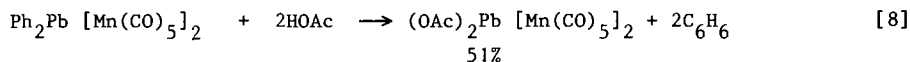


The phosphonium proton in (I) can be substituted by treatment with $i\text{-Pr}_2\text{NLi}$ in $\text{THF}/\text{CH}_2\text{Cl}_2$. $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Pb}$ failed to react with phosphonium ions (21).

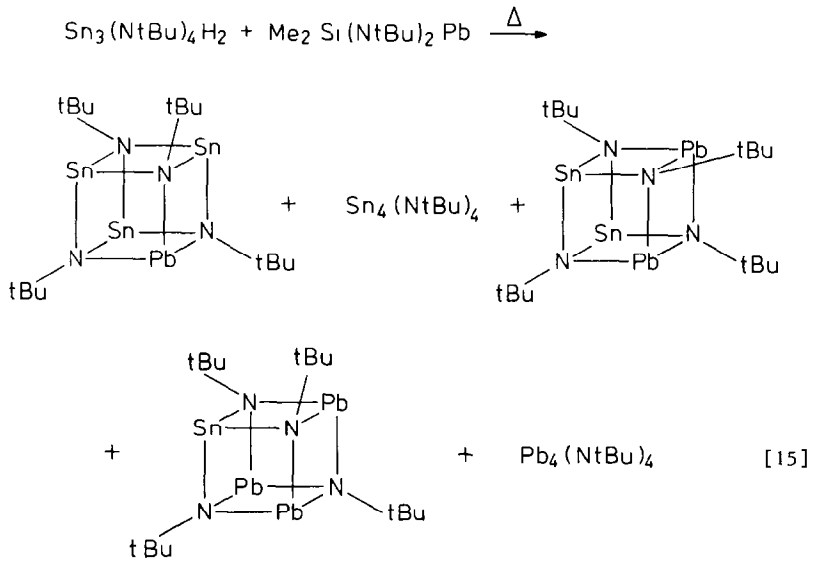
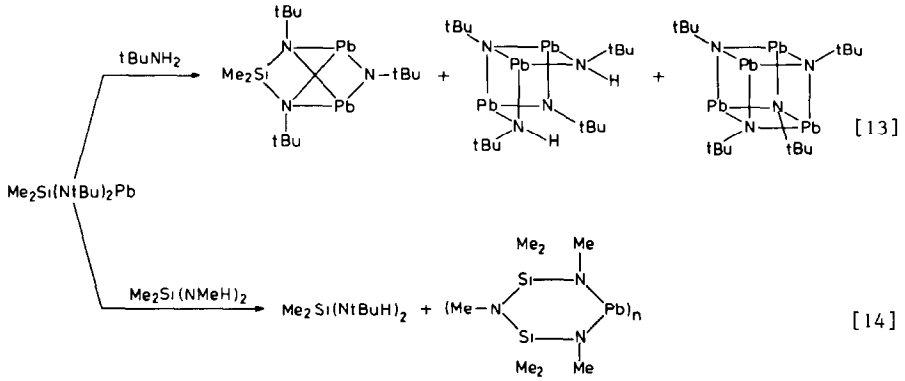
The metallotropy of (II) and (III), prepared according to eqns [6] and [7], has been studied: values of 2.7 and 10.5 kcal/mol have been found for the activation energy (22).



The arenetricarbonylchromium complexes $(\text{CH}_3)_2\text{Pb}(\text{C}_6\text{H}_5)_2[\text{Cr}(\text{CO})_3]$ and $(\text{CH}_3)_2\text{Pb}(\text{C}_6\text{H}_5)_2[\text{Cr}(\text{CO})_3]_2$ have been synthesized. The $^{207}\text{Pb}-^1\text{H}$ coupling constants suggested 4 coordination for Pb: $J(^{207}\text{Pb}-^1\text{H}(\text{CH}_3))$ 69.9 Hz and 74.0 Hz. IR (and Raman) data for the latter compound have been assigned: $\nu_{\text{asym}}\text{Pb-CH}_3$ 489 (483), $\nu_{\text{sym}}\text{Pb-CH}_3$ 474 (471) cm^{-1} (23). The acetolysis of phenylleadmanganese carbonyls has been found to proceed according to [8] and [9]. The new orange or yellow compounds were monomeric in solution; IR data indicated that Pb was in octahedral coordination (24).

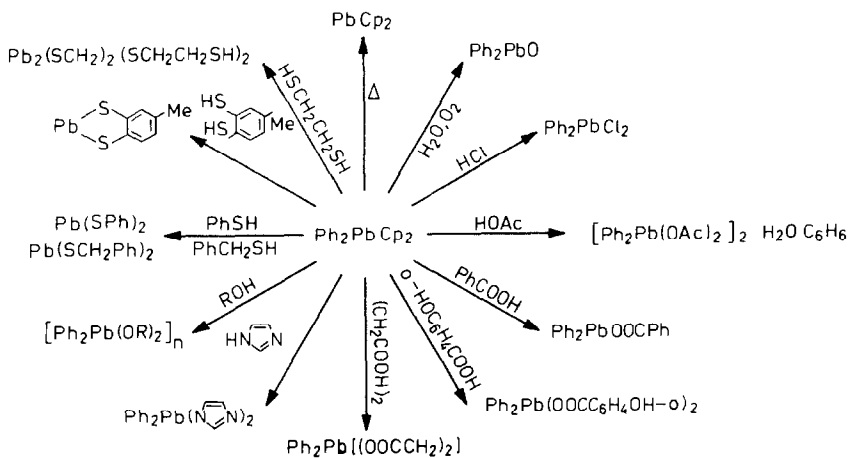
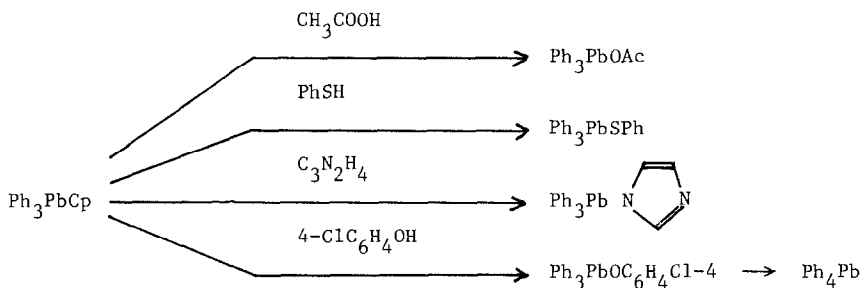


The blue, air stable complexes $[\text{Pb}\{\text{Co}(\text{CO})_3(\text{L})\}_4]$ (L=tertiary arsine, phosphine, or phosphite) have been obtained as the sole and unexpected products from the reactions in boiling benzene in yields of 50 - 75% of a wide variety of ionic and covalent lead (II) and lead (IV) compounds as well as metallic

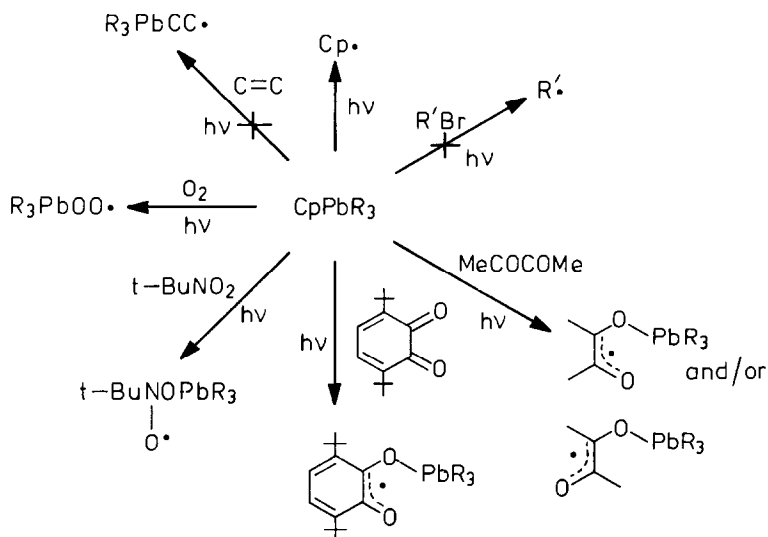


III. Reactions

Synthesis, properties and reactions of Ph_3PbCp and Ph_2PbCp_2 have been described. Crystals of Ph_3PbCp comprise discrete non-interacting molecules with a distorted tetrahedral geometry: $\text{Pb}-\text{C}(\text{Cp})$ 2.30 Å, $\text{Pb}-\text{C}(\text{Ph})$ 2.22 Å. The Cp group is fluxional in both compounds. These compounds are light sensitive. Reactions of Ph_3PbCp are presented in Scheme 1, reactions of Ph_2PbCp_2 in Scheme 2 (30).

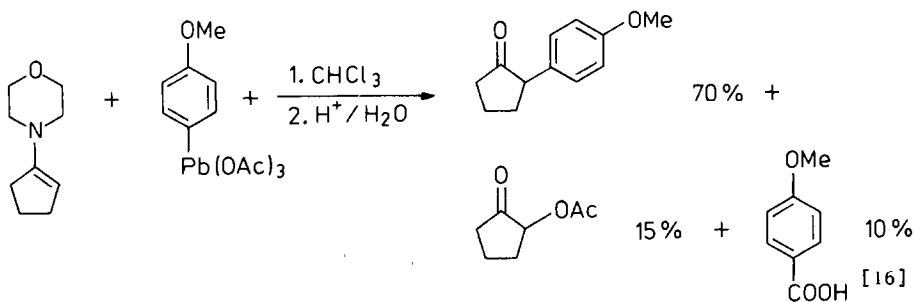


Compounds of the type CpPbR_3 ($\text{R}=\text{Me,Et,Ph}$) and Cp_2PbPh_2 have been photolyzed with UV light. The ESR spectra and reactivity of the radicals have been studied (Scheme 3). The lead (III) radicals have a chemistry very similar to that of the corresponding tin (III) radicals, though with lower reactivity: no bromine abstraction or alkene addition (31).



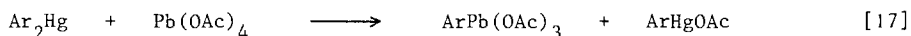
Scheme 3

Pinhey et al. have continued their studies on the chemistry of aryllead (IV) tricarboxylates. The arylation of enamines has been demonstrated to be a facile and useful synthetic reaction.

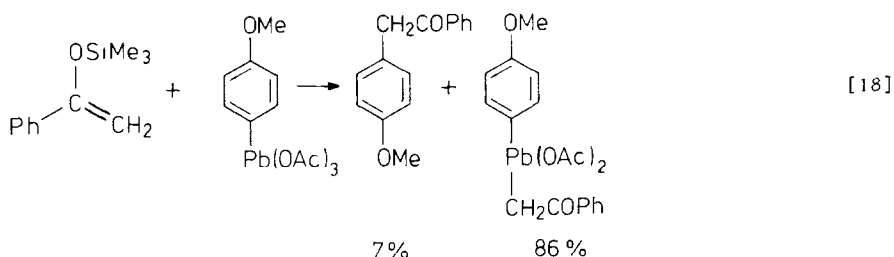


A range of enamines has been arylated with several aryllead (IV) tricarboxylates leading to α -arylketones in yields of 4-83% and/or α -acetoxyketones in yields of 1-65%. Enamines of cyclic ketones showed in general poor reactivity. A larger ring size favours acetoxylation to arylation. Where acetoxylation

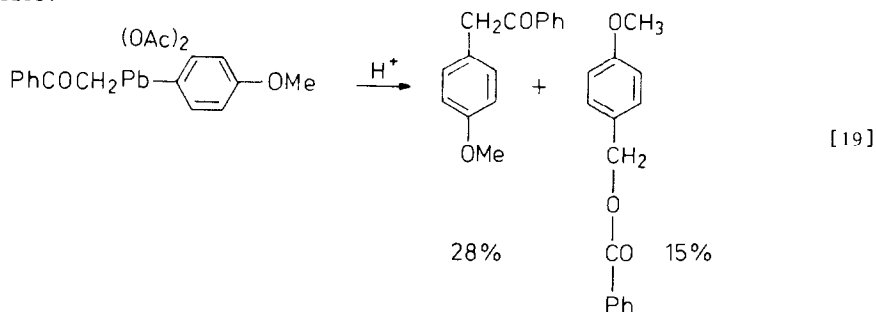
occurs, also anisole is found in about equal amounts. Steric hindrance plays an important role in both acetoxylation and arylation. Reaction of cyclic dienamines with ArPb(OAc)_3 led to oxidation: aromatization of the dienamine. 17 β -Acetoxy-3-morpholinoandrosta-3,5-diene gave arylation (40%) as well as acetoxylation (45%) at the 6-position: 6 α - and 6 β -aryl, but only 6 β -acetoxy (32). The reaction of Criegee [17] has been applied to the preparation of aryllead triacetates for use in situ to acylate substrates such as 2-oxocyclopentanecarboxylate and 2-nitropropane in yields of 62-78% (33).



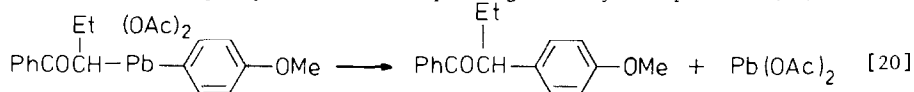
Aryllead (IV) tricarboxylates can act as plumbylating agents. *p*-Methoxyphenyllead triacetate reacts with the trimethylsilyl enol ether of acetophenone according to [18]. The coupling constant between ^{207}Pb and the methylene proton was 193 Hz.



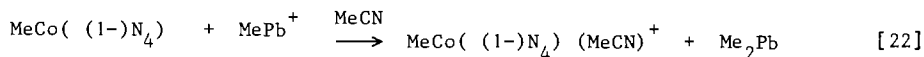
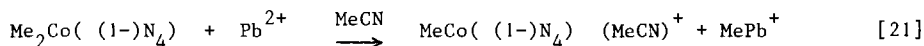
A number of phenacyllead (IV) derivatives has been prepared. These compounds have been allowed to react with trifluoroacetic acid and/or aromatic substrates. Reaction products were ArH , PhCOCH_2R , PhCOCH(R)Ar^1 and PhCOCH(R)Ar^2 in various ratios.



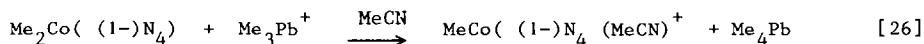
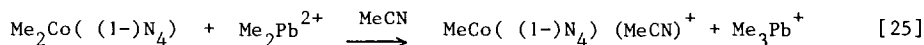
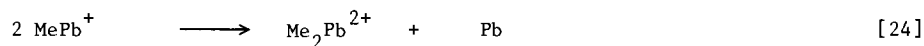
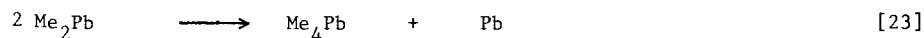
Thermolysis of a phenyllead (IV) compound gave only one product (34).



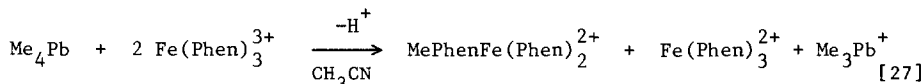
The methyl transfer from trans-dimethyl-cobalt (III) complexes to $\text{Me}_2\text{Pb}^{2+}$, Me_3Pb^+ and Pb^{2+} ions has been investigated. A series of subsequent methylations may take place:



Disproportionation of Me_2Pb or MePb^+ may occur :

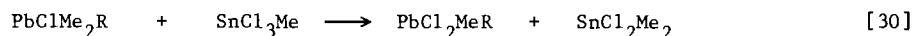
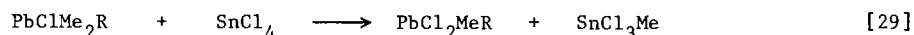
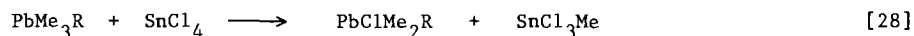


Evidence was shown for the presence of $\text{Me}_2\text{Pb(II)}$ and MePb(II)^+ species (35). Phenanthroline has been methylated during the oxidation of Me_4Pb with tris(phenanthroline)iron (III) in a yield of 96%.



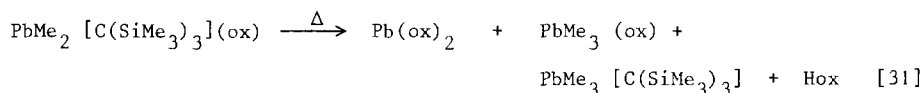
The reaction has been found to be a homolytic process leading to substitution at the 4-position of phenanthroline. Also the tris (α, α' -bipyridine) complex of iron (III), $\text{Fe}(\text{bpy})_3^{3+}$ reacted readily with Me_4Pb to afford the 4-methylbipyridine complex. Inner-sphere electron transfer has been shown to be the reaction mechanism (36).

Reactions of compounds $\text{PbMe}_3[\text{C}(\text{SiMe}_3)_3]$ (VII) have been studied. With equimolar ratios of VII and Cl_2, Br_2 or I_2 selective cleaving of one methyl group was achieved, while in the presence of excess of Cl_2 or Br_2 a second one was slowly cleaved. Redistribution reactions occurred with SnCl_4 .

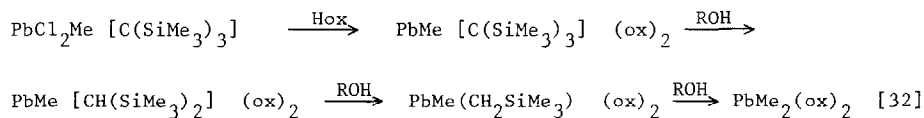


The compounds dialkyl PbCl_2 decomposed to PbCl_2 . Acetolysis reactions have also been investigated. Compounds $\text{PbMe}_2\text{R}(\text{OOCR}^1)$ were formed, no diesters were observed. Ester exchange was only achieved in the presence of a stronger acid. The formate ester decomposed on heating in benzene. ^1H - and ^{13}C -NMR data have been reported: a linear relationship between $^1\text{J}^{207}\text{Pb}-^{13}\text{C}$ and $^2\text{J}^{207}\text{Pb}-^1\text{H}$ was found. In the mass spectra no parent ions (p) were seen but intensive peaks of $(\text{p-Me})^+$ ions (37).

On prolonged heating the complex $\text{PbMe}_2[\text{C}(\text{SiMe}_3)_3](\text{ox})$ undergoes redistribution and reductive elimination reactions.

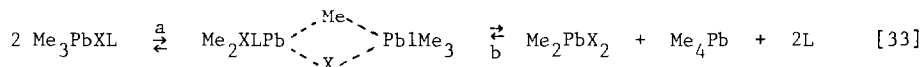


Synthesis and reactions of lead dioxinates have been investigated.



The probable change from 5 to 6 coordination in the mono- and dioxinato complexes results in two additional bands in the UV vis spectra near 260 and 380 nm; $^2\text{J}^{207}\text{Pb}-\text{C}^1\text{H}_3$ and $^1\text{J}^{207}\text{Pb}-^{13}\text{CH}_3$ values increase also considerably (38).

The kinetics of the redistribution reaction of $\text{Me}_{4-n}\text{Pb} [\text{M}(\text{CO})_5]_n$ ($\text{M}=\text{Mn}, \text{Re}; n=1,2$) have been described.



L^- ligand

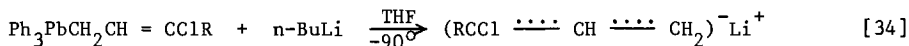
Conproportionation (b) was faster than disproportionation (a); both reactions were solvent dependent (39). Reaction of $\text{cis-CpW}(\text{CO})_2(\text{CS})\text{PbPh}_3$ ($\nu(\text{CS}) 1237 \text{ cm}^{-1}$) with H_2NMe smoothly transformed the CS to a $\text{C}=\text{N}-\text{Me}$ ligand in the products cis- and $\text{trans-CpW}(\text{CO})_2(\text{CNMe})\text{PbPh}_3$. The formation of the trans isomer is favoured in polar solvents (40).

The kinetics of exchange between PhLi and Ph_4Pb has been investigated in the systems: $\text{Ph}_4\text{Pb} + \text{PhLi}$, $\text{MePh}_4\text{Pb} + \text{PhLi}$, $\text{Ph}_4\text{Pb} + \text{MePhLi}$ and $\text{MePh}_4\text{Pb} + \text{MePhLi}$. The magnitudes of dipole moments, effective radii and charge separation in the starting materials and in the transition state were in agreement

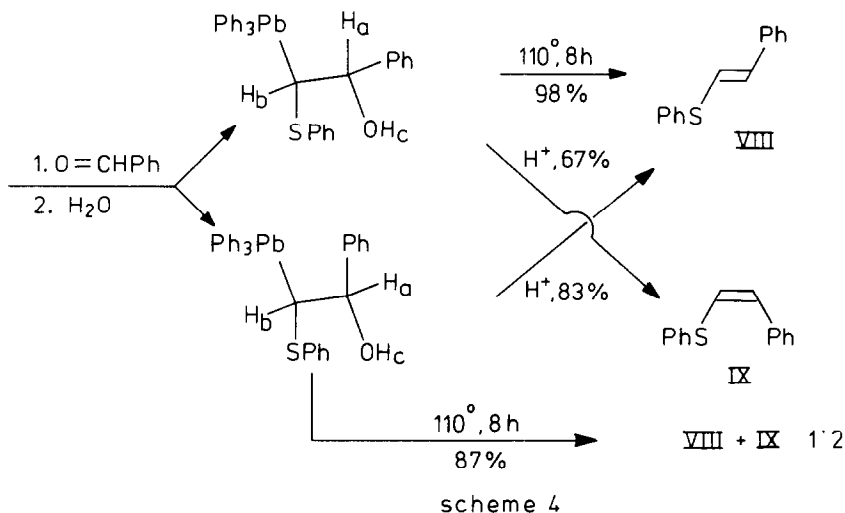
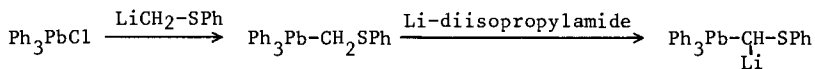
with the proposed molecular mechanism for the exchange reaction (41,42).

1,3-Dimetallopropanes $\text{Me}_3\text{M}(\text{CH}_2)_3\text{M}'\text{Me}_3$ (M and M' = C, Si, Ge, Sn and Pb) have been reacted with Ph_3C^+ to remove hydride. The rate constants followed a Hammett-type relationship. An increase in the reaction rate was found in the series $\text{Si} < \text{Ge} < \text{Sn} < \text{Pb}$. The transition state is favoured by vertical stabilization through σ - π conjugation (43).

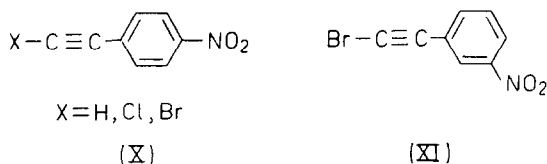
Ph_4Pb reacted with $\text{CH}_2=\text{CHCO}_2\text{H}$ and H_2PtCl_6 in HOAc to give 30% of $\text{PhCH}=\text{CHCO}_2\text{H}$ (44). Chloroalkyllithium (R=H) and gem-chloro(methyl) alkylolithium (R= CH_3), prepared from the corresponding Ph_3Pb compound, react readily with aliphatic and aromatic esters (45).



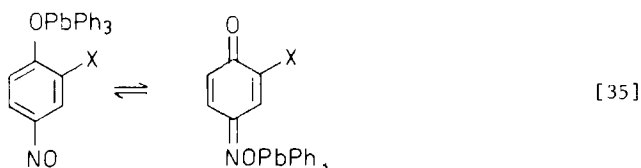
Stereospecific carbonyl olefination was achieved with the aid of a plumblyl leaving group (46).



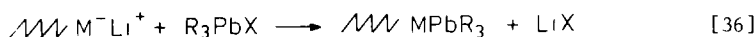
Irradiation of Ph_3PbH with nitrophenyl-acetylenes (X) and (XI) resulted in the formation of metalloxy-nitroxides as found by their ESR characteristics. The Ph_3Pb radical preferentially adds to the nitro group (47).



The nitrosophenol-quinone oxime tautomers have been investigated in PhMe , THF and Me_2SO . In the latter two solvents the equilibrium shifted towards the quinone oxime form. The nitrosophenol derivatives were ionized in Me_2SO or $(\text{Me}_2\text{N})_3\text{PO}$ (48,49). A temperature rise from 25 to 90° favoured the formation of the nitrosophenol compound.

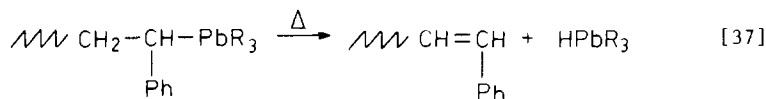


Polystyrene lead triethyl has been prepared according to [36].



M = monomer R = Et

Thermally β -hydrogen abstraction occurs yielding inactive products.



The reaction of $\sim\sim\sim \text{MPbR}_3$ with silver salts in the presence of methyl methacrylate has been examined. The use of crown ethers and transition metal salts has been shown to promote the formation of block copolymer via active polystyryl radicals (50).

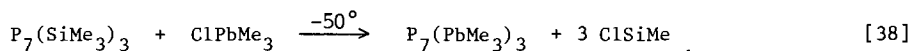
The unimolecular decomposition of compounds MMe_4 (M=C, Si, Ge, Sn and Pb) was studied with the aid of a neutral-fragment mass spectrometer. The most abundant neutral species was excited $\text{M}(\text{Me})_4^*$. Me radicals produced from these compounds by dissociative ionization are vibrationally excited in a state

corresponding to the first symmetrical stretch. Atomic ions Pb^+ are formed by dissociative ionization and from an autoionizing state (51). The kinetics of the gas-phase oxidation of organic compounds of silicon subgroup elements by ozone have been reported. The reactions of Me_4Pb and of binary mixtures with compounds containing other metals proved to be isokinetic in the gas and liquid phase (52).

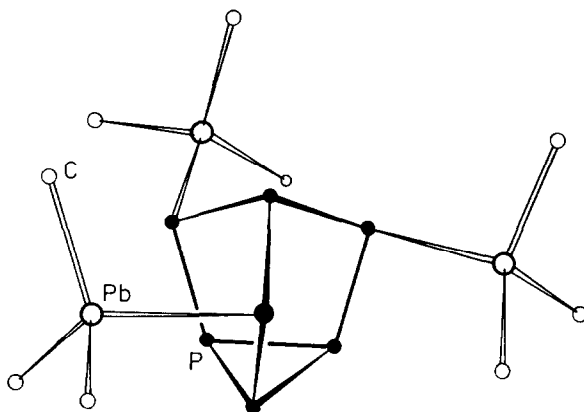
IV. Physical Chemistry

The crystal and molecular structure of $\text{Ph}_2\text{Pb}(\text{OAc})_2 \cdot 2\text{H}_2\text{O} \cdot \text{C}_6\text{H}_6$ has been described. Lead is coordinated by a distorted pentagonal bipyramid with the axial positions being occupied by the phenyl groups. The chelation of all four acetate groups is unsymmetrical with Pb-O bond distances in the range 2.32-2.72 Å. The Pb-O (H_2O) distance is 2.58 Å (53).

The colorless compound $\text{P}_7(\text{PbMe}_3)_3$ (m.p. 120-140° dec.) has been prepared according to [38].



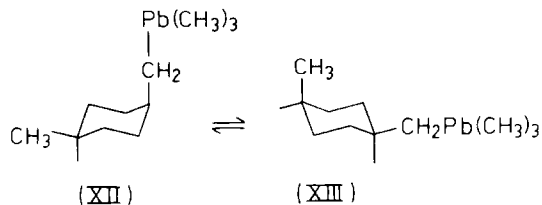
IR data have been presented: $\nu_{\text{Pb-Me}_3}$ 455 and 472 cm^{-1} , $\nu_{\text{P-Pb}}$ 115 and 310 cm^{-1} . The crystal structure of $\text{P}_7(\text{PbMe}_3)_3$ revealed that of this chiral molecule only one enantiomer is present in the crystal (P-Pb 261.1 pm) (54).



Relations between $^1\text{J}(\text{M}-^{13}\text{C})$ values (M=Hg,Sn,Pb) have been discussed for symmetrically and asymmetrically substituted compounds (55,56). The ^{195}Pt NMR spectrum at 21.31 MHz of $\text{cis-Pt}(\text{PPh}_3)_2(\text{Ph})(\text{PbPh}_3)$ has a central doublet of doublets resulting from coupling to the different phosphor atoms and two sets of ^{207}Pb satellites not symmetrically disposed about the central multiplet,

their median position being 180 Hz above the frequency of the main multiplet. The ^{207}Pb NMR spectrum at 20.84 MHz is of similar appearance with ^{195}Pt satellites unsymmetrically disposed about the central multiplet by 180 Hz to the lower frequency side of the spectrum. Spectra recorded at higher field (^{195}Pt at 42.70 and ^{207}Pb at 41.76 MHz) show that the asymmetry is decreased to 85 Hz supporting that the phenomenon is attributable to second-order coupling effects in the satellite spectrum rather than to a large isotope effect (57). ^{31}P -, ^{195}Pt - and ^{207}Pb -NMR data have been reported for a series of platinum complexes of the type $\text{cis-Pt}(\text{PPh}_3)_2(\text{R})(\text{PbR}_2\text{R}')$ and $\text{trans-Pt}(\text{PBu}_3)_2(\text{PbR}_3)_2$ ($\text{R}=\text{Ph}$, 4-MePh, 4-MeOPh, 4-ClPh, 4-FPh; $\text{R}'=\text{R}, \text{Br}, \text{I}$).

$\text{Cis-Pt}(\text{PPh}_3)_2(\text{Ph})(\text{PbPh}_3)$ $\delta(^{207}\text{Pb})$ -100 ppm, $^2\text{J}(^{207}\text{Pb}-^{31}\text{P trans})$ 3460 Hz, $^2\text{J}(^{207}\text{Pb}-^{31}\text{P cis})$ 260 Hz, $^1\text{J}(^{207}\text{Pb}-^{195}\text{Pt})$ 18380 Hz; $\text{trans-Pt}(\text{PBu}_3)_2(\text{PbPh}_3)_2$ $\delta(^{207}\text{Pb})$ 76 ppm, $^2\text{J}(^{207}\text{Pb}-^{31}\text{P cis})$ 240 Hz, $^1\text{J}(^{207}\text{Pb}-^{195}\text{Pt})$ 14395 Hz (58). Among inductive substituent constants from olefinic geminal ^1H -coupling constants also a value for PbR_3 was mentioned (59). ^{207}Pb spin-lattice relaxation studies of $\text{Pb}(\text{NO}_3)_2$, PbMe_4 and PbMe_3Cl indicated field dependence only for the latter compound. Interplay was demonstrated between the spin-rotation and the chemical-shift anisotropy mechanisms (60). ^{13}C -NMR data have been measured of cyclohexyl CH_2PbMe_3 compounds. $^1\text{J}(^{207}\text{Pb}-^{13}\text{C}) > ^3\text{J}(^{207}\text{Pb}-^{13}\text{C}) > ^2\text{J}(^{207}\text{Pb}-^{13}\text{C})$. ^3J vicinal coupling constants were largely regulated by the dihedral angle (Karplus type dependence). For the equilibrium of (XII) and (XIII) - ΔG° was found to be $1.81 \text{ kcal mol}^{-1}$ (61).



^{207}Pb -NMR spectra of seven coordinated lead chelates $\text{MePb}(\text{pan})(\text{X})$ ($\text{pan} = 1-(2\text{-pyridylazo})-2\text{-naphtholate}$, $\text{X} = \text{acetylacetonate}$, $\text{hexafluoroacetylacetonate}$, oxinate and acetate) showed ^{207}Pb values moving downfield in the order $\beta\text{-diketonates} > \text{oxinate} > \text{acetate}$ (62).

With the aid of relativistically parameterized extended Hückel calculations Pyykkö has interpreted nuclear spin-spin coupling constants in organo-lead compounds. It is concluded that the isotropic coupling constants are mainly "contact", i.e. $\text{AO}'\text{s}$ on both nuclei. The non-contact parts are important only for the anisotropic part of the K tensor. The large variations in $^1\text{K}(\text{PbM})$ and $^1\text{K}(\text{PbC})$ are due to changes in the mutual polarisability π . In particular the

negative values of ${}^1K(\text{PbC})$ in some $\text{R}_3\text{PbC} \equiv$ systems and the small ${}^1K(\text{PbPb})$ in Pb_2Me_6 are attributed to a node near the Pb nucleus in the highest occupied σ MO, whose variations mainly determine those of the total K. The sensitivity of these coupling constants to substituents is thus a frontier-orbital effect. Due to the relativistic stabilization of the Pb 6 s shell, most of the 6 s character resides in deeper MO's. Contributions from these to spin-spin coupling do not necessarily vanish, but are less sensitive to substitution (63).

Linear correlations have been described between the spectral intensities of $\nu(\text{Ar})$ and $\nu_s(\text{NO}_2)$ and the electron-donating properties of XMPb_n groups in compounds $\text{Ph}_n\text{MXC}_6\text{H}_4\text{NO}_2$ ($\text{M}=\text{Sn}, \text{Hg}, \text{Pb}, \text{Sb}$; $\text{X}=\text{O}, \text{S}, \text{NR}$). The electron donating properties depended on the nature of the solvent and on the heteroatom X; σ constants were determined (64). The general inertia defect was calculated for molecules as PbMe_4 and used to estimate rotational constants (65). Normal coordinate analysis of several organolead amines has been carried out: $(t\text{-C}_4\text{H}_9)_3\text{PbNH}_2$, $[(i\text{-C}_3\text{H}_7)_3\text{Pb}]_2\text{NH}$ and $[(\text{CH}_3)_3\text{Pb}]_3\text{N}$. In agreement with the ionic character of the Pb-N bond a Pb-N force constant of $1.95 \times 10^2 \text{ N/m}$ was calculated (66). The vibrational spectra of the organolead amines R_3PbNH_3 ($\text{R} = t\text{-C}_4\text{H}_9$), $(\text{R}_3\text{Pb})_2\text{NH}$ ($\text{R} = i\text{-C}_3\text{H}_7, t\text{-C}_4\text{H}_9, (\text{CH}_3)_3\text{CCH}_2$) and $(\text{R}_3\text{Pb})_3\text{N}$ ($\text{R}=\text{CH}_3$) and their ND - and ${}^{15}\text{N}$ -isotopomers have been assigned and discussed. $(t\text{-C}_4\text{H}_9)_3\text{PbNH}_2$, $\nu(\text{PbN})$ free 454 cm^{-1} , $\nu(\text{PbN})$ ass. 464 cm^{-1} ; on hydrolysis $\nu_{\text{as}}(\text{Pb}_2\text{O})$ 681 cm^{-1} of the plumboxide; $\nu(\text{Pb}_2\text{N})$ 603 cm^{-1} , $\nu_{\text{as}}(\text{Pb}_2\text{O})$ 665 cm^{-1} of the plumboxide of $[(i\text{-C}_3\text{H}_7)_3\text{Pb}]_2$ and $\nu_{\text{as}}(\text{PbO})$ 490 cm^{-1} of $(i\text{-C}_3\text{H}_7)_3\text{PbOH}$; $\nu_e(\text{Pb}_3\text{N})$ 590 cm^{-1} and $\nu_s(\text{Pb}_3\text{N})$ 545 cm^{-1} in $[(\text{CH}_3)_3\text{Pb}]_3\text{N}$, after hydrolysis $\nu_{\text{as}}(\text{Pb}_2\text{O})$ 565 cm^{-1} of $[(\text{CH}_3)_3\text{Pb}]_2\text{O}$ and $\nu(\text{PbO})$ 490 cm^{-1} of $(\text{CH}_3)_3\text{PbOH}$ (67). Modes of carboxylate binding in carboxylate complexes have been derived from IR frequencies (68).

Electron transfer reactions and their activation barriers have been investigated by chemical and electrochemical methods by Kochi et al. Activation barriers for homo- and heterogeneous processes may be related quantitatively by the Marcus theory if both proceed by outer-sphere mechanism. CIDEP has been applied to the quenching by Me_6Pb_2 and Ph_6Pb_2 of carbonyl triplets from various quinones. Cyclic voltametric data have been given of Et_4Pb and its oxidation by $\text{Fe}(\text{bpy})_3^{3+}$ (69-71).

The exchange ability of the $p\text{-FC}_6\text{H}_4\text{CO}_2$ group in mixtures of $p\text{-FC}_6\text{H}_4\text{CO}_2\text{H}$ and $p\text{-FC}_6\text{H}_4\text{CO}_2\text{MR}_n$ increased in the order $\text{SnPh}_3, \text{PbPh}_3 < \text{SbPh}_2 < \text{HgPh}, \text{SbPh}_4$ as found by ${}^{19}\text{F}$ -NMR (72).

The results of relativistic quantum mechanical calculations on the electronic states of Pb_2 allow interpretation of mass spectroscopic data (73). The fragmentation characteristics of the trimethylplumbyl cation have been

studied using mass analyzed ion kinetic energy and metastable monitoring techniques. Only losses of methyl groups and of CH_2 have been found. The importance of lead (II) leads to the dominance of C_2H_6 loss in both the low and high energy processes. The weakness of the lead-carbon bond is the factor influencing the fragmentation (74). Pulsed ion cyclotron double resonance spectroscopy has been employed to obtain the heat of formation of e.g. 1,1-dimethylplumbaethylene, derived from trimethylplumbyl cation in the gas phase: heat of formation 59 kcal mol^{-1} , π -bond energy 30 kcal mol^{-1} (75).

Values for the standard free energies of solutions have been tabulated: e.g. for Et_4Pb $-4.46 \text{ kcal mol}^{-1}$ in CCl_4 and $-1.24 \text{ kcal mol}^{-1}$ in nitromethane at 298 K (76). The two lowest Pb atom metastable levels $6p^2\ ^3P_1$ $6p^2\ ^3P_2$ have been studied by stimulated Raman scattering using a XeCl laser pump (77). Numerical calculations performed in order to explain experimental findings of Pb atoms in $\text{H}_2\text{-N}_2\text{-O}_2$ flames indicated bound excited states of PbH (78). High resolution phosphorescence spectra have been measured at 4.2 and 1.2 K for Ph_4Pb . The position of the 0-0 band was 29063 cm^{-1} at 4.2 K. The phosphorescence decay rate constant at 4.2 and 1.2 K was 303 s^{-1} (79). He (I) ultraviolet spectra have been studied for $(\eta^5\text{-C}_5\text{H}_5)_2\text{Pb}$ and $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Pb}$. Computed as well as experimental ionization energies are compared with those of tin analogues. The ionization energies pertaining to electron ejection from the central atom lone pair MO's are larger for the lead than the tin analogues. This has been attributed to the larger ring centroid-metal-ring centroid angle for the lead compounds, implying that the lead lone pairs involve more valence s character than the corresponding tin lone pairs (80).

V. Applications

Several reports have been published on the use of tetraalkylleads as antiknock additives in gasoline: dependence of the effectiveness on the distillation range and content of aromatic hydrocarbons (81), oxidation in a diesel engine (82), influence on the lubricating properties of oil (83), establishment of a standard of 1.10 g/gal. for the average Pb content of leaded gasoline in the USA (84), inhibition of oxidation during storage (85), and addition to ethanol containing fuels (86).

Bis (triphenylplumbyl) chromate has been used as a catalyst to polymerize ethylene: activity 44.5 g of polyethylene/g of catalyst per hour (87), and as a sensitizer in etch gravure pigment paper (88).

Thin polymer films prepared i.a. from trimethylvinyllead contained crystalline and amorphous phases (89). Polymers containing different amounts of highly dispersed lead have been prepared by thermal decomposition of

Ph_4Pb in several copolymers (90). Homogeneous Pb silicate films with various PbO content were formed on Si substrates by codecomposition of a vapour mixture of tetraethylorthosilicate and Et_4Pb (91). Controlled release surfaces containing Ph_3PbOAc have been investigated in the Corbicula fouling in power plants (92).

VI. Analysis

Hydride generation combined with atomic absorption spectrophotometry was used for the fractional determination of Et_3PbCl , Et_2PbCl_2 , inorganic Pb and total Pb in urine. The Pb hydrides formed by reaction with NaBH_4 were trapped at liquid N_2 temperature and fractionated by volatilization. Recovery rates and detection limits were Et_3Pb^+ 99.7%, 0.005 $\mu\text{g Pb}$; $\text{Et}_2\text{Pb}^{2+}$ 97.3%, 0.005 $\mu\text{g Pb}$ and Pb^{2+} 91.4%, 0.1 $\mu\text{g Pb}$ (93). Four novel cells for the determination of volatile organometallic compounds by coupled gas chromatography-flame atomic absorption spectrometry have been described. Detection limits for Et_4Pb and Me_4Pb were 17 μg (94). A method for the determination of Pb in gasoline by atomic absorption has been presented (95). Chromatographic assays of organoleads have been described (96). Glc has been applied for monitoring of the manufacture of organolead compounds (97) and for the determination of Et_4Pb in air (98). Specific element detection is used in the glc of PbR_4 compounds by microwave-induced and sustained He plasma atomic emission (99). Gas chromatography on PEG 400 and Aerosil and mass spectrometry were applied to identify impurities in Et_4Pb . Compounds such as BuEt_3Pb and iso-Bu Et_3Pb were found (100).

Based on selective organic phase extraction coupled with differential pulse electrochemical detection techniques, a process has been described for consecutive detection in natural waters of Me_4Pb , Et_4Pb , Me_3PbI , Et_3PbI , Me_2PbI_2 , Et_2PbI_2 and Pb (101). Ionic alkyl Pb species have been determined in marine fauna by differential pulse anodic stripping voltametry after toluene extraction. The detection limit was 0.01 mg/kg (102). Et_4Pb has been collected on activated carbon and determined by anodic stripping voltametry (103).

Lead in aqueous samples was extracted in CHCl_3 as the dithiocarbamate complex followed by methylation with MeLi to form Me_4Pb . In this way Pb^{2+} could be detected with a limit of 5 ng (104). Et_4Pb has been determined in wastewater (105). Ion-selective electrodes have been used for the potentiometric determination of Et_4Pb in gasolines (106). An assay for Et_4Pb in wastewater is based on the measurement of O_3 during its reaction with Et_4Pb in CCl_4 . The detection limit is 0.1 mg/l (107). Gas detection sensors resistant

to leaded gasoline have been developed (108).

VII. Wastes, Pollution and Industrial Hygiene

The removal of tetraalkyllead compounds from petrol has been advocated in discussion on the health hazards of leaded gasoline (109-120). The current acceptable limit of $1.4 \mu\text{mol/l}$ ($30 \mu\text{g}/100 \text{ ml}$) may be too high for children on the basis of slight but statistically significant differences on psychological testing and behavioural rating between two groups of children with different low blood lead concentrations (110).

Alternatives for lead in petrol have been discussed (116). In addition to lead from automotive emissions, paint applied to steel structures e.g. bridges is a thusfar less well recognized source of lead exposure (121). Lead emissions from gasoline combustion have been discussed (122-124). Average atmospheric R_4Pb concentrations in Antwerp, Belgium were $\leq 13\%$ of the inorganic Pb concentrations. All 5 tetraalkylleads with Et or Me groups have been detected. The alkyllead pattern reflected the average gasoline used. No indications of natural methylation processes for inorganic Pb compounds have been found. Elimination of R_4Pb occurs probably via tri- and dialkylated lead salts (123). Near central Glasgow, Scotland, the average 24 h tetraalkyllead concentration was 32 ng/m^3 . The daytime maximum concentration of 144 ng/m^3 greatly exceeded the overnight levels of $2.7\text{--}30 \text{ ng/m}^3$. At quieter urban sites and a rural site 24 h tetraalkyllead levels averaged only 16 and 3.9 ng/m^3 , respectively (124).

After the Cavtat incident it has been found that *Mytilus galloprovincialis* accumulated more alkylleads than *Halocynthia papillosa*. In *Phallusia mamillata* 1.06-1.24 ppm of alkylleads and 28.51-34.48 ppm of mineral lead were present (125).

The effectivity of various types of ozonization apparatus in treating tetraethyllead containing wastewaters is discussed (126).

Regeneration of lead catalysts in the treatment of exhaust gases from gasoline engines is reported (127).

Contrary to earlier reports new results indicate that methylation of lead (II) acetate does not occur in the environment to form tetraalkylleads. Me_4Pb was formed in tests in which aluminium foil was present in a mixture of aqueous lead (II) acetate and MeI by reaction of the finely divided lead formed with MeI. No Me_4Pb was observed in the absence of aluminium (128). MeI reacted with lead metal in an aqueous medium to Me_4Pb . When MeI was reacted with Pb(II) salts in aqueous media with or without the presence of magnesium, no volatile lead containing products could be detected by head space analysis (129).

The photolytic decomposition of Et_4Pb into Et_3Pb and Et_2Pb derivatives and into Pb has been investigated. Et_3Pb derivatives, the toxic substances formed upon illumination of Et_4Pb , cause the several inhibiting effects in cultures of *P.malhamensis* poisoned by Et_4Pb (130). The fate and toxicity of tetraalkyllead and derivatives in aquatic environments have been discussed. Triethyllead compounds are extremely toxic and accumulate in the aquatic medium owing to their water solubility (131). The formation of Me_4Pb from Me_3PbOAc increased with increasing pH and proceeded through both biological and chemical methylation mechanisms (132).

VIII. Toxicology

Chemical specifications, determination, toxicity and octanol-water partition coefficients of alkyllead compounds have been listed and discussed (133). A series of compounds has been synthesized in order to study their activity towards cockroaches and *Staphylococcus aureus* and *Sorsena-lutea* i.a. $\text{Ph}_3\text{Pb}(\text{N}=\text{PPh}_3)$ (134).

In the continuing discussion on lead in petrol the relation between low-level lead exposure and childhood intellectual development has been questioned (135). The mutagenity and neurotoxicity of lead additives have been discussed. Et_3PbCl increased the rate of sister chromatide exchange in human lymphocytes. Long-term health implications of the addition of lead to petrol remain to be assessed in detail (136). With respect to lead in petrol it was emphasized that an additional detrimental effect on neuro-behavioural and neuropsychological functions may occur in children (137).

Female mice were injected intraperitoneally (ip) with Et_3PbCl (3.0 or 6.0 mg/kg body weight) once a day and on days 3-4 after mating. At the time of the blastocyst implantation the plasma level of progesterone was significantly lower in females given 3.0 mg/kg and the plasma levels of 17 β -oestradiol and progesterone were significantly lower in females given 6.0 mg/kg than in control animals. Probable causes could be: (i) inhibition of synthesis or release of gonadotropic releasing hormone (GnRH) in the hypothalamus (ii) inhibition of synthesis or release of luteinizing hormone (LH) and/or follicle stimulating hormone (FSH) (iii) reaction between organic lead and gonadotropins in plasma and (iv) direct effect on the synthesis of steroids in the gonads and/or adrenals (138). The acute toxicity of Ph_3PbOAc and $\text{Bu}_2\text{Pb}(\text{OAc})_2$ in the rat appeared to result from their irritating properties to membranes regardless of the route of administration. A single oral dose inhibited gastric emptying with resulting fluid distension. Analysis of gastric fluid from pyloric ligated rats following an oral organolead dose

showed increased concentrations of Na^+ and glucose and decreased concentrations of H^+ and K^+ . Dilation of the gastric mucosal microcirculation was also observed along with desquamation of surface mucous cells which resulted in shallow erosions of the upper portions of the gastric glands. Oral dosing of organoleads causes erosion of the gastric mucosa and increases permeability of the mucosal microcirculation, leakage of plasma constituents into interstitial fluid and ultimately the gastric lumen with back diffusion of H^+ . Such a lesion would impair gastric function and reduce normal food and water consumption. Starvation and dehydration may then be important factors for death that follows oral dosing with organoleads (139).

Rabbits were intravenously (iv) injected with Et_4Pb (12 mg/kg) and the fate of Et_4Pb was studied. One day after injection total Pb in the urine consisted of 69% Et_2Pb derivatives, 27% inorganic Pb salts and 4% Et_3Pb derivatives; the ratio of the compounds remained unchanged even after 7 days. Total Pb in the feces consisted of 85% inorganic Pb salts, 9% Et_2Pb derivatives and 6% Et_3Pb derivatives 2 days post injection; the ratio changed after 7 days to 95%, 1% and 4%. After 24 h Et_3Pb derivatives accounted for 84% of the total Pb in the liver, 68% in the kidney and 59% in the blood, while Et_2Pb derivatives accounted for 93% of the total Pb in the bile and inorganic Pb salts made up 90% in the cecal, the colonic and the rectal contents. When Et_2Pb derivatives were incubated with the cecal contents, mineralization within the incubation time occurred. Apparently Et_2Pb compounds are formed by organ metabolism from Et_4Pb and eliminated into urine and bile. Et_2Pb compounds from the bile are converted into inorganic Pb salts in the intestines (140).

Muscle tissue of mice intoxicated with Me_4Pb and Et_4Pb showed more anomalies than after intoxication with $\text{Pb}(\text{NO}_3)_2$. Dense bodies of various size and structure were observed between myofibrils in direct contact with the mitochondria and the reticulum sarcoplasmatic tubules. Also thickening of the inner part of the arteries was seen (141). Et_3PbCl was given ip to rabbits at doses of 1, 1.5 and 2.5 mg/kg/day during alternating days or weekly. The largest accumulation was found in liver and kidney. Blood levels of organic Pb disappeared after the first day. Only chronic exposure to organic Pb results in its accumulation in the brain (142). A dose dependent decrease in the content of glutathione was found in the brain of rats following treatment with Et_3Pb compounds (143). The effect of Et_3PbCl on the membrane bound SH-enzymes, Na,K-dependent-ATPase and pyruvate dehydrogenase (PDH) were studied in relation to the effect on the galactosyl ceramide sulfotransferase (CST). Morphologic changes were induced as well as a reduction of CST activity. A less pronounced reduction of Na,K-dependent-ATPase was found. PDH activity was not affected (144). The effectiveness of organolead compounds as inhibitors

of dopamine sensitive adenylate cyclase (competition for the DA-1 receptor) and of basal adenylate cyclase has been investigated. With trisubstituted alkyllead compounds the inhibition was a function of the chain length of the hydrocarbon attached to lead. R_3Pb derivatives were more effective inhibitors of the first system, $PhPb(OAc)_3$ inhibited more effectively the second adenylate cyclase system (145).

Cultured cells from chick embryo brains were studied for their sensitivity to Et_3PbCl . The [^{35}S] sulfate labeling of sulfatides was reduced to 50%, the [3H] serine labeling of cerebroside with α -hydroxy fatty acids was not influenced and that with non-hydroxy fatty acids was 40% inhibited in 1- and 2- but not in 3-week old cultures. Apparently neurons are more sensitive than glia cells and the labeling of sulfatides can be affected more than that of cerebroside (146). The ip neurotropic selectivity in mice of several toxic compounds has been found largest for Et_4Pb (147). The effect of Et_3Pb derivatives on the entry of newly synthesized proteins into myelin was studied in an in vitro system of brain stem slices prepared from actively myelinating young rats. A specific effect towards posttranslational metabolism of integral myelin metabolism was observed (148).

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IX. References

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