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SYNTHESIS AND SPECTROSCOPIC STUDIES OF PHENYLLEAD HALIDE AND THIOCYANATE ADDUCTS WITH HEXAMETHYLPHOSPHORAMIDE

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Summary

Hexamethylphosphoramide (HMPA) adducts of the type $Ph_3PbX\cdot HMPA$ (X=Cℓ, Br, I, and NCS), $Ph_2PbX_2\cdot 2HMPA$ (X=Cℓ, Br and I), and $Ph_2PbX_2\cdot HMPA$ (X=Br and I), have been prepared and characterized by infrared, Raman, mass, and ^{31}P nmr spectroscopy. Molecular weight and infrared solution data show that $Ph_3PbX\cdot HMPA$ adducts dissociate in benzene, the degree of dissociation being NCS<<Cℓ<Br<I. The thiocyanate adducts $Ph_3PbNCS\cdot HMPA$ and $Ph_2Pb(NCS)_2\cdot 2HMPA$ have ν(CN) and ν(CS) frequencies in the solid state, and ν(CN) frequencies and absorptivities in benzene solution consistent with N-bonded thiocyanate in the solid state and in benzene solution. Vibrational frequencies are reported in the range 260 to 80 cm^{-1} and assignments are made for ν(Pb-X), ν(Pb-O), and ν(Pb-NCS) modes. The 1:1 adducts $Ph_3PbX\cdot HMPA$ are monomeric and trigonal bipyramidal, whereas the 1:2 adducts $Ph_2PbX_2\cdot 2HMPA$ are monomeric

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and cis-octahedral and the $Ph_2PbX_2 \cdot HMPA$ appear to be halogen bridged polymers with lead six-coordinate. Coordination of HMPA causes a small upfield change in ^{31}P chemical shift values, and $^2J(Pb-P)$ values vary with X in the order: NCS>I~Br>Cℓ for $Ph_3PbX \cdot HMPA$ adducts. Corresponding tin and lead adducts are compared with respect to mode of adduct formation.

Introduction

Much less is known of phenyllead halide adducts compared with the analogous tin compounds (1). A few diphenyllead halide adducts with O-donor ligands have been prepared but no spectroscopic data were recorded (2,3), apart from ^{13}C and ^{207}Pb nmr data for solutions of phenyllead halides in O-donor solvents (4,5).

Recently, several adducts of $Ph_2Pb(NCS)_2$ including some with O-donors were prepared (6) and "NCS-group" vibrational data determined. In particular, $Ph_2Pb(NCS)_2 \cdot 2HMPA$ (HMPA=hexamethylphosphoramide) was found to be monomeric and undissociated in benzene thus raising the possibility of solution studies on organolead halide adducts with HMPA. As part of our continuing interest in the adducts of phenyllead and -tin halides and pseudohalides, we report the preparation and characterisation by infrared, Raman, mass, and ^{31}P nmr spectroscopy of adducts of diphenyl- and triphenyl-lead halides and isothiocyanates with HMPA. Our purpose is to investigate the effect of change in X and number of phenyl groups on adduct formation and properties, and to compare the lead adducts prepared here with the analogous tin compounds (7). Crystal data for $Ph_3PbC\ell \cdot HMPA$ were reported earlier (8).

Experimental

Triphenyllead chloride, and diphenyllead dichloride were commercial products dried in a vacuum before use. Triphenyllead bromide and iodide were prepared by the reaction of triphenyllead acetate with potassium halide in ethanol-water. Literature methods were used to prepare triphenyllead isothiocyanate (9) and diphenyllead dibromide and di-iodide (10). Benzene, pentane, and HMPA were dried and stored over molecular sieves before use.

Microanalyses for C,H,N, and halogen were done by Chemalytics, Tempe, Arizona, while molecular weights were determined by Galbraith Laboratories, Knoxville, Tennessee, using vapour pressure osmometry. Spectroscopic measurements (infrared, Raman, ^{31}P nmr, mass spectra) were made as described elsewhere (7).

Preparations

The parent phenyllead halide or isothiocyanate (2-5 gm) dissolved in a solution of HMPA (3-5 mℓ) in benzene (20-30 mℓ) and the adduct precipitated after pentane (50-100 mℓ) was added to the cooled solution. Where possible, crude products were recrystallised from benzene-pentane. Yields: 75-90%. Recrystallisation of the di-adducts of diphenyllead halides gave the mono-adduct. $Ph_2Pb(NCS)_2 \cdot 2HMPA$ was prepared as previously described (4).

Results and Discussion

Analytical data for the new adducts included in the present study are given in Table I. All adducts are air-stable crystalline solids with sharp melting points, and the triphenyllead halide adducts are soluble in many non-polar solvents such as benzene and dichloromethane but are insoluble in pentane. However, adducts in the $Ph_2PbX_2 \cdot nHMPA$ series (except $Ph_2Pb(NCS)_2 \cdot 2HMPA$ (6)) are only slightly soluble in benzene. The least soluble adduct was $Ph_2PbCℓ_2 \cdot 2HMPA$ which yielded $Ph_2PbCℓ_2$ when recrystallised from benzene, while $Ph_2PbX_2 \cdot 2HMPA$ (X=Br,I) gave the mono-adducts. Molecular weight and infrared solution data (Table II) show that most $Ph_3PbX \cdot HMPA$ adducts dissociate in benzene, the degree of dissociation being: NCS<<Cℓ<Br<I. For Ph_2PbX_2 adducts

TABLE I - Analytical Data [a]

Compound	Colour	MPt(°C)	%C	%H	%N	%X[b]
$Ph_3PbCl \cdot HMPA$	White	166-7	44.3 (44.1)	5.05 (5.1)	6.3 (6.4)	4.8 (5.4)
$Ph_3PbBr \cdot HMPA$	white	154-5	41.4 (41.3)	4.65 (4.8)	5.65 (6.0)	11.6 (11.45)
$Ph_3PbI \cdot HMPA$	cream	134-5	38.55 (38.7)	4.4 (4.5)	5.65 (5.6)	16.6 (17.0)
$Ph_3PbNCS \cdot HMPA$	white	120	44.0 (44.4)	4.7 (4.9)	8.1 (8.3)	-
$Ph_2PbCl_2 \cdot 2HMPA$	white	153-4	36.35 (36.5)	5.7 (5.9)	10.35 (10.6)	8.8 (9.0)
$Ph_2PbBr_2 \cdot 2HMPA$	white	162-3	32.1 (32.8)	5.2 (5.3)	9.1 (8.6)	18.6 (18.2)
$Ph_2PbI_2 \cdot 2HMPA$	pale-yellow	139	29.3 (29.6)	4.6 (4.8)	8.8 (8.6)	26.1 (26.1)
$Ph_2PbBr_2 \cdot HMPA$	white	179	30.7 (30.9)	4.0 (4.0)	5.8 (6.0)	22.9 (22.8)
$Ph_2PbI_2 . HMPA$	pale-yellow	124	27.0 (27.2)	3.35 (3.55)	5.6 (5.3)	32.5 (31.95)

[a] Calculated values in parentheses.

[b] X is halogen.

(X=Cℓ,Br,I), only infrared measurements on saturated solutions (<0·01M) could be made. Although some adduct is found in solution as confirmed by ^{31}P nmr studies, no trends in dissociation can be deduced from these results because any equilibria present must involve both the solid adduct and parent halide.

TABLE II - Solution data

Compound	Molecular[a] weight	$\nu(P{=}O)$[b] (cm^{-1})	^{31}P nmr[c]	
			δ_P (ppm)	$^2J_{Pb-P}$ (Hz)
$Ph_3PbCl\cdot HMPA$	387 (653)	1196m 1212wm	24.5	85
$Ph_3PbBr\cdot HMPA$	396 (698)	1195m 1213wm	24.2	100
$Ph_3PbI\cdot HMPA$	409 (745)	1198wm 1214m	23.3	100
$Ph_3PbNCS\cdot HMPA$	687 (676)	1192m 1212sh	24.8	125
$Ph_2PbCl_2\cdot 2HMPA$	d	1194m 1212s	24.8	184
$Ph_2PbBr_2\cdot 2HMPA$	d	1195s 1213m	24.7	186
$Ph_2PbI_2\cdot 2HMPA$	d	1197m 1214s	24.3	183
$Ph_2Pb(NCS)_2\cdot 2HMPA$ (6)	840 (836)	1193s	23.5	206
$Ph_2PbBr_2\cdot HMPA$	d	1192s 1211m	23.8	168
$Ph_2PbI_2\cdot HMPA$	d	1196s 1213sm	24.1	not obs.

[a] In benzene, at 39°C; conc. 0.01M; theoretical values are in parentheses.

[b] In benzene; conc. 0.05M or saturated solution; for free HMPA, $\nu(P{=}O)$ is $1214cm^{-1}$.

[c] In $CDCl_3/CH_2Cl_2$ eutectic at 190K; chemical shifts are positive downfield from 85% H_3PO_4 external reference; for free HMPA, δ_P is 26.5 ppm.

[d] Insufficiently soluble for molecular weight measurement.

Vibrational Spectra

For $Ph_3PbNCS \cdot HMPA$, NCS-group vibrational data both in the solid state; ν(CN), 2050s (R), 2057 vs (IR); ν(CS) 799w(R), 797vw(IR); and in benzene solution; ν(CN), 2043(R), 2042(IR), with $A_{CN} = 12 \times 10^4\ M^{-1}cm^{-2}(NCS)^{-1}$, indicate predominantly N-bonded thiocyanate is present, as was found earlier for $Ph_2Pb(NCS)_2 \cdot 2HMPA$ (6)(from solid-state data) and the corresponding tin compounds (7). In benzene solution $Ph_2Pb(NCS)_2 \cdot 2HMPA$ shows ν(CN) at 2041 cm^{-1} (R), 2030 cm^{-1}(IR), with $A_{CN} = 17 \times 10^4 M^{-1}cm^{-2}(NCS)^{-1}$, all consistent with the presence of N-bonded thiocyanate.

Skeletal frequencies in the region below 250 cm^{-1} for these compounds, are given in Tables III to V; weak peaks (130-160 cm^{-1}) due to the phenyl group (x) vibration have been omitted. The assignments given were based on those for the parent phenyllead halides reported by Clark et al(11). Lead-oxygen stretching modes were assigned to the 200-220 cm^{-1} region, slightly lower than in the corresponding tin compounds. Since no crystal structures of phenyllead halide adducts have yet been published, only tentative structural conclusions can be reached on the basis of the vibrational data reported here. Only recently were the crystal structures of Ph_3PhX(X=Cℓ,Br) determined (13) although that of $Ph_2PbC\ell_2$ has been known for some time (14).

The triphenyllead halide adducts show a single lead-halogen stretching mode both infrared and Raman active and two lead-phenyl stretches, one strongly infrared active (asymmetric) and the other only Raman active(symmetric). In addition, for $Ph_3MX \cdot HMPA$(M=Sn or Pb) pairs, values of the ratios ν(Pb-X)/ν(Sn-X)* are 0.86(X=Cℓ), 0.95(X=Br), 0.96(X=I) and 0.86(X=NCS), while for

(Continued on p. 425)

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* Values of the ratio ν(Pb-X)/ν(Sn-X) for representative pairs of isostructural lead and tin halide species are: $MC\ell_4$, 0.87; $MC\ell_6^{2-}$, 0.89; Ph_3MX, 0.89(X=Cℓ), 0.83(X=Br), 0.96(X=1)(7,15).

TABLE III - Skeletal Frequencies (cm^{-1}) for $Ph_3PbX \cdot HMPA$

X=Cl		X=Br		X=I		X=NCS		ASSIGNMENT
IR	R	IR	R	IR	R	IR	R	
224sh	229m	224vs	228m	232 225 vs	229m	235sh 230vs	235 230 m	ν_{as}(Pb-Ph) (t)*
217vs	216m							ν(Pb-Cl)
				215s	218m			2ν(Pb-I)
207sh	208vw	204m		202vs		208vs	207sh	ν(Pb-O)
	195vs		199vs		199vs		198vs	ν_s(Pb-Ph) (t')*
187s 171sh	169vw	182m	184sh	177m	184m	176s	184m	(u)*
						162vs,br		ν(Pb-NCS)
		140s	140s					ν(Pb-Br)
				108vs	108vs			ν(Pb-I)
123w 103w 87vw	123w 105wm	118vw 96vw 86w		98sh 88vw		102sbr 89sh		deformations

* Whiffen's notation (12)

TABLE IV. Skeletal Frequencies (cm^{-1}) for $Ph_2PbX_2 \cdot 2HMPA$

X=Cl		X=Br		X=I		X=NCS		Assignment
IR	R	IR	R	IR	R	IR	R	
253m		252s	253w	247s	251vw	257m	263wbr	(y')*
232s	232s	230s	233w	224s	227w	235m		ν_{as}(Pb-Ph) (t)*
	221sh							$2\delta(PbCl_2)$
212vs	210sh							ν(Pb-Cl)
		213wsh		213wsh				ν(Pb-O)
203vw		206bsh			207sh			
	198vs	201w	198vs	193m	194vs	200mbr	205vs	ν(Pb-Ph) (t')*
188s								see below**
		177vw		174w	173sh			(u)
		163vw		166vw				
						160 145 vs,br	155 135 vw,br	ν(Pb-NCS)
		140vs	140m					ν(Pb-Br)
				112vs	115s 112sh			ν(Pb-I)
112wm	113m							$\delta(PbCl_2)$
103w						114sh		Deformations
95wm					93sh	92sh		
87wm	86vs	88wmbr		88w				
	78m		77vs		80m			

* Whiffen's notation (12)

** Assigned to ν_{as}(Pb-Ph)(t') modified by Fermi resonance with a combination mode, perhaps (86+103) or (78+103).

TABLE V - Skeletal Frequencies (cm^{-1}) for $Ph_2PbX_2 \cdot$HMPA

X=Br		X=I		Assignment
IR	R	IR	R	
252m	253vw	249s	249vw	(y')*
222s	226w		223w	ν_{as}(Pb-Ph) (t)*
		215vs		
214s	218w		210w	ν(Pb-O)
202vw	198vs	198m	194s	ν_s(Ph-Ph) (t')*
189w	190s	188sh		
		169vw		(u)*
156vs	157m			ν_t(Pb-Br) (terminal)
		127vs	131vs	ν_t(Pb-I) (terminal)
121vs	121m			ν_b(Pb-Br) (bridging)
		100 vs	99m	ν_b(Pb-I) (bridging)
99m	105m			Deformations
	84sh		85w	
77s				

* Whiffen's notation (12).

X=Cℓ or Br, the ν(Pb-X) values are above those found for solid Ph_3PbX where lead is five-coordinate with strong halogen bridges (13). These results indicate a monomeric trigonal-bipyramidal structure like that of $Ph_3SnX \cdot$HMPA for $Ph_3PbX \cdot$HMPA with axial HMPA and X ligands and all phenyl groups equatorial. As in the tin analogues, splitting of the ν_{as}(Pb-Ph) band shows a lowering of the trigonal local symmetry around the lead caused by the asymmetric HMPA ligand.

Since lead unlike tin readily achieves a coordination greater than six*, the slight solubility of the di-adducts,

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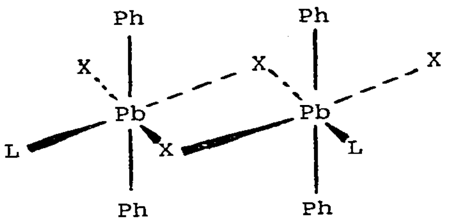
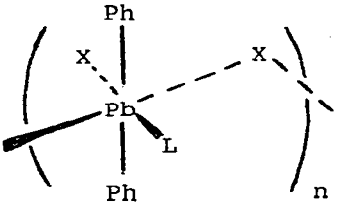
* For example, compare the behaviour of $Me_2Pb(ox)_2$ in O-donor solvents with that of $Me_2Sn(ox)_2$(16), and the formation of adducts by $Me_2Pb(OBz)_2$ with both benzoate groups retaining bidentate co-ordination(17).

$Ph_2PbX_2\cdot 2HMPA$ (X=Cℓ,Br,I) could imply a polymeric structure involving halogen bridges as found in $Ph_2PbC\ell_2$(14). However, the sharp melting points and the ν(Pb-X)/ν(Sn-X) values of 0.95(X=Cℓ), 1.00(X=Br) and 0.98(X=I) for these compounds suggest that like their tin counterparts, they have a monomeric six-coordinate octahedral structure, with either cis or trans arrangements of the halide and HMPA ligands. The coincidence of infrared and Raman values for ν(Pb-X) and the Raman activity of ν_{as}(Pb-Ph) and infrared activity of ν_s(Pb-Ph), all favour the cis structure for these adducts. The same structure was proposed earlier for $Ph_2Pb(NCS)_2\cdot 2HMPA$ based on thiocyanate group frequencies (6).

The mono-adducts with Ph_2PbX_2(X=Br,I) could be five-coordinate like their tin analogues. However, ν(Pb-X) values in the same range as for the di-adducts and splitting of ν_s(Pb-Ph), presumably due to coupling between adjacent Ph_2Pb units, suggest structures (II) using halogen bridges to achieve six-coordinate lead for these compounds.



IIa



IIb

The two lead-halogen stretching frequencies observed, both infrared and Raman active, are thus assigned to terminal (higher) and bridging (lower) ν(Pb-X) modes. Indeed, the ν_b(Pb-Br) value for $Ph_2PbBr_2\cdot HMPA$(121 cm^{-1}) is the same as that found for solid Ph_2PbBr_2 (122 cm^{-1}) which is polymeric (11).

^{31}P nmr Spectra

All adducts gave a single sharp peak at room temperature in $CD\ell_3/CH_2C\ell_2$ (Table II) indicating fast exchange of coordinated and free ligands. A temperature of 190-200K was required to resolve separate free and coordinated ligand peaks in $CD\ell_3/CH_2C\ell_2$ eutectic as solvent.

Peaks may be uniquely assigned for solutions of $Ph_2Pb(NCS)_2\cdot$2HMPA which is undissociated at room temperature and for solutions of $Ph_3PbX\cdot$HMPA where only one adduct is possible. However, for the rest of the diphenyllead halide adducts, without solution molecular weight data, the nature of the solute species for these compounds is uncertain and no definite assignments can be made.

Coordination of HMPA in all cases causes a small upfield movement in δ_P as in the corresponding tin adduct (7), presumably because any decrease in electron density at phosphorus due to oxygen coordination is compensated by electron donation from the $-\ddot{N}Me_2$ groups.

Lead-phosphorous coupling constants show more variation with adduct type than do chemical shift values. For the $Ph_3PbX\cdot$HMPA series, ^2J(Pb-P) varies with X in the order: NCS>I~Br>Cℓ, which differs from that found for the tin series:I>NCS>Br>Cℓ. Thus, the nmr "trans-influence" (18) of an anion X^- cannot be automatically assumed to be the same in an analogous series of tin and lead compounds. For the diphenyllead halide adducts ^2J(Pb-P) values appear to increase with increasing coordination but, without definite assignments, the effect of X on ^2J(Pb-P) values cannot be discussed further.

Mass Spectra

As expected for compounds of this type over sixty percent of the ion current in most cases is due to $HMPA^{\cdot+}$ and its fragmentation products $(Me_2N)_2PO^+$ and Me_2NPOH^+. The lead-containing

TABLE VI - Mass spectral data (lead-containing ions)*

$Ph_3PbX\cdot HMPA$				$Ph_2PbX_2\cdot nHMPA$					
ION	X=Cl	X=Br	X=I	ION	X=Cl n=2	X=Br n=2	X=Br n=1	X=I n=2	X=I n=1
$Ph_2PbX\cdot HMPA^+$	1.4	0.3	-	$Ph_2PbX\cdot HMPA^+$	0.6	0.3	0.4	0.4	0.5
$Ph_3Pb\cdot HMPA^+$	0.5	0.1	0.2	$PbX\cdot HMPA^+$	-	0.3	0.6	1.2	1.1
$PhPb\cdot HMPA^+$	0.5	0.1	-	$Pb\cdot HMPA^{+\cdot}$	1.3	0.3	0.4	0.8	1.7
$PbX\cdot HMPA^+$	1.4	0.4	-	$Ph_2PbX_2^{+\cdot}$	-	0.3	0.2	-	-
$Pb\cdot HMPA^+$	1.4	0.5	-	Ph_2PbX^+	10.2	15.2	17.8	24.9	11.2
Ph_2PbX^+	16.6	22.9	0.9	$PhPbX_2^+$	2.6	4.3	4.3	0.2	0.3
Ph_3Pb^+	11.4	6.0	28.0	$PhPbX^{+\cdot}$	1.9	1.1	0.6	1.0	0.6
$PhPbX^{+\cdot}$	-	0.9	-	$PhPb^+$	9.6	4.5	6.4	10.4	14.6
$Ph_2Pb^{+\cdot}$	-	0.9	-	$PbX_2^{+\cdot}$	-	8.8	2.5	7.9	5.6
PbX^+	23.7	22.0	9.9	PbX^+	23.1	41.7	33.0	25.0	25.4
$PhPb^+$	14.2	17.9	32.0	$Pb^{+\cdot}$	50.6	23.3	33.8	21.3	39.0
$Pb^{+\cdot}$	28.9	28.0	29.0						

* Percentage of the total positive ion current carried by metal-containing ions.

ions (Table VI) are dominated by the even electron species Ph_3Pb^+, Ph_2PbX^+, $PhPb^+$, and PbX^+, following the general trend observed in the mass spectra of organometallic compounds of Group IV elements (19). The only abundant (>10%) odd-electron lead-containing species is $Pb^{+\cdot}$. No parent ion was observed for adducts of either Ph_3PbX or Ph_2PbX_2 and only for $Ph_2PbBr_2\cdot nHMPA$ was an ion corresponding to the parent Lewis acid observed. Several species are observed with one HMPA coordinated which may be formed by loss of phenyl or halogen from the parent molecule-ions. Interestingly, the HMPA bonds sufficiently to lead so that $Pb\cdot HMPA^{+\cdot}$ is observed in all but one spectrum. However, there is always the possibility of these ions containing HMPA being formed by recombination in the mass spectrometer.

Comparison of lead-containing ion abundance data for $Ph_3PbX\cdot HMPA$ and the parent Lewis acids (20) shows significant differences when X=Cℓ and Br. For X=Cℓ, the metal ion Pb^+ is less abundant in the adduct spectrum (29%) than in fact of the parent chloride (38%), while for bromide species differences mainly occur in the abundance of three coordinate species, adduct 23% and 6%, parent bromide 18% and 17%, of Ph_2PbBr^+ and Ph_3Pb^+ respectively. This indicates that coordinated HMPA affects the fragmentation of these adducts, perhaps following a pattern like that suggested for the corresponding tin compounds (7). However, these differences are not as great as those between $Ph_3SnC\ell\cdot HMPA$ and $Ph_3SnC\ell$, which together with the smaller abundances of HMPA-containing metal ions and a greater fraction of total ion current carried by $HMPA^{+\cdot}$ and its fragmentation products in the lead cases, would suggest that loss of HMPA before or after ionisation is more important for $Ph_3PbX\cdot HMPA$ (X=Cℓ, Br) than for $Ph_3SnC\ell\cdot HMPA$. For $Ph_3PbI\cdot HMPA$, the principal metal ions (>20%) are Ph_3Pb^+, $PhPb^+$, and $Pb^{+\cdot}$, as is also found for Ph_3PbI and Ph_4Pb (21), showing loss of $I^\cdot$ and HMPA to give Ph_3Pb^+ is the main fragmentation process of the iodide adduct. Unfortunately, like other Group IV derivatives, no metastable ions were observed and therefore no detailed fragmentation pattern was proposed for the triphenyllead halide adducts studied here.

Mass spectral data for Ph_2PbX_2(X=Cℓ, Br, I) are not yet available and thus the effect of coordinated HMPA on the fragmentation of the diphenyllead halide adducts cannot be assessed. The ion $Pb^{+\cdot}$ is unusually abundant (75%) in the lead-ion spectrum of $Ph_2PbC\ell_2$, while the lead-containing ion abundance data for the mono- and di-adducts of Ph_2PbX_2(X=Br, I) show distinct differences perhaps due to the different numbers of HMPA ligand molecules present in these adducts.

Comparison of Phenyl-tin and -lead Halides and their HMPA Adducts.

A recent review of crystal structures of tin compounds (22) shows phenyl-tin chlorides, bromides, and iodides are mainly molecular in the solid state with weak halogen-bridging interactions causing some distortions from a regular tetrahedral arrangement around tin. These compounds are low melting and freely soluble in a range of non-coordinating solvents. In contrast, X-ray studies (13, 14) and vibrational results (11) indicate phenyllead chlorides and bromides are polymeric with strong halogen-bridging sufficient to render Ph_2PbX_2(X=Cℓ, Br) insoluble in non-coordinating solvents. Iodide bridges are weaker causing Ph_2PbI_2 to be soluble in benzene as are all Ph_3PbX(X=Cℓ, Br, I). Melting points of all phenyllead halides are higher than those of their tin counterparts the difference being least for iodides. Both di- and tri-phenyl-tin and lead-thiocyanates (6, 23) are polymeric as are Ph_3SnNCO(24) and Ph_3PbNCO(25), in all cases using the ambidentate —NCS— or —NCO— groups.

The HMPA adducts of di- and triphenyltin and lead halides and thiocyanates are more similar in structure and properties as compared with the parent compounds. Thus all $Ph_3MX\cdot HMPA$ (M=Sn, Pb) are five-coordinate monomers, soluble in benzene, with very similar melting points. Only for X= NCS is there a noteworthy difference in melting points. The di-adducts with Ph_2MX_2(M=Sn, Pb) all have monomeric six coordinate structures, with a trans Ph_2M group. However, the tin compounds with the trans-X_2-trans-L_2 configuration are in general lower melting and more soluble in benzene than the lead compounds which have the cis-X_2—cis-L_2 configuration. Factors influencing the choice of trans or cis MX_2L_2 configurations in $Ph_2SnX_2L_2$ systems are not well understood (22) and as well as the nature of L or X, a change from tin to lead also has an effect. Interestingly, both $Ph_2M(NCS)_2\cdot 2HMPA$ species, although monomeric and soluble in benzene, have the same high melting point (~230°C).

The essential difference in the phenyl -tin and -lead halide systems is shown by the mono-adducts, $Ph_2MX_2\cdot HMPA$. For M=Sn, the adducts are monomeric five coordinate, soluble in benzene, with melting points between those of the di-adduct and parent halide. With M=Pb, six-coordination is probably retained due to halogen bridges, causing the adducts to be only very slightly soluble in benzene. For X=Br, melting points lie in the order Ph_2PbBr_2>mono-adduct>di-adduct, but for X=I, the opposite order occurs, presumably connected with the much weaker bridging in Ph_2PbI_2 compared with Ph_2PbBr_2(11).

Adduct formation by phenyl-tin halides occurs by the forming of tin-ligand bonds causing an increase in the coordination number of the central tin atom. In contrast, in the lead case, no change in coordination occurs and adduct formation requires that halogen bridges (sometimes strong) be broken. Thus, while one would expect analogous tin and lead compounds not to differ greatly in acceptor strength, because of the two different processes apparently used for adduct formation, it is unwise to extrapolate too closely the formation, structure, and properties of phenyl -lead halide adducts from the better known tin compounds.

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