Some complexes of phenyllead halides

Although organotin halides react with many electron-pair donors to form addition compounds[1,2], little is known of corresponding organolead adducts. Pfeiffer[3] reported the preparation of some addition compounds of diphenyllead salts with pyridine $(C_6H_5)_2PbX_2 \cdot 4py$, ($X = NO_3$, Cl and Br). These compounds were unstable, readily losing pyridine in air, giving in the case of the dinitrate, a stable bispyridinium complex. The decomposition products of the other compounds were not characterized. Matwiyoff and Drago[4] recently reported the formation in solution of some 1:1 complexes of trimethyl- and triethyllead chlorides with Lewis bases.

We have investigated the reactions of donor molecules with some organolead compounds and have isolated several solid adducts (see Table 1). Diphenyllead dichloride is insoluble in most organic solvents, but can be recrystallized from pyridine, N,N-dimethylformamide and dimethyl sulphoxide to give 1:2 solvated addition compounds. The dibromide appears to form similar complexes, but only the dimethyl sulphoxide adduct is stable. Under the same conditions triphenyllead chloride does not form complexes, but reaction with tetramethylammonium chloride gives a 1:1 addition compound. The bidentate chelating ligands 2,2′-bipyridine and 1,10-phenanthroline give 1:1 adducts with diphenyllead dichloride.

TABLE 1

Compound	*M.p. °C*	*Analyses* *calcd.*/*found* *C*	*H*	*Pb*
$(C_6H_5)_2PbCl_2 \cdot 2py$	did not melt	44·73	3·41	35·08
	below 300	44·46	3·40	34·98
$(C_6H_5)_2PbCl_2 \cdot 2DMSO$	decomp.	32.64	3·77	35·21
	168–170	32.64	3·74	35·50
$(C_6H_5)_2PbCl_2 \cdot 2DMF$	decomp.	37·38	4.18	35·82
	76–80	37·38	4·37	35·70
$(C_6H_5)_2PbCl_2 \cdot bipy$	decomp.	44.88	3.08	35·21
	250	44.86	3.09	35·53
$(C_6H_5)_2PbCl_2 \cdot phenan$	did not melt	47·07	2.96	33·82
	below 300	46.08	3.00	34·33
$(C_6H_5)_2PbBr_2 \cdot 2DMSO$	165–170	28.37	3·27	30.59
		28.47	3·22	30.49
$(C_6H_5)_3PbCl \cdot (CH_3)_4NCl$	decomp.	45·27	4.66	35·51
	298	45·34	4.65	35·47

In the case of the diphenyllead adducts the mole ratios of acceptor/donor of 1:2 (monodentate) and 1:1 (bidentate) are expected on the basis of six-co-ordinate mononuclear lead, with octahedral distribution about the central metal atom. With triphenyllead chloride:tetramethylammonium chloride, the combining ratio can be explained by postulating the formation of a salt, $[(CH_3)_4N][(C_6H_5)_3PbCl_2]$, analogous to the substituted ammonium organohalostannates, *e.g.* $[(C_2H_5)_4N][(CH_3)_3SnBr_2]$ reported by Seyferth and Grim[5]. It is unlikely that the compound is a simple five-coordinate donor–acceptor adduct.

Experimental

The phenyllead halides were prepared from tetraphenyllead using well established procedures[6]. N,N-Dimethylformamide, pyridine and dimethyl sulphoxide were purified by distillation from the appropriate drying agent. Tetramethylammonium chloride was recrystallized from absolute alcohol. Commercial 2,2'-bipyridine and 1,10-phenanthroline (Eastman) were used as received. Melting points were determined using a Thomas-Hoover melting point apparatus.

$(C_6H_5)_3PbCl\cdot(CH_3)_4NCl$. An ethanol solution (100 ml) of triphenyllead chloride (4.7 g, 10 mmole) was boiled under reflux with tetramethylammonium chloride (2.42 g, 22 mmole) for 4 h. The solvent was removed and the residue extracted with (i) hot water and (ii) boiling benzene to remove starting materials. Recrystallization from absolute ethanol gave pure triphenyllead chloride:tetramethylammonium chloride (4.25 g, 81 %), decomp. 298° (sealed tube).

$(C_6H_5)_2PbCl_2\cdot bipy$. A suspension of diphenyllead dichloride (2.16 g, 5 mmole) in ethanol (100 ml) was boiled under reflux with 2,2'-bipyridine (3.43 g, 22 mmole) for 6 h. The solvent was removed and the residue extracted with benzene. Recrystallization of the insolubles from a large volume of absolute ethanol gave diphenyllead dichloride bipyridine (2.05 g, 55 %). The 1,10-phenanthroline adduct (30 % yield) was prepared in the same manner. The other addition compounds were prepared by recrystallizing the halides twice from the donor solvents and drying to constant weight at room temperature and 1 mm pressure. The "solvents of crystallization" could be removed at 1 mm pressure by heating at the boiling point of the solvents. The adducts themselves are insoluble in common organic solvents.

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U. S. Army Natick Laboratories,
Natick, Massachusetts (U.S.A.)

Kenneth Hills
Malcolm C. Henry

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