LEAD

ANNUAL SURVEY COVERING THE YEAR 1973

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Reviews

In a number of reviews the following aspects of organolead chemistry have been dealt with: acetylenic organolead compounds [1]; organolead compounds with lead-metal bonds [2]; electroorganic synthesis of tetraethyllead [3]; stability of organolead complexes with anionic and neutral ligands [4]; autoxidation of organolead compounds [5].

Preparations

A new type of bivalent organolead compound has been prepared by Holliday et al. [6]:

$$(C_5H_5)_2Pb + HX \longrightarrow C_5H_5PbX + C_5H_6 \qquad (X = Cl, Br, OAc) \qquad (1)$$

C_5H_5PbX is insoluble in non-polar solvents and is believed to be polymeric with bridging X groups. Excess acid produces PbX_2.

Davidson and Lappert [7] report on another new bivalent organolead compound (eqn. 2).

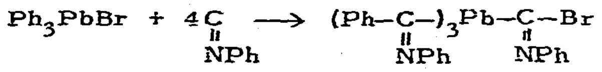
$$2(Me_3Si)_2CHLi + PbCl_2 \longrightarrow [(Me_3Si)_2CH]_2Pb \qquad (2)$$

The purple compound melts at 43-45°, is air-sensitive and soluble in non-polar media.

Kunze and Huber [8] have succeeded in preparing for the first time a tetra-nitrophenyllead compound by hydrazine-induced disproportionation of Ar_2PbX_2. The compound shows the usual chemical and physical properties of tetraaryllead compounds.

$$(3\text{-}O_2NC_6H_4)_2PbX_2 \xrightarrow[Na_2CO_3]{N_2H_4} \underset{\text{m.p. } 179.5^{\circ}}{(3\text{-}O_2NC_6H_4)_4Pb} \qquad (3)$$

Meiler et al. [9] have found that phenyl isocyanide inserts into lead-carbon bonds as well as lead-halogen bonds:


(4)

$$Ph_3PbBr + 4\underset{NPh}{\overset{}{\underset{\|}{C}}} \longrightarrow (Ph{-}\underset{NPh}{\underset{\|}{C}}{-})_3Pb{-}\underset{NPh}{\underset{\|}{C}}{-}Br \qquad (4)$$

Matteson et al. [10] in their study on tetraborylmethanes prepared also a lead derivative (eqn. 5). Only the dilead compound was obtained. The monolead compound $Ph_3PbC[B(OMe)_2]_3$ seems to disproportionate extremely readily and so escapes isolation.

$$2C[B(OMe)_2]_4 \xrightarrow[LiOMe]{BuLi\ or} 2^-C[B(OMe)_2]_3 \xrightarrow{Ph_3PbCl} 2[Ph_3PbC[B(OMe)_2]_3]$$

$$(Ph_3Pb)_2C[B(OMe)_2]_2 + C[B(OMe_2)]_4 \longleftarrow \qquad (5)$$

Tetrakis(trimethylenedioxyboryl)methane, $C(BO_2C_3H_6)_4$, was found [11] more suited for the synthesis of organometallic derivatives. In this case the monolead compound, $Ph_3PbC(BO_2C_3H_6)_3$, could be isolated. Also the mixed lead-tin, lead-germanium, and even the lead-tin-germanium compound $(Ph_3Pb)(Ph_3Sn)(Ph_3Ge)CBO_2C_3H_6$ were prepared although the last product was not fully characterized.

Huber et al. [12] have synthesized $Ph_2Pb[Mn(CO)_5]_2$ (C_{2v} symmetry, $P2_1/c$ space group) by the alkali salt method of Gorsich (eqn. 6). Halogen eliminates two phenyl groups in $CHCl_3$ at -60° (eqn. 7) ; similarly an ethyl group is removed from $Et_3PbMn(CO)_5$ at 25° (eqn. 8). $Br_2Pb[Mn(CO)_5]_2$ in acetone decomposes at 25° (eqn. 9).

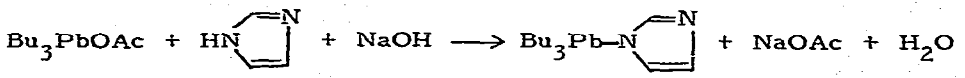
$$Ph_2PbCl_2 + 2NaMn(CO)_5 \longrightarrow Ph_2Pb[Mn(CO)_5]_2 \qquad (6)$$

$$Ph_2Pb[Mn(CO)_5]_2 + X_2 \longrightarrow X_2Pb[Mn(CO)_5]_2 \qquad (7)$$

$$Et_3PbMn(CO)_5 + X_2 \longrightarrow Et_2ClPbMn(CO)_5 \qquad (8)$$

$$Br_2Pb[Mn(CO)_2]_5 \xrightarrow[25^0]{acetone} PbBr_2 + Mn_2(CO)_{10} \qquad (9)$$

A patent [13] describes the preparation of (tributylplumbyl)imidazole from Bu_3PbOAc in one step (eqn. 10). The reaction is carried out in benzene in the presence of NaOH and the water formed is distilled off azeotropically.



(10)

Ermolova and Komarev [14] have prepared alkynyloxy-lead derivatives as follows:

$$\mathrm{Me_3PbOH + HO{-}CR_2{-}C{\equiv}CH \longrightarrow Me_3Pb{-}O{-}CR_2{-}C{\equiv}CH} \qquad (11)$$

Organolead nitronates (eqn. 12) were prepared by Lorberth and Lange [15]. ^{1}H NMR and mass spectra indicate that, in contrast with expectation, bonding of the organometallic moiety occurs via an oxygen atom to the nitronate ligand.

$$\mathrm{R_3PbNR_2 + CH_3NO_2 \longrightarrow R_3Pb{-}O{-}N(O){=}CH_2 + HNR_2} \qquad (12)$$

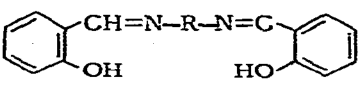
Kunze and Huber [16] determined conditions under which reaction (13) occurs. In general, diaryllead dihalides (aryl = Ph, 3-$NO_2C_6H_4$) are easily prepared from diaryllead diacetates in acetic acid. A complex, $[Ph_4P]_2[3\text{-}NO_2C_6H_4)_2PbBr_4]$, was also isolated.

$$\mathrm{Ar_2Pb(OAc)_2 + 2\,HX \longrightarrow Ar_2PbX_2 + 2\,HOAc} \qquad (13)$$

Syutkina et al. [17] synthesized diaryllead diacetate via a mercury-catalyzed redistribution reaction of lead tetraacetate with organotin compounds (eqn. 14).

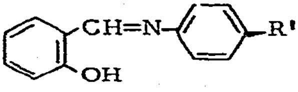
$$\mathrm{R_2SnAr_2 + Pb(OAc)_4 \xrightarrow{Hg^{2+}} R_2Sn(OAc)_2 + Ph_2Pb(OAc)_2} \qquad (14)$$

Diphenyllead complexes, Ph_2PbL or $Ph_2PbL'_2$, with ligands of the type:



H_2L

or



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have been prepared by Poddar and Das [18] by the reaction of the sodium derivative of the ligand with Ph_2PhX_2 in dry methanol. UV and IR data are discussed.

De Vos et al. [19] have continued their study of the plumbylation of benzene derivatives. The preparation of a series of new aryllead triacylates (eqn. 15) in benzene in the presence of excess trichloroacetic acid is reported.

$$\mathrm{Pb(OAc)_4 + ArH \longrightarrow \underset{Ar\,=\,4\text{-alkoxy-3-halo}}{ArPb(OAc)_3}} \tag{15}$$

In the presence of trifluoroacetic acid even halobenzenes can be plumbylated in the para-position [20].

$$\mathrm{Pb(OAc)_4 + 4\,CF_3COOH \leftrightarrows Pb(O_2CCF_3)_4 + 4\,HOAc} \tag{16}$$

$$\mathrm{Pb(O_2CCF_3)_4 + X\text{-}C_6H_5 \leftrightarrows \underset{X\,=\,F,\,Cl,\,Br}{p\text{-}X\text{-}C_6H_4Pb(O_2CCF_3)_3} + HO_2CCF_3} \tag{17}$$

Reactions

Evidence has been provided by Plazzogna et al. [21], that hexaphenyldilead does not disproportionate into tetraphenyllead and diphenyllead (eqn. 19). The reaction of Ph_6Pb_2 with C_6D_5Li did only give $Ph_3PbC_6D_5$ and not a trace of Ph_4Pb.

$$\mathrm{Ph_6Pb_2 + C_6D_5Li \longrightarrow Ph_3PbC_6D_5 + Ph_3PbLi} \tag{18}$$

$$\mathrm{\not\longrightarrow\ \rightleftarrows Ph_4Pb + Ph_2Pb \xrightarrow{C_6D_5Li} Ph_4Pb + Ph_2C_6D_5Li} \tag{19}$$

Garg and Rai [22] studied the thermal decomposition of organolead compounds using an automatic recording thermobalance and concluded that the following decomposition reaction takes place:

$$\mathrm{2\,Ph_6Pb_2 \longrightarrow 3\,Ph_4Pb + Pb} \tag{20}$$

$$\mathrm{3\,Ph_3PbCl \longrightarrow 2\,Ph_4Pb + PbCl_2 + PhCl} \tag{21}$$

$$\mathrm{2\,Ph_3PbOH \longrightarrow Ph_4Pb + Ph_2PbO + H_2O} \tag{22}$$

Clinton et al. [23] determined the acetolysis rates of mixed methyl-ethyl-lead compounds, $Me_{4-n}PbEt_n$ (n = 0-4): $\underline{k}(Me_4Pb)$ $7.3 \cdot 10^{-6}$/sec, $\underline{k}(Et_4Pb)$ $4.9 \cdot 10^{-6}$/sec. The influence of an ethyl group on the acetolysis rate of an alkyl group is about twice that of a methyl group.

A patent [24] describes the synthesis of dialkyltin dichlorides from tetraalkyllead compounds.

$$SnCl_4 + R_4Pb \longrightarrow R_2SnCl_2 \qquad (23)$$

Pant [25] has used aryl-lead compounds to prepare aryl-tellurium compounds, e.g. by stirring triphenyllead chloride with $TeCl_4$ in dioxane. The reaction proceeds further to give Ph_2TeCl_2, if excess Ph_3PbCl is present.

$$Ph_3PbCl + TeCl_4 \longrightarrow Ph_2PbCl_2\downarrow + PhTeCl_3 \qquad (24)$$

$$Ph_3PbCl + PhTeCl_4 \longrightarrow Ph_2PbCl_2\downarrow + Ph_2TeCl_2 \qquad (25)$$

Clinton and Kochi [26] have considered two mechanisms for the reaction of tetraethyllead with CuX_2.
Scheme 1

$$Et_4Pb + CuX_2 \longrightarrow Et_4Pb^{\cdot +} + CuX_2^- \qquad (26)$$

$$Et_4Pb^{\cdot +} \longrightarrow Et_3Pb^+ + Et^\cdot, \text{ etc.} \qquad (27)$$

Scheme 2

$$Et_4Pb + CuX_2 \longrightarrow Et_3PbX + EtCuX \qquad (28)$$

$$EtCuX \longrightarrow CuX + Et^\cdot, \text{ etc.} \qquad (29)$$

From kinetic studies on reaction of mixed methyl/ethyl-lead compounds with $CuCl_2$ and from selectivities in the mass spectral fragmentation pattern of these tetraalkyllead compounds it is concluded that scheme 2 pertains to the actual reaction.

The same authors [27] studied the reaction of tetraethyllead with silver trifluoromethanesulphonate in acetic acid and in tetrahydrofuran (THF).

$$Et_4Pb + AgO_3SCF_3 \longrightarrow Et_3PbO_3SCF_3 + EtAg$$

$$EtAg \longrightarrow C_2H_6 + C_2H_4 + Ag \qquad (30)$$

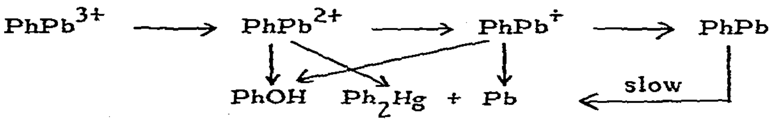
$$EtAg \longrightarrow C_4H_{10} + Ag \qquad (31)$$

In THF excess of Ag^+ produces much butane whereas with excess of Et_4Pb much ethane is produced.

Physical chemistry

Doe et al. [28] have concluded from infrared data that $(MeC_5H_4)_2Pb$ is isostructural with the analogous tin compound.

Colliard and Devaud [29] found that the polarographic reduction of phenyllead triacetate in aqueous/alcoholic media takes place in three stages with formation of diphenylmercury, phenol and lead.



(32)

The relative and absolute intensities of the chemiluminescence of tetraethyllead with atomic oxygen were compared by Vanpee and Yaron [30] with those of other compounds:

$$Me_3Al > NO > Fe(CO)_5 > Et_4Pb$$

Lorberth et al. [31] concluded from infrared spectra of trialkyllead nitronates, $R_3Pb{-}O{-}N(O){=}CR'R''$, that the R_3Pb moiety has local D3h symmetry, and the $-O-N(O){=}CR'R''$ moiety has C_{2v} symmetry.

The infrared integrated absorption coefficients, $\Sigma(A/\nu^2)$, of the valence vibration of the C≡C triple bond have been reported in a series of $R_3MC{\equiv}CH$ compounds (M = C, Si, Ge, Sn, Pb) to vary linearly with the acetylenic proton NMR chemical shifts. Guillerm et al. [32] interpreted these results in terms of $\pi(\underline{d}-\underline{p})$ bonding between the heteratom (lead) and the unsaturated bond.

Bosworth et al. [33] have reported on vapour phase Raman spectra of spherical top molecules (a.o. Me_4Pb).

Maciel and Dallas [34] found ^{207}Pb pulse Fourier transform

NMR a promising tool for studies in lead chemistry. Using $\mathrm{Me_4Pb}$ in toluene as a standard (0 ppm) they report a.o. the following chemical shifts:
$\mathrm{Et_4Pb}$ (neat) 70.6 ppm, $\mathrm{Ph_6Pb_2}$ ($\mathrm{CS_2}$) -73 ppm, $\mathrm{Me_3PbOAc}$ (HOAc) 408.1 ppm, $\mathrm{Pb(OAc)_2}$ (water) -1337 ppm, $\mathrm{Pb(NO_3)_2}$ (water) -2961.2 ppm.

Kravtsov et al. [35] have correlated the structure of organolead derivatives of 2,6-dichlorothioanisole and 2,6-dichlorothiophenol with their chlorine-35 NQR spectra.

ESR spectra of the trimethyllead radical were recorded by Bennett and Howard [36] after trapping these radicals from a reaction of $\mathrm{Me_3PbCl}$ with sodium at 77° K in a variety of matrices. The $\underline{g}$ tensors appeared to be anisotropic: g_{xx} 2.1055, g_{yy} 2.0973, g_{zz} 1.9139. The hyperfine coupling to $^{207}\mathrm{Pb}$ is extremely large and anisotropic. It is concluded that the radical is not planar.

Cooper et al. [37] photolyzed hexamethyldilead, which gave a lead mirror but no ESR spectrum attributable to $\mathrm{Me_3Pb^{\bullet}}$. However, the intermediacy of $\mathrm{Me_3Pb^{\bullet}}$ radicals followed from the reaction with reactive halides giving $\mathrm{Me_3PbX}$. The following reactivity order was found: allyl bromide > $\mathrm{CCl_4}$ > alkyl bromides > allyl and alkyl bromides. Tetraethyllead photolyzed with formation of ethyl radicals (observed in the ESR spectrum). Trialkyllead radicals were not found to add to multiple bonds.

Mansell and Hiller [38] determined tetraethyllead in gasoline by destruction in a Parr Acid Digestion Bomb followed by measurement with atomic absorption spectrometry.

Applications

According to a patent [39] trimethyllead tetrafluoroborate is suited as a redistribution catalyst for mixtures of $\mathrm{Me_4Pb}$ and $\mathrm{Et_4Pb}$:

$$\underset{50}{\mathrm{Me_4Pb}} + \underset{50}{\mathrm{Et_4Pb}} \xrightarrow[\mathrm{r.t.}]{\mathrm{Me_3PbBF_4}}$$

$$\longrightarrow \underset{5.1}{\mathrm{Me_4Pb}} + \underset{23.6}{\mathrm{Me_3EtPb}} + \underset{42.3}{\mathrm{Me_2Et_2Pb}} + \underset{23.6}{\mathrm{MeEt_3Pb}} + \underset{5.4\ \%}{\mathrm{Et_4Pb}} \qquad (33)$$

Tetrabenzyllead and tetravinyllead are suitable starting materials for the preparation of organoalkali earth metal compounds, useful as polymerization catalysts [40].

$$R_4Pb \xrightarrow{Ca, Sr} R_2M \qquad (34)$$

According to Lorenz [41] good protection against marine and freshwater fouling (without the usual need for Cu_2O and resin binder) was provided by incorporation of both bis(tributyltin) oxide and triphenyllead acetate in paints.

Da Costa and Osborne [42] investigated the effect of chemical structure on the toxicity of organolead compounds to wood-destroying fungi. Tripropyl-, tributyl- and tripentyllead salts were generally the most effective.

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