STUDIES IN GROUP IV ORGANOMETALLIC CHEMISTRY

XIII*. ORGANOMETALLIC COMPOUNDS WITH FIVE METAL ATOMS IN NEOPENTANE CONFIGURATION

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INTRODUCTION

In our paper of ref. 2 an organolead compound of the structure $(Ph_3Pb)_4Pb$ was described. One of the surprising properties of this compound is its relatively high stability which we attribute to its symmetry. It seemed worthwhile to attempt the synthesis of a series of compounds with the general formula

$$(Ph_3M)_4M'$$

in which M and M' are Pb, Sn or Ge in all possible combinations. Once formed these compounds were expected to be stable: (*a*) because the stability of organic compounds of the Group IV elements increase in the order Pb < Sn < Ge < Si; (*b*) because the symmetry is not lowered when M and M' are different. A point of special interest was that they would represent the first compounds with lead–tin and lead–germanium bonds.

Only one compound of this series has been described in the literature, *viz.* $(Ph_3Sn)_4Sn$. As long ago as 1923 Böeseken and Rutgers[3] obtained this compound in a small yield from the reaction between tin dichloride and phenylmagnesium bromide, hexaphenylditin being the main product. Their structural assignment was based on analyses and thermal decomposition behaviour, and these authors must be credited for a conclusion which certainly was not very obvious at that time.

PROCEDURE

For the preparation of the compounds $(Ph_3M)_4M'$ four equivalents of Ph_3MLi (M being Pb, Sn or Ge) were reacted with a Group IV metal tetrachloride, $M'Cl_4$ (M' being Sn or Ge), in diethyl ether or tetrahydrofuran at low temperature:

$$4Ph_3MLi + M'Cl_4 \longrightarrow (Ph_3M)_4M' + 4LiCl \quad (1)$$

After hydrolysis the compounds $(Ph_3M)_4M'$ could be isolated in varying yields, depending on the nature of M and M'. Varying amounts of the compounds Ph_6M_2 were

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* For Part XII in this series see ref. 1.

always formed as a by-product as a result of exchange reactions (see below), and final "yields" of the required compounds are thus to some extent dependent on the separability of the two types of product by crystallization techniques.

For compounds containing lead as the central atom the procedure had to be slightly modified because it is known that lead tetrachloride is much less suitable for organylation than the other Group IV metal tetrachlorides, owing to its oxidizing nature and general instability. Fortunately, in organolead chemistry this can be overcome by starting from lead dichloride instead of lead tetrachloride[4,5]. The diorganolead compound initially formed easily disproportionates into the tetraorganolead and lead. This proved to be applicable to the preparation of the compounds $(\mathrm{Ph_3M})_4\mathrm{Pb}$ as well and consequently these were isolated from the reactions of two equivalents of $\mathrm{Ph_3MLi}$ with lead dichloride:

$$2\mathrm{Ph_3MLi} + \mathrm{PbCl_2} \longrightarrow [(\mathrm{Ph_3M})_2\mathrm{Pb}] + 2\mathrm{LiCl} \qquad (2)$$

$$2[(\mathrm{Ph_3M})_2\mathrm{Pb}] \longrightarrow (\mathrm{Ph_3M})_4\mathrm{Pb} + \mathrm{Pb} \qquad (3)$$

It seems that the formation of the compounds $(\mathrm{Ph_3M})_4\mathrm{M'}$ proceeds more easily the larger the metal atoms (see Table 1). This holds true for the surrounding atoms M as well as, though to a lesser extent, for the central atom M'. All compounds $(\mathrm{Ph_3Pb})_4\mathrm{M'}$ are easily accessible and only a little hexaphenyldilead is formed. The isolation of the compounds $(\mathrm{Ph_3Sn})_4\mathrm{M'}$ is rather difficult owing to the low yield and the presence of hexaphenylditin.

It was not possible to isolate compounds of the type $(\mathrm{Ph_3Ge})_4\mathrm{M'}$ in the pure state although indications were present that they were formed. As a result of the attempt to prepare $(\mathrm{Ph_3Ge})_4\mathrm{Pb}$, a yellow product was obtained which is probably a mixture of the desired product and $\mathrm{Ph_6Ge_2}$, but these products could not be separated [the yellow colour strongly suggests the presence of $(\mathrm{Ph_3Ge})_4\mathrm{Pb}$.]. Further, where M' is Sn or Ge, small fractions were obtained which are probably mixtures of $(\mathrm{Ph_3Ge})_4\mathrm{M'}$ and $\mathrm{Ph_6Ge_2}$. In all preparations starting with triphenylgermyllithium large amounts of bis(triphenylgermanium) oxide were isolated in addition to some hexaphenyldigermane.

These observations can be explained by assuming a lithium–chlorine exchange reaction (4) which has been suggested by Gilman and Gerow[6], *e.g.*:

$$\mathrm{Ph_3GeLi} + \mathrm{SnCl_4} \longrightarrow \mathrm{Ph_3GeCl} + [\mathrm{LiSnCl_3}] \qquad (4)$$

$$\mathrm{Ph_3GeCl} + \mathrm{Ph_3GeLi} \longrightarrow \mathrm{Ph_6Ge_2} + \mathrm{LiCl} \qquad (5)$$

$$2\mathrm{Ph_3GeCl} + \mathrm{H_2O} \longrightarrow (\mathrm{Ph_3Ge})_2\mathrm{O} + 2\mathrm{HCl} \qquad (6)$$

The triphenylgermanium chloride formed (4) reacts partly with unconverted triphenylgermyllithium to give hexaphenyldigermane (5) and the remaining triphenylgermanium chloride is converted into bis(triphenylgermanium) oxide on hydrolysis of the final reaction mixture (6). To minimize this exchange Wiberg *et al.*[7] have suggested working at temperatures below 0°.

If this explanation is correct, the tendency towards lithium–chlorine exchange must decrease in the order $\mathrm{Ph_3GeLi} > \mathrm{Ph_3SnLi} > \mathrm{Ph_3PbLi}$. The same order has

TABLE I

DATA AND ANALYSES OF $(Ph_3M)_4M'$

$(Ph_3M)_4M'$	Solvent for recrystallization	Decompn. point	Colour	Isomorphism[a]	% Yields[b]			Analyses					
								Calculated			Found		
					$(Ph_3M)_4M'$	Ph_6M_2	Ph_3MX	C	H	Mol.wt.	C	H	Mol.wt.[c]
$(Ph_3Pb)_4Pb^{d,e}$	$CHCl_3$	...	red	•	30			44.09	3.08	1961			1760
$(Ph_3Pb)_4Sn$	$CHCl_3$	± 160	yellow	•	54	23	...	46.18	3.23	1873	46.30	3.43	1830
$(Ph_3Pb)_4Ge$	$CHCl_3$-petr.ether	± 210	yellow	+	10	23	...	47.35	3.31	1827	47.51	3.46	1824
$(Ph_3Sn)_4Pb^e$	$CHCl_3$-petr.ether	± 200	yellow	•	55			53.81	3.76	1607	53.41	3.94	1403
$(Ph_3Sn)_4Sn^f$	CS_2-acetone	± 280	white	•	22	37		56.94	3.98	1519	57.15	4.07	1514
$(Ph_3Sn)_4Ge^g$	benzene	± 324	white	•?	4	68		58.72	4.11	1473	58.53	4.17	1467
$[(Ph_3Ge)_4Pb]^{e,h}$	benzene		yellow		23	11	45	60.78	4.25	1423	63.98	4.46	885
$[(Ph_3Ge)_4Sn]^h$						20	56						

[a] Compounds with the same sign are isomorphous.
[b] No attempts have been made to obtain optimal yields; these values should be taken as indicative rather than exact.
[c] Osmometrically in CH_2Cl_2.
[d] This compound has been included for comparison; for details see ref. 2.
[e] Solutions are not stable and become turbid after a while; this is probably why the molecular weights found are too low.
[f] Found: Sn, 38.68. $C_{72}H_{60}Sn_5$ calcd.: Sn, 39.08%.
[g] Found: Ge, 4.98; Sn, 32.57. $C_{72}H_{60}Ge_4Sn$ calcd.: Ge, 4.93; Sn, 32.24%.
[h] $(Ph_3Ge)_4M'$ could not be isolated in the pure state.

been found[8] for the capacity of these compounds to metalate fluorene (where a lithium-hydrogen exchange takes place).

Structural proof for the compounds under discussion depends on the following data and considerations:

(*a*) the method of preparation;

(*b*) the analyses and molecular weight determinations;

(*c*) the isomorphism of several of these compounds with $(Ph_3Pb)_4Pb$ as revealed by X-ray analyses*. The structure of the compound $(Ph_3Pb)_4Pb$ had already been determined independently[2].

The method used for the preparation of $(Ph_3Pb)_4Pb$ (the simultaneous hydrolysis and oxidation of triphenylplumbyllithium[2]) is not applicable to the preparation of the other Group IV derivatives; only in the case of tin could very small amounts of $(Ph_3Sn)_4Sn$ be isolated. But even if it had worked, this method would have yielded compounds containing only one kind of metal.

On the other hand, $(Ph_3Pb)_4Pb$ could not be prepared from triphenylplumbyllithium and lead dichloride because of its instability in ethereal medium. Only transient yellow or red colours were observed, which disappeared within the time required for isolation.

In the solid state all compounds prepared are stable at room temperature. In solution the compounds with lead as the *central* atom, $(Ph_3M)_4Pb$, are unstable, as the rapid development of turbidity shows, and this explains the too low molecular weights found; whereas the compounds with lead atoms as the *surrounding* metal atoms, $(Ph_3Pb)_4M'$, show much higher stability in solution.

Spectral data regarding this series of compounds will be discussed elsewhere[9].

EXPERIMENTAL

The starting materials: triphenylplumbyllithium[10], triphenylstannyllithium[11], and triphenylgermyllithium[12], were prepared according to established procedures in an atmosphere of pure nitrogen; Ph_3PbLi was obtained from the reaction of $PbCl_2$ with 3 equivalents of PhLi in diethyl ether; Ph_3SnLi and Ph_3GeLi were prepared by treating Ph_3SnCl and Ph_3GeCl respectively with lithium in tetrahydrofuran.

General procedure for the preparation of the compounds $(Ph_3M_4)M'$

The preparations were carried out under nitrogen in a 250 ml three-necked round-bottomed flask provided with a magnetic stirrer, a thermometer and a nitrogen inlet tube. Into this flask 0.02 mole of Ph_3MLi ($M = Pb$, Sn or Ge) in 50 ml of ether (or THF) was introduced and the whole was chilled to about —50° by external cooling with dry ice-acetone. Subsequently, 0.01 mole of $PbCl_2$ (5.6 g) [or 0.005 mole of $SnCl_4$ (0.57 ml) or 0.005 mole of $GeCl_4$ (0.57 ml) respectively] was added and with constant stirring the reaction mixture was allowed to come to room temperature. In the case of $PbCl_2$ black metallic lead separated and in the other cases the mixtures turned slightly yellow and then light grey. The mixture was stirred for one hour at

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* X-ray analyses have been carried out at the Institute for Crystal Chemistry of the State University of Utrecht under the direction of Prof. A. F. PEERDEMAN. The results will be published separately.

room temperature. Hydrolysis was achieved by adding small pieces of ice. The organic solvent was removed from the hydrolyzed mixture by vacuum distillation under stirring. The precipitate was filtered off, dried and extracted with chloroform. Repeated concentration of the chloroform extract gave several crops of crystals; the identical crops were combined and recrystallized from the appropriate solvent. For data and analyses see Table 1.

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SUMMARY

The preparation of stable, crystalline compounds of the type $(Ph_3M)_4M'$ is described. They are obtainable according to the following reaction equation:

$$4Ph_3MLi + M'Cl_4 \longrightarrow (Ph_3M)_4M' + 4LiCl \qquad M = Pb, Sn; M' = Sn, Ge$$

The compounds with $M' = Pb$ are obtained as follows:

$$4Ph_3MLi + 2PbCl_2 \longrightarrow (Ph_3M)_4Pb + Pb + 4LiCl$$

Lead compounds are prepared most easily; $(Ph_3Ge)_4M'$ could not be obtained.

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