LEAD

ANNUAL SURVEY COVERING THE YEAR 1974

J. Wolters

Rijksuniversiteit Leiden (The Netherlands)

Reviews

In the following reviews specific aspects of organolead chemistry have been dealt with: organolead compounds [1,2,3]; tetraalkyllead poisoning [4]; characteristic vibrational frequencies of i.a. organolead compounds [5]; lead-boranes [6]; gas chromatography [7] and radiochemistry [8] of organolead compounds; ^{13}C NMR chemical shifts and coupling constants of organolead compounds [9]; structure determination of organolead compounds [10,11]; cycloalkenes containing heterocyclic lead [12]; organolead compounds and living organisms [13]; organoleadperoxides [14]; fluxional main group IV organometallic compounds, including some organolead compounds [15]; O-organometal hydroxylamines and oximes including organolead [16]; organolead electrochemistry [17,18,19]; decomposition of organolead compounds [20]; organolead intermediates in catalytic reactions [21].

Preparations

Williams and Cook [22] have prepared alkyllead-silicon compounds as follows:

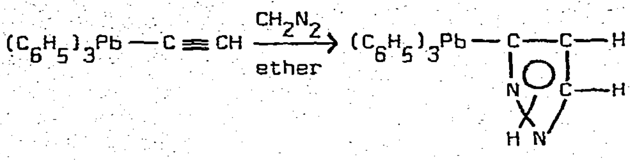
$$RCl + Mg + PbCl_2 \longrightarrow R_3PbMgCl \qquad (1)$$

$$R_3PbMgCl + ClCH_2SiMe_3 \longrightarrow R_3PbCH_2SiMe_3 \qquad (2)$$

(R = Me, Et)

Lead, Annual Survey covering the year 1973 see J. Organometal. Chem., 95(1975)291-300.

Guillerm et al. |23| in their study on 1,3-dipolar cycloaddition reactions of diazoalkanes to group IV B, V B and VI B acetylene derivatives prepared a (triphenylplumbyl) pyrazole.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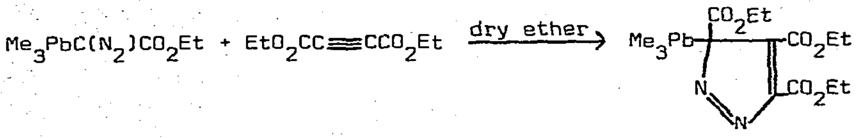
Grüning and Lorberth |24| have continued their study on organometallic diazoalkanes. Cycloaddition reactions of trimethyllead diazoacetic acid ethyl ester, $Me_3PbC(N_2)CO_2Et$, with activated alkenes and acetylenes are described, e.g. (eqn.4):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The structure of the resulting organometallic pyrazoles and pyrazolines is discussed on the basis of the IR, Raman, PMR and mass spectra.

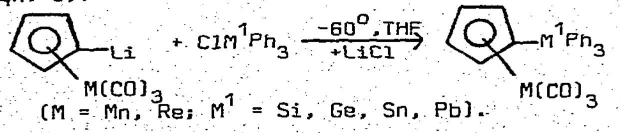
Organolead diazo compounds |25| are prepared by treating silazane derivatives of lead with appropriate diazo compounds (eqn.5).

$$Me_3PbN(SiMe_3)_2 + HC(N_2)R \longrightarrow Me_3PbC(N_2)R + HN(SiMe_3)_2 \quad (5)$$

$(R = CO_2C_2H_5,\ COCH_3,\ COC_6H_5,\ Me_3Pb)$

The compounds are characterized by their ^1H NMR, mass and IR spectra and elemental analyses.

Nesmeyanov et al. |26| report on the preparation and properties of triphenyllead derivatives of manganese and rhenium π-cyclopentadienyltricarbonyls (eqn. 6).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$(M = Mn, Re;\ M^1 = Si, Ge, Sn, Pb).$

In the triphenyllead derivatives the C_{Cp} - Pb bond is broken rapidly (10-15 min) under the influence of HCl, with the quantitative liberation of π-cyclopentadienyltricarbonylmanganese and π-cyclopentadienyltricarbonylrhenium.

Chelated derivatives of salicylaldehyde, acetylacetone and 8-hydroxyquinoline with lead (II), diphenyllead (IV) and triphenyllead (IV) have been obtained by Gopinathan and Pandit |27| by the reaction of HL or NaL with PbO, Ph_2PbCl_2, or Ph_3PbCl. IR spectra are discussed.

A patent |28| describes the preparation of organometallic phosphites, $(RO)_2POMR^1_3$ (R,R^1 = alkyl, aryl; M = Group IV A metal), by treating the corresponding $[(RO)_2P]_2O$ with the appropriate $R^1_3MOR^2$ (R^2 = alkyl) under an inert gas atmosphere.

Trimethyllead methyl-dichlorophosphate (eqn. 7) was prepared by Dehnicke et al. |29|. IR and Moessbauer spectra suggest that the compound is polymerized through O - P - O bridges whereby the Pb atom has coordination no. 5 (D3h).

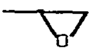
$$Me_3PbCl + [Cl_2P(O)]_2O \longrightarrow Me_3Pb(O_2PCl_2) \qquad (7)$$

Rzaev et al. |30| have described the synthesis and free radical copolymerization of triphenylplumbyl cinnamate. Triphenylplumbyl cinnamate was prepared by reacting triphenylplumbanol with cinnamic acid.

Barbieri and Borelli |31| have reinvestigated the synthesis of triphenylvinyllead (eqn. 8).

$$\underset{(A)}{H_2C = CHMgBr} + \underset{(B)}{Ph_3PbCl} \xrightarrow{THF} Ph_3PbCH = CH_2 + MgBrCl \qquad (8)$$

The yield was increased to 90% by increasing the molar (A)/(B) ratio up to 2.5:1.

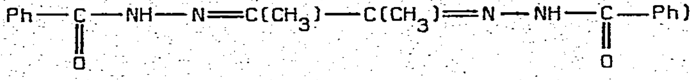
Triphenyllead epoxide, Ph_3Pb, was prepared by Barbieri |32|, by the epoxidation of triphenylvinyllead with F_3CCO_2OH (yield 31%).

In his studies |33,34| on organometallic-mercury compounds, $R_3C - Hg - MR^1_3$ (M = Si,Ge,Sn,Pb), Mitchell describes the synthesis of N-plumbylketeneimines by transmetalation of the corresponding N-silylketeneimines.

$$PhCH{=}C(CN)_2 + t\text{-}BuHgSiMe_3 \xrightarrow{C_6H_6/CH_2Cl_2} PhCH\text{-}t\text{-}Bu.C(CN){=}C{=}NSiMe_3 + Hg \qquad (9)$$

$$PhCH\text{-}t\text{-}Bu.C(CN){=}C{=}NSiMe_3 + R_3PbOR^1 \longrightarrow PhCH\text{-}t\text{-}Bu.C(CN){=}C{=}NPbR_3 + Me_3SiOR^1 \qquad (10)$$

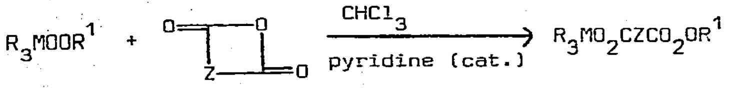
(R = Alkyl; R^1 = Me, COMe)

The chelating behaviour of diacetylbisbenzoylhydrazone (H_2DB) with Sn(IV), Pb(II) and Pb(IV) has been reported by Cefalù et al. |35|. The diphenyllead complex, Ph_2PbDB (H_2DB =  $Ph{-}\underset{\underset{O}{\|}}{C}{-}NH{-}N{=}C(CH_3){-}C(CH_3){=}N{-}NH{-}\underset{\underset{O}{\|}}{C}{-}Ph$), was prepared by the reaction of Ph_2PbX_2 with the base in its dianion form in dry methanol. Vibrational, electronic and PMR data indicate that the ligand is tetradentate in all of the complexes except $Sn(DB)_2$.

1:1 adducts of Ph_2PbCl_2 and Me_2PbCl_2 with N,N'-ethylenebis (salicylideneiminato) nickel (II) and bis(β-mercaptoethylamine) nickel (II) were synthesized by Pellerito et al. |36|. Their configurations were investigated in the solid state by IR and electronic spectroscopy and by magnetic measurements.

Tetraphenylarsonium and tetramethylammonium salts of the complex anions $Ph_3Pb(N_3)_2^-$, $Ph_3Pb(N_3)(NCS)^-$, $Ph_2Pb(N_3)_4^{2-}$ and $Ph_2Pb(N_3)(NCS)_2^-$ were prepared and characterized |37|. Trigonal and octahedral structures were proposed.

Razuvaev et al. |38| have prepared organometal salts of peroxy ester acids as follows (eqn. 11):

 (11)

(R = alkyl, aryl; Z = alkylene; R^1 = tert-alkyl; M = group IV A metal)

Me_4Pb or Et_4Pb is prepared from finely powdered metallic Pb, an alkaline earth metal, esp. Mg, and the corresponding alkyl halide at 0-100° in the presence of Bu_4NI, and an ether, e.g., $EtO(CH_2)_2\ O(CH_2)_2\ OEt$ |39|.

The yield and thermal stability of Et_4Pb from the reaction of a Pb alloy with an alkali metal and EtCl with subsequent distillation with superheated steam in the presence of an $FeCl_3$-based additive to prevent nodulizing of the solid mass, were improved by using 0.3-0.8 wt. % $FeCl_3$ and 0.01-0.03 wt. % Nekal BX as the additive |40|.

Hackett and Manning |41| attempted to prepare the compound $[n-Bu_3\ PCo(CO)_3]_3PbH$.

Ephritikhine and Levisalles |42| have isolated a lead (IV) containing intermediate from the reaction of $PbF_2(OAc)_2$ and pregnenolone. Some of its reactions are described.

Reactions

Batalov |43| has studied the reaction of tetraethyllead with ethyl-^{14}C bromide in sealed evacuated molybdenum-glass ampules. $(C_2H_5)_4$ Pb and $^{14}C_2H_5Br$ reacted at 140^{o} to form $(C_2H_5)_3$ PbBr, $PbBr_2$, gas and C_4H_{10}. The amount of hydrocarbon increased with duration of reaction. Examination of the tag position indicated the following steps:

$$(C_2H_5)_4\,Pb \longrightarrow (C_2H_5)_3\,Pb^{\cdot} + C_2H_5^{\cdot} \tag{12}$$

$$(C_2H_5)_3\,Pb^{\cdot} + {}^{14}C_2H_5Br \longrightarrow (C_2H_5)_3\,PbBr + {}^{14}C_2H_5^{\cdot} \tag{13}$$

$$(C_2H_5)_3\,PbBr + C_2H_5^{\cdot}\,({}^{14}C_2H_5^{\cdot}) \longrightarrow C_4H_{10}\,({}^{14}C_4H_{10}) + (C_2H_5)_2\,Pb^{\cdot}Br \tag{14}$$

$$(C_2H_5)_2\,\dot{P}b^{\cdot}Br + {}^{14}C_2H_5Br \longrightarrow (C_2H_5)_2\,PbBr_2 + {}^{14}C_2H_5^{\cdot} \tag{15}$$

$$(C_2H_5)_2\,PbBr_2 \longrightarrow 2C_2H_5^{\cdot} + PbBr_2 \tag{16}$$

Clarke and Wardell |44| report on the reactions of aryl triphenyllead sulphides, Ph_3PbSAr, with halogens, sulphur (II) halides, carbon halides and mercury halides. Unlike the analogous tin and germanium reactions, the reactions of the organolead sulphides do not lead exclusively to cleavage of the metal-sulphur bond. Ph-P cleavage, decomposition to Pb (II) inorganic species and photochemical reaction with e.g. CCl_4, were observed. The reactions of R_3MSAr ($R \neq H$; M = C, Si, Ge, Sn, Pb) are compared.

Gardner and Kochi |45| emphasized the importance of one-electron transfer in the reactions of metal alkyls in the facile reactions between Me_nPbEt_{4-n} ($4 \geqslant n \geqslant o$) and hexachloroiridate (IV). Kinetic and product studies are augmented by electrochemical oxidation potentials, and spin-trapping experiments to support cation radicals $R_4Pb^{\overset{+}{\cdot}}$ as the key intermediates from which alkyl transfer proceeds.

Scheme :

$$R_4Pb + Ir\,(IV)\,Cl_6^{2-} \xrightarrow{k} R_4Pb^{\overset{+}{\cdot}} + Ir\,(III)\,Cl_6^{3-} \tag{17}$$

$$R_4Pb^{\overset{+}{\cdot}} \xrightarrow{fast} R^{\cdot} + R_3Pb^{+} \tag{18}$$

$$R^{\cdot} + Ir\,(IV)\,Cl_6^{2-} \longrightarrow RCl + Ir\,(III)\,Cl_5^{2-}\text{ , etc.} \tag{19}$$

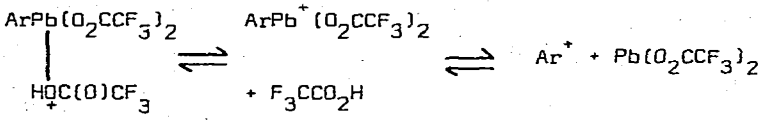
Bell et al. [46] have continued their study on the chemistry of aryllead (IV) tricarboxylates (eqn. 20):

$$RC_6H_4Pb(OAc)_3 + F_3CCO_2H \xrightarrow{r.t.} RC_6H_5O_2CCF_3 \qquad (20)$$

$$77.6 - 96.7\%$$

(R = p-Me, H, p-Ph, p-OMe, m-OMe, o-Me)

They propose that the conversion of the aryllead compounds into the aryltrifluoroacetates proceeds through the aryl cation, and involves the following equilibria (eqn. 21):



$$\begin{array}{c} ArPb(O_2CCF_3)_2 \\ | \\ H\underset{+}{O}C(O)CF_3 \end{array} \rightleftharpoons \begin{array}{c} ArPb^+(O_2CCF_3)_2 \\ + F_3CCO_2H \end{array} \rightleftharpoons Ar^+ + Pb(O_2CCF_3)_2 \qquad (21)$$

The preparation of some para-R-phenyllead triacetates by direct plumbylation of PhR with $Pb(OAc)_4$ and a haloacetic acid followed by metathesis with AcOH, is reported. Biaryls are synthesized by reaction of aryllead (IV) tricarboxylates with aromatic compounds [47], e.g. p-$FC_6H_4Pb(OAc)_3$ with F_3CCO_2H in the presence of mesitylene gave 67-88% 2,4,6-$Me_3C_6H_2C_6H_4F$-p.

The reaction of Me_3Al with PbS was studied by Boleslawski et al. [48].

$$4Me_3Al + 2PbS \xrightarrow{xylene} Me_4Pb + Pb + 2(Me_2Al)_2S \qquad (22)$$

Under the experimental conditions the maximum degree of conversion of the Me groups was 22.5% (0.5 h, 135°). The products were analyzed by NMR. An intramolecular alkylation mechanism was proposed.

Cookson et al. [49] reported on the structures and thermal decomposition of some diphenyllead bispolyfluorobenzoates. $Ph_2Pb(O_2CR)_2$ ($R = C_6F_5$, p-$MeOC_6F_4$ or p-$EtOC_6F_4$), obtained from $Ph_2Pb(OAc)_2$ and the appropriate polyfluorobenzoic acids, are considered to have associated structures with bridging bidentate carboxylate groups in the solid state and to be predominantly monomeric with chelating carboxylate groups at low concentration in $CHCL_3$. Thermal decomposition of e.g. $Ph_2Pb(O_2CC_6F_5)_2$ in boiling pyridine gave $Ph_2Pb(C_6F_5)_2$ and a low yield of $Ph_3PbC_6F_5$. The decomposition products are formed by competing decarboxylation, rearrangement, and (under vacuum) homolysis reactions of the diorganolead dicarboxylates, and by further reactions of the rearrangement products.

Seyferth et al. [50] have prepared gem-dichloroallyllithium as follows:

$$Ph_3PbCH_2CH = CCl_2 + n - BuLi \xrightarrow[THF]{-95^o} n - BuPbPh_3 + Li(CCl_2CHCH_2) \qquad (23)$$

Metal-proton and metal-metal exchange reactions have been studied by PMR for triphenyllead derivatives of thiophenol, 2-methylthiophenol, 2,6-dimethylthiophenol and benzylmercaptan [51]. The reaction pathway involves an associative mechanism with a cyclic transition state.

Physical Chemistry

Heumann et al. [52] studied fragmentations and ion yields of the tetramethyl compounds of silicon, germanium and lead in dependence on the electron impact energy. In all cases the Me_3M^+ ions showed the highest intensity in the complete 15-100 eV electron impact energy range apparently due to their even electron no. The ion yields of the sum of all fragments containing a metal atom reached a maximum for Me_4Ge and decreased from Me_4Ge to Me_4Pb and could be related to the electronegativities.

Husain and Littler [53] described a kinetic study of lead atoms (6 $^3P_0$) by atomic absorption spectroscopy. Pb(6^3 P_0) is generated by the pulsed irradiation of $Pb(Et)_4$ and monitored photoelectrically in absorption by time-resolved attenuation of atomic resonance radiation at λ= 283.3 nm.

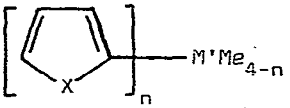
Pellerito et al. [54,55] concluded from PMR, infrared and ultraviolet spectra of the solid N,N'-ethylenebis (acetylacetoneimine) complex of Ph_2PbCl_2 that it had an octahedral bipyramidal configuration, in which the planar Ph_2PbCl_2 moieties were axially bridged by the imino ligand. Osmometry and conductivity of the complex in MeOH indicated that the complex was dissociated in free ligands and solvated Ph_2PbCl_2.

Mass spectra of certain spiro compounds with a group IV B element central atom, e.g. 4-plumbaspiro|4.4|nonane, were recorded by Orlov et al. [56] and correlated with structure.

Tsvetkov et al. [57] have determined mutual solubility and critical temperatures of the dissolution of alkyl compounds of silicon, germanium, tin, and lead with methanol, aniline, and diethyl oxalate. Viscosity and density are given for e.g. Et_4Pb. The critical solution temperatures of solutions containing Et_4M decreased with increasing at. no. of M.

Cooper et al. [58] have reported ^{207}Pb chemical shifts for compounds $Me_{4-n}PbX_n$ (n = 1-4, X = 4-FC_6H_4; n = 1,2,4, X = Me C$\equiv$C; n = 1,4, X = CH_2= CH; n = 1, X = Cl, MeO, $MeCO_2$). ^{1}H and ^{19}F NMR spectra of the 4-fluorophenyllead compounds are also given. The trends in ^{207}Pb chemical shifts are compared with those for ^{29}Si and ^{119}Sn chemical shifts in Si and Sn analogues. A correlation between δ(^{207}Pb) and δ(^{19}F) for the fluorophenyl derivatives is discussed. This correlation supports the theory that the ^{207}Pb chemical shifts in these compounds are strongly influenced by π-bonding effects (pπ - dπ bonding). The ^{207}Pb chemical shifts of propynyllead compounds have been measured in both benzene and pyridine solution. In all cases the ^{207}Pb resonance moved to higher field in pyridine solution, the maximum solvent shift being +13.4 ppm for $Pb(C\equiv CMe)_4$, suggesting that this had the strongest acceptor properties.

Doddrell et al. |59| continued their study on ^{13}C NMR of organometallics. ^{13}C chemical shift variation within a series of phenyl, furyl and thienyl organometallics, e.g. $Ph_{4-n}MMe_n$ (n = 0,2,3; M = Si, Ge, Sn, Pb, C) and



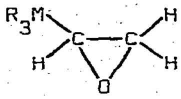
(X = O, S; M' = Sn, Pb, Hg; n = 1,2,4) are best understood rather in terms of alkyl and aryl substituent effects on ^{13}C chemical shifts than of variations in dπ-pπ metal-aryl interactions. Large changes in ^{13}C-metal coupling constants are observed suggesting that other factors besides the s-character of the C-metal bond are responsible in determining the coupling constants.

^{13}C chemical shifts and coupling constants are reported for Me_3PbCH_2Ph |60| The value of J(^{207}Pb - ^{13}C (4)) exceeds that of J(^{207}Pb - ^{13}C (3)): 32.4 Hz vs. 26.4 Hz. This phenomenon has its origin in carbon-metal (σ-π) hyperconjugation.

Sorriso et al. |61| determined dipole moments and molecular conformations of the four series $C_6H_5SM(CH_3)_3$, m- and p-$ClC_6H_4SM(CH_3)_3$ and $|(CH_3)_3M|_2S$ (M = C, Si, Ge, Sn, Pb). From the results for the meta derivatives it is inferred that the phenyl ring in the asymmetric compounds is forced almost 90° out of the plane containing the CSM atoms, ruling out a phenyl-sulphur conjugative interaction.

Samodelov and Bryuzgina |62| have concluded from measurements of the cathodic polarisation of a lead electrode in acid solution that the main process on the electrode is a chemical reaction involving the formation of lead hydrides.

In their PMR study on metal-substituted oxiranes, Barbieri and Taddei |63| also reported on the proton signals of



(M = Pb; R = Ph).

Chemical shifts and coupling constants are discussed in terms of possible electronic interaction between M and the oxirane ring.

Yushin and Mikheev |64| have calculated the thermodynamic functions of gaseous PbH_4 in the range 298-1500° K.

A pseudopotential method |65| was applied to calculate the valence local orbitals of the ground states of the hydrides XH_4 (X = C, Si, Ge, Sn, Pb). The computed values of the bond lengths X-H and the force constants for the totally symmetrical vibrational mode agree with available experimental values. A correlation between the valence orbital parameters and the electronegativity of the X atoms was found.

Barker and Clarke |66| made an attempt to determine the stability constants for the chloro complexes of triethyllead, $Et_3PbCl_n^{1-n}$, in varying aqueous acid solutions using an amine extraction technique at 20°.

Brown et al. |67| studied the reduction of EtI on rotating disk Pb cathodes in DMF and in EtOH by means of steady-state polarization data and analysis of the product, Et_4Pb. Under optimum conditions, which include the use of quaternary ammonium salts, the reaction is essentially quantitative. Inferior yields are obtained when EtOH is used as solvent.

In their study on vibrational spectra and structure of some aromatic derivatives of mercury,tin and lead, Rodionov et al. |68| have determined the IR spectra in the 200-3500 cm^{-1} range for aryllead compounds, $Ar_2Pb(OAc)_2$ ($Ar = Ph, p\text{-}MeC_6H_4$, 1-naphthyl, $p\text{-}ClC_6H_4$), and Ph_4Pb.

Beckwith et al. |69,70| offer evidence for the intermediacy of organolead compounds in the lead tetraacetate decarboxylation of tertiary carboxylic acids, e.g. 2,3,3-trimethyl butanoic- and adamantane-2-carboxylic acid.

Gash et al. |71| have reported on the synthesis, structure, and bonding of bis(tetrachloroaluminato)-π-benzene lead (II) - benzene,

$\pi - C_6H_6Pb(AlCl_4)_2 \cdot C_6H_6$:

Pb - C (benzene ring) 3.08 - 3.13 Å and Pb - Cl ($AlCl_4^-$) 2.952 - 3.218 Å.

The bonding in the molecule is discussed in terms of a qualitative molecular orbital scheme: 6 s and 6 p and no 6 d orbitals are utilized for bonding with chlorine and with the ring carbons (unlike in ferrocene-type structures).

Albers and Van Hoof |72| have studied the enhanced conversion of X-rays into visible light in thin composite anthracene-$PbCl_2$ layers.

Boleslawski et al. |73| investigated the structure and properties of a trimethyllead chloride complex with methylaluminium dichloride, $Me_3PbCl \cdot MeAlCl_2$, by NMR, IR and Raman spectroscopy and by molecular weight and electrolytic conductance measurements.

Bertazzi |74| studied the anion exchange on the trimethyllead (IV) thiocyanate aqueous complex system.

Distefano et al. |75| have reported on mass spectrometry measurements for Ph S Pb Me_3. An ionization energy of 7.75 eV was found. Appearance potentials and bond dissociation energies were determined. The results discussed in connection with mass spectrometric data on other main group IV organometallic compounds suggest the presence of a $p_\pi - d_\pi$ contribution to the S-Pb bond.

The UV photoelectron spectra for $CH_3SPb(CH_3)_3$ and $S|Pb(CH_3)_3|_2$ are reported |76|. The electronic interactions between the $Pb(CH_3)_3$ substituent and the sulphur $n\pi$ orbital are discussed in terms of the relative importance of hyperconjugation (n-σ mixing), (p-d)π-bonding and electrostatic interactions.

Kennedy and McFarlane |77| determined the magnitude and sign of $^1J(^{207}Pb - ^{207}Pb)$ in hexamethyldilead by heteronuclear double resonance: + 290 Hz This surprising small value suggests a low s-overlap integral for the metal-metal bond.

Aritomi and Kawasaki |78| have studied the interaction of dimethylbis (substituted oxinato) lead with donors such as pyridine, DMSO and HMPA. The changes of the $J(^{207}Pb - CH_3)$ values are due to the decrease of the excitation energy by the accumulation of negative charge around the lead atom.

Kato et al. |79| have recorded the IR and Raman spectra of $CH_3CS_2Pb(C_2H_5)_3$. Characteristic absorption bands of the C(S)-S group are found near 880-860 cm^{-1}.

Anderson et al. |80| reported an ESR study on radical anions of Me_3PbCl, Ph_3PbCl and Ph_3PbBr. The ^{207}Pb hyperfine coupling was considerably greater than for R_3Pb radicals.

Stafford et al. |81| have investigated the behaviour of Ph_3PbX and Ph_2PbX_2 (X = Cl, Br, I), in methanol solution by means of UV spectroscopy and by conductometric and potentiometric measurements. Binuclear complexes, e.g. Ph_4PbI_4 are formed.

Solution absorption and luminescence studies of Ph_4Pb were reported by Gouterman and Sayer |82|. The phosphorescence emission is red shifted, which is attributed to formation of a triplet excimer.

Applications

Organolead compounds such as triphenyllead acetate or tributyllead acetate were used as toxicants in solvent dispersions of synthetic rubbers for antifouling paints which did not develop surface chalking |83|.

Kochkin et al. |84| studied the antifungal activities of triethylchloroplumbane and polytriethylmethacryloxyplumbane in the protection of wood with organotin and organolead compounds.

Dibutyllead diacetate, triethyllead acetate, trimethyllead acetate and esp. tributyllead acetate are used as effective wood preservatives |85|.

A patent |86| describes the solidification of tetraalkyllead with benzylidenesorbitol.

Smoke-retardant styrene polymer compositions containing tetraphenyl lead are reported |87|.

Shephard |88| continued his study on the redistribution of mixtures of Me_4Pb and Et_4Pb in the presence of trimethyllead tetrafluoroborate as a redistribution catalyst:

$$\underset{50}{Me_4Pb} + \underset{50}{Et_4Pb} \xrightarrow[\text{r.t.}]{75\%\ \text{aq. } Me_3PbBF_4} \underset{24}{Me_3EtPb} + \underset{42}{Me_2Et_2Pb} + \underset{24}{MeEt_3Pb} \qquad (24)$$

The stabilizing activity of organolead compounds (e.g. triphenyllead isocyanate) and their mixtures with organic phosphites (e.g. tributyl phosphite) during the thermal degradation of PVC is reported |89|. Triphenyllead isocyanate is prepared by heating triphenyllead hydroxide with urea in xylene for 4 hr at 130° under nitrogen.

According to ref. [90] the sensitivity of radiation-sensitive polyyne compounds (e.g. monomethylester of 10,12-docosa-diynedioic acid) is extended into the X-ray region by the use of organometallic sensitizers, such as hexaphenyldilead.

Anti-corrosive paints containing organic lead polymers are used for electrostatic coating [91].

Triamyllead acetate, prepared by the reaction of triamyllead bromide with AgOAc, may be used as a slimicide in wet hydrocarbon fuels, as a pesticide, as a stabilizer for chlorinated polymers, and as a resicant in military gases, fogs and sprays [92].

Pesticidal trialkyllead acetates, $R_3Pb(OAc)$ (R = Bu, amyl, isoamyl), were prepared by the reaction of R_3PbX (X = Cl, Br) with AgOAc [93].

Viventi [94] has studied the light-induced vulcanization of polysiloxanes in the presence of Et_4Pb.

The Pb content of ethylated gasoline was unaffected by contact with H_2O or NaCl solutions for 4 years under laboratory and practical conditions [95].

Organolead compounds, e.g. tributyllead acetate, are used as paint-biocides [96]. Their effectiveness is comparable to that of organomercury and organotin compounds.

Analysis

Lead in gasoline is determined by using the oxygen bomb and an a.c. polarographic method which is simpler than the conventional methods [97].

Lead may be determined in organic compounds by decomposing the sample, adding 8-hydroxyquinoline to precipitate the metal-hydroxyquinoline complex at pH 9.25 and determining excess 8-hydroxyquinoline polarographically at $E_{1/2} = -1.39$ V vs. SCE [98].

Segar [99] has determined lead in volatile alkyllead compounds of gasoline by using flameless atomic absorption gas chromatography. The sensitivity for Me_3EtPb was 10^{-8} g Pb / 2 µl.

The determination of small amounts of lead in gasoline by atomic absorption spectrometry with a carbon rod atomizer is reported by Kashiki et al. |100|, detection limit 0.001 ppm Pb.

Heistand and Shaner |101| have developed an automated atomic absorption determination of low levels of lead in gasoline with a precision of 0.0036 g in the range 0.007 - 0.1 g Pb/gallon.

Pb present in gasoline in the range 0.002 - 5 g / gal was determined by a method based on the use of Compton scattering as an internal standard and on comparison of the unknown with a blank and with a saturated solution |102|.

Wastes

According to ref. |103| dissolved organic lead compounds are removed from aqueous media, e.g. tetraalkyllead manufacture waste water, by treatment with activated lead. The activated lead is produced by extracting the non-lead component from a lead compound, e.g. NaPb, by means of water, alcohol, acid, or alkyl halide.

Common mussels (Mytilus edulis) are suitable indicator organisms for lead in sea-water |104|.

In a series of patents |105,106,107| the reduction of the organolead compound content of aqueous solutions by electrolysis is described.

Metal halides, esp. $SnCl_4$ or $SbCl_5$, bonded to a solid substrate by tertiary amine or alkyl halide functional groups, selectively remove lead alkyls from gasoline |108|.

Heilweil |109| has developed a lead trap for removing Et_4Pb from gasoline.

Toxicology

Bagirov |110| studied the effect of Et_4Pb on hemopoiesis on long exposure to ethylated gasoline. Prolonged action of Et_4Pb on the organism may result in quantitative changes in blood composition as well as in profound qualitative changes in the hemopoietic system up to the development of leukosis.

The contamination by Et_4Pb and its prevention is described |111|. The antidote is Ca EDTA.

In refs. |112, 113, 114|, the chronic toxic actions of leaded gasoline 78 vapors in rabbits are reported.

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