Organolead Chemistry. Part I. Some Dimethyl-lead Dialkoxides

By **R. J. Puddephatt*** and **G. H. Thistlethwaite**, Donnan Laboratories, The University of Liverpool, Grove St., P.O. Box 147, Liverpool L69 3BX

Dimethyl-lead dialkoxides have been prepared by treating dimethylbispropynyl-lead with alcohols. The dialkoxides are polymeric in the solid state and the strength of the association is dependent on the size of the alkoxide group.

THERE have been several recent studies of the preparation and properties of trialkyl-lead alkoxides.[1-3] The lead–oxygen bond in these compounds is very reactive and the alkoxides are useful reagents for the preparation of other organolead compounds and also in some catalytic processes. In view of the greater reactivity of the Pb–O bond compared with the Sn–O bond in similar compounds [2] and the interesting properties of the di-

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[1] E. Amberger and R. Hönigschmidt-Grossich, *Chem. Ber.*, 1965, **98**, 3795.

[2] A. G. Davies and R. J. Puddephatt, *J. Chem. Soc.* (*C*), 1967, 2663; 1968, 317, 1479.

[3] R. Hönigschmidt-Grossich and E. Amberger, *Chem. Ber.*, 1969, **102**, 3589.

alkyl-tin dialkoxides,[4,5] one can predict specific uses for the corresponding dialkyl-lead dialkoxides in chemical synthesis. However these compounds have not been reported.

The trialkyl-lead alkoxides have usually been prepared by treating the trialkyl-lead halide with sodium alkoxide,[1,2] but this method cannot readily be applied to synthesis of dialkyl-lead dialkoxides due to the insolubility of the dialkyl-lead dihalides and the difficulty of separating the desired product from sodium halide.[6] This paper describes a convenient route to dimethyl-lead dialkoxides together with some properties of these compounds.

Preparation of Dimethyl-lead Dialkoxides.—The reversible reaction between organolead alkoxides and alkynes has previously been used to prepare alkynyl-lead compounds.[2,3] We have used the reverse reaction to prepare dimethyl-lead dialkoxides from dimethylbispropynyl-lead [equation (1)].

$$\mathrm{Me_2Pb(C{\equiv}CMe)_2 + 2ROH \longrightarrow Me_2Pb(OR)_2 + 2MeC{\equiv}CH} \qquad (1)$$

Dimethylbispropynyl-lead can be prepared in high yield from dimethyl-lead dichloride and propynyllithium. It is easily purified by vacuum sublimation and may be stored without appreciable decomposition for several months at room temperature in the absence of moisture.

Analytical data and physical properties of the dimethyl-lead dialkoxides

Compound	M.p. (°C)	s.p.[a]	ν(CO)/cm^{-1}	Analysis (%) Calc. (Found) C	H	Pb
$Me_2Pb(OMe)_2$	d. 150		1059s, 1048s	16·05 (16·5)	4·0 (4·3)	69·2 (68·4)
$Me_2Pb(OEt)_2$	146—149d	100—110 (10^{-3})	1102s, 1057s	22·0 (21·7)	4·9 (4·8)	63·3 (62·0)
$Me_2Pb(OEt)_2$ EtOH	d. 100		1102s, 1058s	25·7 (24·8)	5·9 (5·4)	55·5 (56·2)
$Me_2Pb(OPr^i)_2$	80—85	90 (10^{-3})	1160m, 1126s	27·0 (25·9)	5·7 (5·6)	58·3 (57·9)
$Me_2Pb(OBu^t)_2$[b]	100—105	75 (10^{-3})	1190s, 1177sh	31·3 (31·0)	6·3 (6·0)	54·0 (52·9)
$Me_2Pb(OPh)_2$	140—155d			39·7 (39·1)	3·8 (3·9)	48·9 (50·3)

[a] s.p. = Sublimation point, in °C, pressure in mmHg in parentheses. [b] *M*: Calc. 383·5. Found 340 (0·023M solution), 355 (0·039M solution).

The reactions with alcohols were carried out by dissolving the alkynyl-lead compound in the alcohol, sometimes diluted with benzene. Propyne was evolved and the dialkoxide was obtained by evaporation of the solvent *in vacuo*. Methanol and ethanol reacted rapidly at room temperature but isopropyl alcohol and t-butyl alcohol were considerably less reactive. Thus dimethyl-lead di-t-butoxide was obtained by refluxing dimethylbispropynyl-lead in t-butyl alcohol for 45 min. Shorter reflux times gave products, which, from the n.m.r. spectra, appeared to contain mixtures of dimethylbispropynyl-lead, dimethyl-lead di-t-butoxide, and dimethylpropynyl-lead t-butoxide.

The similar alcoholysis of dimethylbis(3,3,3-trifluoropropynyl)lead takes place much more rapidly, but this compound is also considerably more sensitive to atmospheric moisture and is also less readily accessible than the corresponding propynyl derivative. It is therefore a less suitable intermediate for preparing the alkoxides.

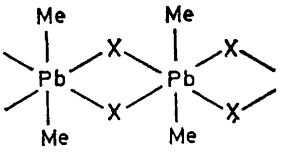
Properties of the Dimethyl-lead Dialkoxides.—The dimethyl-lead dialkoxides are white solids which are hydrolysed in air to dimethyl-lead oxide; dimethyl-lead diphenoxide was stable to moist air. Dimethyl-lead dimethoxide reacted exothermally with chloroform and with carbon disulphide.

The i.r. spectra showed two strong bands due to the C–O stretching vibration (see Table). The band frequencies were close to those for the trialkyl-lead alkoxides, though these gave only a single band.[2]

Dimethyl-lead dimethoxide decomposed when heated *in vacuo* to 150° giving lead dimethoxide, trimethyl-lead methoxide, and dimethyl ether, together with some methanol and carbon dioxide. The mode of decomposition is therefore similar to that of the dialkyl-lead dihalides [7] (equation 2, X = Cl or OMe).

$$\mathrm{2Me_2PbX_2 \longrightarrow PbX_2 + Me_3PbX + MeX} \qquad (2)$$

This observation, together with the high melting point (>150°) and very low solubility of the compound in most organic solvents, suggest that dimethyl-lead dimethoxide may have the same polymeric structure as the dimethyl-lead dihalides [8] (I, X = Cl or OMe).



The high value of the coupling constant $^2J(\mathrm{PbCH_3})$ of 132 Hz in a solution of dimethyl-lead dimethoxide in methanol suggests octahedral co-ordination at lead [9-12] with the extra two co-ordination sites presumably occupied by methanol.

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[6] A. G. Davies and R. J. Puddephatt, unpublished work.

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As the size of the alkoxy group increases, the dimethyl-lead dialkoxides have lower melting points and increased volatility and solubility. Thus dimethyl-lead di-t-butoxide readily sublimes *in vacuo* and is easily soluble in benzene; its n.m.r. spectrum in this solvent suggested that the compound was monomeric with four-co-ordinate lead [${}^2J$(PbMe) = 93·5 Hz] [9–12], and this was confirmed by a molecular-weight determination (Table), though a very accurate value could not be obtained presumably due to partial hydrolysis of the alkoxide during the measurements. We suggest that the steric requirements of the bulky Bu^t group leads to much weaker intermolecular association in this compound.

The structure of the dimethyl-lead dihalides was deduced by analysis of their vibrational spectra in the Pb–Me and Pb–X stretching regions.[8] We have been unable to confirm the structure of the dialkoxides in this way since bands due to Pb–Me and Pb–O stretching vibrations overlap in the region 450—550 cm^{-1}.

EXPERIMENTAL

I.r. spectra of Nujol mulls of solids were recorded on a Unicam SP 200 or Perkin-Elmer 625 instrument. ${}^1H$ N.m.r. spectra were recorded at 33°C using a Varian A 60 spectrometer. Chemical shifts are reported in p.p.m. from tetramethylsilane (TMS) internal standard.

C,H analyses were carried out by Alfred Bernhardt or by Mr. D. Skelding, Associated Octel Company Ltd. Lead analyses were obtained by destroying the organolead compound with bromine and nitric acid followed by titration with ethylenediaminetetra-acetic acid, in a solution buffered to pH 5, using Xylenol Orange as indicator. Molecular weights were determined using a Mecrolab Vapour Pressure Osmometer using benzene solvent.

Organolead alkoxides and acetylides were handled in an atmosphere of dry nitrogen or *in vacuo*. Alcohols were dried by refluxing over magnesium and were then distilled under nitrogen. Other solvents were dried by conventional methods.

Dimethylbispropynyl-lead.—Propyne was bubbled through a solution of methyl-lithium (50 ml, 1·75M in ether, 87·5 mmol) in tetrahydrofuran (60 ml) at −60° for 30 min. The mixture was warmed to room temperature, dimethyl-lead dichloride (10 g, 32·6 mmol) was added, and the mixture was stirred for 1 h at room temperature. The solvent was evaporated *in vacuo* and the *product* sublimed from the reaction mixture as colourless crystals (7·6 g, 74%), sublimes 80—100°, 10^{-2} mmHg, m.p. 112° (Found: C, 30·35; H, 3·8; Pb, 67·2. $C_8H_{12}Pb$ requires C, 30·5; H, 3·8; Pb, 65·7%).

The same product could be obtained from dimethyl-lead dichloride and the propynyl Grignard reagent, after extraction from the reaction mixture with pentane. The yield was 52%.

Dimethyl-lead Dimethoxide.—Methanol (10 ml) was added to a solution of dimethylbispropynyl-lead (1·0 g) in benzene (10 ml). After 10 min the solvents were evaporated *in vacuo* to yield colourless crystals of dimethyl-lead dimethoxide (100%); $\nu_{max.}$ 535sh, 529ms, 511s, 471mw, 462w cm^{-1}; $\delta(CH_3Pb)$ in CCl_4–CH_3OH, 2·07 p.p.m., ${}^2J$(^{207}PbH) 132·0 Hz.

Dimethyl-lead dimethoxide (0·5 g) was heated *in vacuo* to 140°, 10^{-3} mmHg. The gaseous decomposition products were trapped at −190° and later identified as a mixture of methanol, dimethyl ether, and carbon dioxide by the gas phase i.r. spectrum. The sublimate was identified as trimethyl-lead methoxide (0·2 g) and the residue as largely lead(II) dimethoxide (0·2 g) by comparison with authentic compounds.[1,2]

Dimethyl-lead diethoxide was prepared similarly and contained 1 mol of ethanol of crystallisation; $\delta(CH_3Pb)$ in CH_3OH, 1·78 p.p.m., ${}^2J$(^{207}PbH) 132 Hz; $\delta(CH_3CH_2)$, 1·10 p.p.m. (triplet), ${}^3J$(HH) 7·0 Hz; relative areas $CH_3Pb : CH_3CH_2$, 2 : 3.

After prolonged pumping (24 h) at room temperature or on heating to 90° *in vacuo* (30 min) the ethanol of crystallisation was lost; n.m.r. (in CH_3OH) identical with above except that relative areas $CH_3Pb : CH_3CH_2$, 1 : 1. On heating above 100°, 10^{-3} mmHg the ethoxide partly sublimed and partly decomposed. Decomposition products included ethanol and acetaldehyde.

Dimethyl-lead Di-isopropoxide was prepared similarly and purified by vacuum sublimation. $\delta(CH_3Pb)$ (in CCl_4), 2·08 p.p.m.; $\delta(CH_3C)$, 1·40 p.p.m. (d); $\delta(CHO)$, 4·53 p.p.m. (septet), ${}^3J$(HH) 6·2 Hz; relative areas $CH_3Pb : CH_3C$, 1 : 2.

Dimethyl-lead Di-t-butoxide.—Dimethylbispropynyl-lead (1·0 g) was refluxed in t-butyl alcohol (10 ml) for 45 min. The solvent was evaporated, leaving a pale yellow oil from which dimethyl-lead di-t-butoxide was isolated as a white solid (0·3 g) by vacuum sublimation; $\delta(CH_3Pb)$ (in benzene), 0·87 p.p.m., ${}^2J$(^{207}PbH) 93·5 Hz; $\delta(CH_3C)$, 1·03 p.p.m.; relative areas MePb : MeC, 1 : 3.

Dimethyl-lead Diphenoxide was prepared by addition of phenol (0·78 g) in benzene (10 ml) to dimethylbispropynyl-lead (1·19 g) in benzene (10 ml). The *product* was precipitated almost immediately. It was washed thoroughly with dry benzene and dried *in vacuo*; yield 1·07 g. The product was insoluble in methanol, ether, acetone, benzene, and dimethyl sulphoxide.

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