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# PHOSPHORUS, ARSENIC AND ANTIMONY COMPLEXES OF THE MAIN GROUP ELEMENTS

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## CONTENTS

## ABBREVIATIONS

| | |
|---|---|
| QAS | tris(*o*-diphenylarsinophenyl)arsine |
| dpe | 1,2-bis(diphenylphosphino)ethane |
| das | *o*-phenylenebis(dimethylarsine) |
| dee | 1,2-bis(diethylphosphino)ethane |

## A. INTRODUCTION

Transition metal complexes of phosphorus, arsenic and antimony donors have been extensively studied during the past 20 years [1]. The metals of group IA and IIA do not complex with heavy group VB donors *, but the more metallic elements of the *p*-block complex do, under appropriate conditions. The coordination chemistry of the *p*-block elements has attracted much less interest than that of the transition metals — thus the former lack both the '*d*—*d*' spectra and paramagnetism which have prompted so much work on the latter. Main group chemistry also lacks a simple theoretical model, analogous

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* Phosphine complexes of beryllium halides have not been prepared [2], but adducts with organoberyllium compounds are known, e.g. $Ph_2Be \cdot 2Me_3P$ [3].

to ligand field theory, which aids interpretation of the results. This is not to say that main group complexes are of only minor interest; e.g. aluminium complexes are of great importance in Friedel—Crafts and Ziegler—Natta processes.

The present review covers the complexes of the metallic elements of groups IIIB, IVB, with phosphine, arsine and stibine donor ligands (see below). The complexes of boron halides and hydrides have been reviewed several times [4—6] and will not be dealt with here.

|  | B | C | N |
|---|---|---|---|
|  | Al | Si | P |
| Zn | Ga | Ge | As |
| Cd | In | Sn | Sb |
| Hg | Tl | Pb | Bi |

Although there are considerable analogies between the *p*-block and the more familiar *d*-block complexes, there are also some significant differences. Variations in oxidation state and stereochemistry can be controlled in transition metal chemistry to a considerable degree by the experimental conditions and the ligands used. In main group chemistry oxidation states tend to be restricted and less amenable to alteration by small changes in ligand properties.

Many of the *p*-block halides and their complexes are very sensitive to moisture, and oxygen sensitivity is not uncommon, so that preparation and studies must be carried out under rigorously dry conditions and in an inert atmosphere. The complexes often undergo facile isomerism, ionisation or partial dissociation in solution in various solvents, and, especially in some of the earlier work, erroneous conclusions were drawn about solid state structures by extrapolation of data obtained from solution studies. In the absence of spectroscopic data to the contrary it is dangerous to assume that the solid state and solution structures are the same.

In addition to adduct formation, main group halides can react with heavy group VB donor ligands in a number of ways:

(a) oxidation of the ligand, e.g.

$$R_3Sb + SnX_4 \rightarrow R_3SnX_2 + SnX_2$$

(b) scrambling of the substituents

$$BiR_3 + SnX_4 \rightarrow RBiCl_2 + R_2SnCl_2$$

(c) ligands with acidic hydrogen, i.e. primary or secondary phosphines or arsines form unstable adducts which eliminate HX in the presence of a base ($R_3N$ usually) or thermally lose alkane in the cases of organometallic compounds

$$R_3Al + HPR_2 \rightarrow R_2Al \cdot HPR_2 \rightarrow R_2Al{-}PR_2 + RH$$

Very little is known about the intermediate $R_3M{-}PR_2H$ compounds, but the $R_2M{-}PR_2$ (and $-AsR_2$) have been reviewed [6,7].

## B. ALUMINIUM

Despite the extensive use of aluminium chloride as a Lewis acid few reports of the isolation of group VB Lewis base complexes have appeared.

Beattie and Ozin [8] prepared $AlCl_3(Me_3P)_2$ which was assigned a five-coordinate ($D_{3h}$) structure on the basis of the IR and Raman spectral results. The $^{27}Al$ and $^{31}P$ NMR spectra of $AlX_3(Me_3P)$ (X = Cl, Br) in toluene solution were reported by other workers [9], but the preparation of the adducts was not described. The 1 : 1 adduct of $AlBr_3$ and $P^nBu_3$ is a colourless crystalline solid, which can be recrystallised from benzene, in which it exhibits evidence of considerable association [10]. The enthalpy of formation of 1 : 1 alkylphosphine complexes of $AlBr_3$ has been examined. The heats of formation of $AlBr_3(PR_3)$ (R = $Bu^n$, hexyl, octyl) are about 40—50 kcal, but for the arylphosphine analogue the values are much lower, which was interpreted as due to $\pi$-bonding making the lone pair less available for donation to the metal [11,12]. An $(AlBr_3)_2PPh_3$ appears to form in solution in the presence of excess aluminium bromide.

The reaction of triphenylarsine with $AlCl_3$ yields [13] a colourless crystalline 1 : 1 adduct, which is thermally stable at temperatures less than 250° C, but which is readily oxidised by dry air in benzene solution to $Ph_3AsO$. Bromobenzene under reflux converts it to a $Ph_4As^+$ salt. Triphenylstibine and triphenylbismuthine are chlorinated by $AlCl_3$ [14], but $Et_3Sb$ and $AlCl_3$ yield a yellow—green liquid believed to be $AlCl_3(SbEt_3)$ [15]. A large excess of $Et_3Sb$ in this reaction produced a brown solid identified as $AlCl_3(SbEt_3)(SbEt_2Cl)$ [15].

Greenwood et al. [16] were unable to prepare $AlH_3(PMe_3)$; trimethylphosphine did not displace $Me_3N$ from $AlH_3(NMe_3)$, and the reaction of $LiAlH_4$, $PMe_3$ and HCl produced aluminium metal and hydrogen. This suggests that (the unknown) $AlH_3(PMe_3)$ is much less stable than the boron and gallium analogues. Proton NMR spectra showed that aluminium chlorohydrides form only 1 : 1 adducts with $PEt_3$ of types $AlH_nCl_{3-n} \cdot (PEt_3)$ [17].

Aluminium borohydride $Al(BH_4)_3$ forms [18,19] exceedingly moisture-sensitive 1 : 1 adducts with $PMe_3$, $AsMe_3$ and $PPh_3$. The $Al(BH_4)_3AsMe_3$ does not react further with $AsMe_3$, but the trimethylphosphine analogue takes up a further mole of $PMe_3$ to form $Al(BH_4)_3(PMe_3)_2$, which slowly decomposes into $BH_3 \cdot PMe_3$. The complex $Al(BH_4)_3 \cdot PPh_3$, which is monomeric in benzene, also forms $BH_3 \cdot PPh_3$ on thermal decomposition. Adducts of organoaluminium compounds have been reviewed [20].

## C. GALLIUM

Gallium dihalides $Ga^I[Ga^{III}X_4]$ react [21] with the tripod tetraarsine, tris(*o*-diphenylarsinophenyl)arsine (QAS), to form colourless air-sensitive $Ga_2X_4(QAS)$ (X = Cl, Br), formulated as $[Ga^I(QAS)][Ga^{III}X_4]$. This seems to imply the presence of a trigonal pyramidal cation, and a spectroscopic reinvestigation would be interesting.

Gallium(III) chloride and bromide forms 1 : 1 adducts with phosphine, but gallium(III) iodide shows little tendency to take up phosphine. Alkyl and aryl phosphines form 1 : 1 adducts with gallium(III) halides — $GaX_3 \cdot PR_3$ ($X$ = Cl, Br, I, $R_3$ = $Me_3$ [8,22], $Ph_3$ [11,12,23,24], ($p$-tolyl)$_3$ [23,24], ($p$-$MeOC_6H_4$)$_3$ [23,24]; $X$ = Cl, Br, $R_3$ = $Bu^n_3$, hexyl$_3$, octyl$_3$, $PhPr_2$, $Ph_2Et$ [11,12]). Vibrational spectra in the solid state and molecular weight studies in benzene suggest that the trimethylphosphine complexes are monomeric pseudotetrahedral ($C_{3v}$) molecules [8,22]. The tertiary arylphosphine complexes appear to be similar in the solid state, but in solution the structures are solvent dependent. In $CH_2Cl_2$ [24] and $C_6H_6$ [22], the structures appear to remain pseudotetrahedral, but in $CH_3NO_2$ or $(CH_3)_2CO$ [23,24] conducting solutions are formed, with IR spectra consistent with $GaX_4^-$ ions. The cations were not identified.

The bidentate 1,2-bis(diphenylphosphino)ethane (dpe) forms complexes of stoichiometry $Ga_2X_6$(dpe) ($X$ = Cl, Br, I) [23,24]. In the solid state the vibrational spectra for $X$ = Cl, Br, are consistent with an $X_3Ga$—(dpe)—$GaX_3$ structure, but the iodide has a markedly different spectrum and may be ionic [Ga(dpe)$I_2$][$GaI_4$] [24]. $o$-Phenylenebis(dimethylarsine) (das) forms $GaX_3 \cdot 0.5$ (das) ($X$ = Cl), but $GaX_3$(das) ($X$ = Br, I) [25]. These complexes are stable in air for several hours and dissolve in a variety of solvents to give conducting solutions. On the basis of measurements in solution the complexes are formulated [Ga(das)$_2Cl_2$][$Ga_3Cl_{10}$] and [Ga(das)$_2X_2$][$GaX_4$] ($X$ = Br, I) [25], but in the absence of spectroscopic data the presence of a different structure in the solids is not excluded. Tris(ligand) complexes $[Ga(das)_3]^{3+}$ could not be obtained [25].

Greenwood et al. [16,26] obtained several adducts of gallane with monodentate phosphines. Contrary to the reaction with $LiAlH_4$, $PPh_3$ or $PMe_3$ react with $LiGaH_4$ and HCl in ether to form $GaH_3 \cdot PR_3$:

$$LiGaH_4 + PR_3 + HCl \rightarrow GaH_3 \cdot PR_3 + LiCl + H_2$$

Neither the $Me_3N$ nor $AsPh_3$ analogues are formed by this type of reaction. Gas-phase displacement reactions indicate that $Me_3N$ and $PMe_3$ have approximately equal donor strengths towards $GaH_3$ [16]. Dimethylphosphine forms [16] $GaH_3 \cdot PMe_2H$, but this decomposes readily into Ga, $Me_2PH$ and hydrogen, and the complexes with $Ph_2PH$ and $Et_2PH$ are even less stable. Poorly characterised species containing $GaH_3$ and phosphines are mentioned in several patents, e.g. ref. 27, and it is claimed that thermal decomposition of this type of adduct produces gallium phosphide or arsenide semiconductors.

## D. INDIUM

No complexes of indium(I) have been prepared.

Indium(III) halides form a considerable number of phosphine complexes, which are obtained by mixing the constituents in non-aqueous solvents, or in the cases of volatile ligands by reaction in the absence of a solvent. The products are colourless crystalline solids, which are considerably less sensitive to water than the aluminium and gallium analogues. Trimethylphosphine forms [8,28] 2 : 1 adducts with all three indium(III) halides [cf. $GaX_3 \cdot PMe_3$ and $AlCl_3 \cdot (Me_3P)_2$]. A single-crystal Raman study [29] of $InCl_3(PMe_3)_2$ identified the $\nu$(In-P) at 135 $cm^{-1}$, and vibrational spectral data have shown that both the $PMe_3$ and $PEt_3$ complexes have *trans* trigonal bipyramidal ($D_{3h}$) structures [8,28,32]. Dimethylphenylphosphine forms 3 : 1 complexes, $InX_3(PMe_2Ph)_3$ (X = Cl, Br) [28], which lose one equivalent of phosphine upon washing with diethylether to form $InX_3(PMe_2Ph)_2$. Vibrational spectra have shown that the tris complexes are not mixtures of the bis complex and free ligand but were not able to distinguish whether the structure contained *mer* or *fac* isomers. As proton NMR spectra are of little use for structural assignment, owing to rapid ligand exchange [28,30] this problem must await the results of an X-ray study.

Complexes of stoichiometry $InX_3(PR_3)_2$ have been prepared with a range of phosphines (X = Cl, Br, $R_3$ = $Ph_2Et$ [28,30], $Ph_2Me$ [30], $(p\text{-tolyl})_3$ [30,23]; X = Cl, Br, I, $R_3$ = $Ph_3$ [31,33], $Ph_2(p\text{-tolyl})$ [30]; X = Br, $R_3$ = $(C_6H_{11})_3$ [30]; X = Cl, $R_3$ = $(p\text{-MeOC}_6H_4)_3$ [23]). Vibrational spectra are consistent with the presence of discrete five-coordinate trigonal bipyramidal molecules. The structure of $InCl_3(PPh_3)_2$ has been established by an X-ray study [33]. The molecule is a slightly distorted trigonal bipyramid (Fig. 1); the In—Cl distance is reasonable (2.383 Å) for a single bond, but the In—P bonds are unexpectedly long (2.71 Å).

The indium iodide complexes are of uncertain structure. Differences in the far IR spectra of $InCl_3(PPh_3)_2$ and $InI_3(PPh_3)_2$ may suggest that the latter

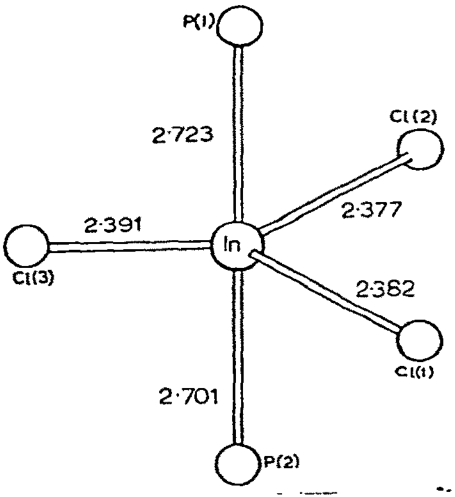

Fig. 1. The structure of $InCl_3(PPh_3)_2$. (Reproduced by permission of The Chemical Society.)

is *cis* trigonal bipyramidal or even an ionic dimer [31]. An X-ray study of one of these iodo complexes is needed to clear up this problem. The iodo complexes $InI_3(PR_3)_2$ also show a marked tendency to lose ligand and become four-coordinate $InI_3 \cdot PR_3$ (R = Ph [34], *p*-tolyl [23], *p*-$MeOC_6H_4$ [23]). Tricyclohexylphosphine normally forms only 1 : 1 complexes [28], but an $InBr_3[P(C_6H_{11})_3]_2$ has been prepared [30]. The 1 : 1 adducts are probably pseudotetrahedral ($C_{3v}$) molecules [28,30]. The flexible aliphatic phosphine $P^nBu_3$ gave only oily products with indium(III) halides [28].

In solution indium—phosphine complexes are labile, undergoing rapid ligand exchange. In nitromethane solution the arylphosphine complexes exhibit significant conductance [23] which was attributed to the formation of $[InL_2X_2][InX_4]$ or $[InL_4X_2]InX_4$, although the nitromethane is probably sufficiently polar to function as a ligand itself. The lability in solution is shown by the rapid formation of the appropriate palladium or platinum complexes on reaction with $Na_2MX_4$, and $InCl_3(PMe_3)_2$ has been proposed as an alternative to $[AgI \cdot PMe_3]_4$ or $AgNO_3 \cdot PMe_3$ as a means of storing trimethylphosphine [28]. In solution the triphenylphosphine complexes were readily oxidised to the corresponding phosphine oxide [34].

Hydrated indium(III) perchlorate reacts [35] with $PPh_3$ under reflux in EtOH—$CCl_4$ to form $In(PPh_3)_4(ClO_4)_3$. Triphenylarsine does not complex in solution, but $In(AsPh_3)_4(ClO_4)_3$ was obtained from the constituents in a sealed tube. IR spectra confirm that the perchlorate groups are ionic and hence the indium is four-coordinate, in contrast with the six-coordination found with sulphur and oxygen donors.

1,2-Bis(diphenylphosphino)ethane forms [31] 1 : 1 $InX_3$(dpe) for X = Br, I but surprisingly not for X = Cl, which is unexpected, and no explanation for this has been forthcoming. These complexes may be *cis* tbp, but this has not been established. Indium perchlorate also forms the four-coordinate $[In(dpe)_2](ClO_4)_3$ [35a]. A 1 : 1 ratio $InX_3$ : das in benzene or diethyl ether produced $InX_3 \cdot$ das (X = Cl, Br) and $InX_3 \cdot 1.5$(das) [25]. Based upon cryoscopic and conductimetry studies on nitrobenzene solutions, these were formulated $[In(das)_2X_2]InX_4$ and $[In(das)_2I_2][In(das)I_4]$, the production of the latter being tentatively attributed to lattice energy factors in the solid state [25]. Again it is necessary to stress that the solution behaviour (which may itself be open to more than one interpretation) may be a poor guide to solid state structures, and a detailed spectroscopic examination would be interesting.

Roundhill [30] has prepared olefin—phosphine complexes of indium iodide — $InI_3(Ph_2PCH{=}CH_2)$ and $InI_3(Ph_2PCH_2CH_2CH{=}CH_2)_2$. The latter is a five-coordinate $InI_3P_2$ moiety, but the former is of uncertain structure. The IR spectrum does not clearly distinguish between a polymer or the presence of indium—olefin coordination. An X-ray examination would be most interesting. The factors influencing the stoichiometry and structure of indium(III) complexes have been discussed in the excellent review of Carty and Tuck [35b].

## E. THALLIUM

Mass spectrometry studies [36] have demonstrated that $TlL^+$, L = $PPh_3$, $AsPh_3$, $BiPh_3$, are formed in the gas phase, but no solid thallium(I) complexes have been isolated. Attempts to prepare complexes of $PPh_3$ [37,38], $AsPh_3$ [37,38], $AsMe_2Ph$ [39] or o-$C_6H_4(AsMe_2)_2$ [25,39] with thallium(III) halides have been unsuccessful, reduction to thallium(I) and oxidation of the ligand occurring. Nyholm and Ulm [25] were also unable to prepare diarsine complexes by reaction of $[Tl(bipy)_2X_2][TlX_4]$ (bipy = 2,2'-bipyridyl) with (das). Triphenylstibine and triphenylbismuthine are also chlorinated by $TlCl_3$ [38, 40,41]. Adducts with organothallium(III) complexes are known, however [42—45].

## F. SILICON

Isslieb and Reinhold [45] obtained 1 : 2 adducts between silicon tetrachloride and a range of tertiary phosphine ($PEt_3$, $P(C_6H_{11})_3$, $PPr_3$). The complexes were described as moisture-sensitive colourless solids, with normal molecular weights in benzene solution. Beattie and Webster [46] demonstrated that under rigorously anhydrous conditions $P(C_6H_{11})_3$ did not complex with $SiCl_4$ in benzene solution and concluded that Isslieb and Reinhold's products may have been phosphonium compounds. Clark et al. [47] also reported that (das) did not complex with $SiCl_4$, and thus it seemed that silicon halides had little or no tendency to complex with phosphorus and arsenic donor ligands. However, the isolation [8] of $AlCl_3 \cdot (PMe_3)_2$ suggested that $[SiCl_3 \cdot (PMe_3)_2]^+$ might be stable and prompted a reinvestigation of the $SiCl_4$—$PR_3$ systems. Reaction of $SiCl_4$ or $SiBr_4$ with $PMe_3$ in the gas phase produced $SiX_4(PMe_3)_2$ which have vapour pressures of less than 2 mm at ambient temperatures [48,49]. Silicon tetrafluoride did not complex with $PMe_3$ at 26°C, but at −78°C there is evidence for the formation of both 1 : 1 and 1 : 2 adducts. The approximate stability relationships $SiF_4 \ll SiCl_4 < SiBr_4$ towards $PMe_3$, but $SiF_4 > SiCl_4 > SiBr_4$ towards $NMe_3$, and $Me_3P > Me_3N$ towards $SiCl_4$ were deduced. Whilst part of these trends are explained by steric factors, these are clearly not sufficient in themselves, and electronic explanations must also be invoked [48]. Trimethylphosphine will displace $NMe_3$ from $[SiCl_3(NMe_3)_2]ClO_4$ in acetonitrile solution to form $[SiCl_3(PMe_3)_2]ClO_4$ [48,49]. Recrystallisation of $SiX_4 \cdot (PMe_3)_2$ from the appropriate halide (X = Cl, Br) failed to yield 1 : 1 complexes, in contrast with the tin analogues [49,50]. The vibrational spectra of $SiX_4 \cdot (PMe_3)_2$ were interpreted in terms of a *trans* pseudooctahedral structure [51], and solution spectra in benzene showed that the structure persists in solution and that dissociation is small. More recently vibration spectra have been recorded using both $SiX_4(PMe_3)_2$ and $SiX_4[P(CD_3)_3]_2$, which makes the assignment of the fundamental vibrational frequencies more certain [52]. The $SiF_4(PMe_3)_n$ gave poor-quality spectra, but the case of $n = 2$ is presumably *trans* pseudooctahedral ($D_{4h}$) and $n = 1$ five-coordinate

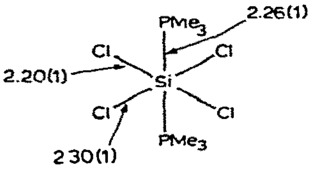

Fig. 2. The structure of $SiCl_4(PMe_3)_2$.

$C_{3v}$ [51]. Preliminary X-ray data on $SiCl_4(PMe_3)_2$ (Fig. 2) confirm the *trans* structure [53].

Isslieb and Reinhold [45] also reported a $SiBr_4(PPh_3)_4$ which does not seem to have been further examined. Silicon tetrachloride converts $BiPh_3$ to $Ph_2BiCl$ and $BiCl_3$ [54].

## G. GERMANIUM

The only germanium(II) complexes are the $GeI_2PR_3$ ($R_3$ = $Ph_3$, $Ph_2Me$, $Ph_2Et$, $Ph_2Pr^i$, $Ph_2Bu^n$, $Ph_2H$, $^nBu_3$) of King [55]. They form yellow solids which turn red in the presence of traces of oxygen. A complex $(GeI_2)_2Ph_2PCH_2CH_2PPh_2$ was also obtained in low yield [55].

Germanium tetrafluoride is reported to form white 1 : 1 complexes with $PH_3$ and $PMe_3$, which can be sublimed with some decomposition in vacuo at 25° C [56]. It was suggested that the solids contain six-coordinate germanium fluoride bridged polymers. Germanium tetrachloride forms $GeCl_4(PMe_3)_2$ on direct reaction with $PMe_3$ [51], and on recrystallisation from excess $GeCl_4$ this is converted [50] into $GeCl_4 \cdot PMe_3$ (cf. $SiCl_4(PMe_3)_2$ which does not give a 1 : 1 adduct). Germanium(IV) bromide forms only a 1 : 1 adduct with $PMe_3$ [50]. Vibrational spectra suggest [50—52] that the 1 : 2 adducts are pseudo-octahedral ($D_{4h}$), and the 1 : 1 trigonal bipyramidal ($C_{3v}$) with axial $PMe_3$. Analogous to $SiCl_4$, $GeCl_4$ does not complex with *o*-phenylenebis(dimethylarsine) [47].

## H. TIN

Mössbauer spectra have been reported for $SnX_2PPh_3$ (X = Cl, Br) and for frozen solutions of $SnX_2P^nBu_3$ (X = Cl, Br, I) [57]. The preparation and properties of the complexes were not described. The isomer shifts of the complexes were less than those of the free halides, consistent with the substitution of the weak bond from the tin to a bridging halide by a stronger P—Sn bond [57].

Allison and Mann [58] prepared tin(IV) complexes with monodentate phosphines in 1949. The complexes $SnX_4 \cdot (PR_3)_2$ (X = Cl, Br, R = Pr, Et) were isolated, but with $SnI_4$ the products were too unstable to be isolated. In the presence of HX (or water which generates HX), phosphonium hexahalogenostannates(IV) $[PR_3H]_2SnX_6$ were produced [58]. Novel mixed tin—mercury compounds $SnHg(PR_3)_2Cl_6$ were also prepared, but their structures were not elucidated [58].

The ease with which tin Mössbauer spectra can be obtained has resulted in numerous recent studies of tin(IV) coordination complexes. The majority of phosphine complexes are the 1 : 2 type $SnX_4(PR_3)_2$ (X = Cl, Br) and are usually prepared by reaction of stoichiometric amounts of the phosphine and halide in non-polar solvents under rigorously anhydrous conditions. The reported complexes are $SnCl_4(PR_3)_2$ [$R_3$ = $Me_3$ [51,52], $Et_3$ [58—60], $Pr_3$ [58,60], $Bu_3$ [59,60], $(octyl)_3$ [61], $PhMe_2$ [60,61], $Ph_2Me$ [59,60], $PhEt_2$ [59,60], $Ph_2Et$ [60], $Ph_2OMe$ [60], $Ph_3$ [59—63], $Ph_2(C{\equiv}CMe)$ [60]. Similar tin(IV) bromide complexes have been prepared with $PPh_3$ [64], $PBu_3$ [59], $Me_2PhP$ [61], $P(octyl)_3$ [61], $PEt_3$ [58], $PPr_3$ [58].

The vibrational spectra of $SnCl_4 \cdot (PMe_3)_2$ were interpreted [51,52] as due to a *trans* octahedral complex, and this has been confirmed by subsequent IR and Raman spectral studies on other phosphine complexes [59—61,63,64]. Final confirmation of the structure was obtained by an X-ray study [65] of $SnCl_4(PEt_3)_2$ (Fig. 3), the results of which suggested that there was a high 5s character in the Sn—P bonds. Malone and Mann [66] measured the $^1J(^{117,119}Sn—^{31}P)$ coupling constants in $SnCl_4(PR_3)_2$ ($R_3$ = $Et_3$, $PhEt_2$) and observed that, by analogy with transition metal complexes, the spectra could be interpreted as due to *cis*-$SnX_4P_2$ moieties (which is incorrect) illustrating that care must be taken in applying criteria from *d*-block complexes to main group analogues. Subsequently an explanation of the variation in $^1J(M—P)$ was offered [65]. The $^{31}P$ NMR spectrum of $SnCl_4(P^nBu_3)_2$ has been briefly reported [67].

A number of 1 : 1 complexes $SnX_4 \cdot PR_3$ ($R_3$ = $Ph_3$ [59—61], $(C_6H_{11})_3$, $Me_3$ [50]) have been prepared. The vibrational spectra and X-ray powder

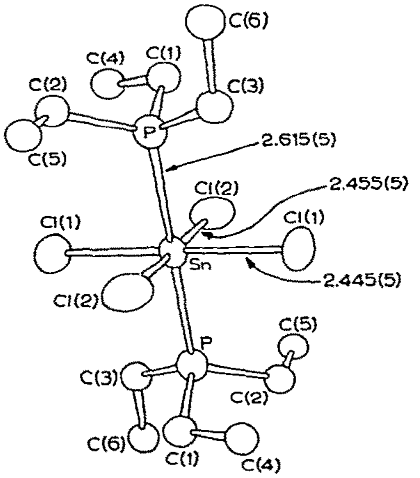

Fig. 3. The structure of $SnCl_4(PEt_3)_2$. (Reproduced by permission of The Chemical Society.)

pattern of $SnX_4PMe_3$ are consistent with a trigonal bipyramidal monomer [50], but there are conflicting reports on $SnCl_4 \cdot PPh_3$. The IR spectrum and molecular weight in $CH_2Cl_2$ of $SnCl_4 \cdot PPh_3$ correspond to a dimeric structure [63], and the Mössbauer spectrum [59] favours six-coordination. However, Carty et al. [60] report that recrystallisation of $SnCl_4 \cdot PPh_3$ from $CH_2Cl_2$ produces $[PPh_3H]_2SnCl_6$ and interpreted the vibrational and Mössbauer spectra of their product in terms of a five-coordinate monomer. The reported [59—61] isomer shifts are widely different and the nature of the various "$SnCl_4 \cdot PPh_3$" is unclear.

Triphenylarsine [59,61,63,64] and triethylarsine [58,59] form only 1 : 2 complexes with $SnCl_4$ and $SnBr_4$. In a number of cases the group VB ligands coordinated to tin(IV) have shown a marked tendency to air oxidise; the reported data [62] on $SnBr_4(PPh_3)_2$ have been shown to be consistent [59,61] with $SnBr_4(OPPh_3)_2$. Tin(IV) fluoride complexes have not been prepared. Triphenylstibine and $SnX_4$ (X = Cl, Br) form yellow products initially which become white on keeping [59]. Mössbauer spectra showed the yellow solids to contain Sn(IV), but the white are $SnX_2 + Ph_3SbX_2$ [59].

Bidentate group VB ligands form 1 : 1 adducts with $SnCl_4$ and $SnBr_4$: *o*-$C_6H_4(AsMe_2)_2$ [58,68], *o*-$C_6H_4(AsEt_2)_2$ [69], *o*-$C_6H_4(PPh_2)_2$ [61], *o*-$C_6H_4(PPh_2)(AsPh_2)$ [68], *o*-$C_6H_4(PPh_2)(NMe_2)$ [61], $Ph_2PCH_2PPh_2$ [59,68], $Ph_2P(CH_2)_2PPh_2$ [60,68,70], $Ph_2As(CH_2)_2AsPh_2$ [68], *cis*-$Ph_2PCH{=}CHPPh_2$ [68], *cis*-$Ph_2PCH{=}CHAsPh_2$ [68], $Ph_2P(CH_2)_2AsPh_2$ [68] and *cis*-$Ph_2AsCH{=}CHAsPh_2$ [68], but further substitution to give $[Sn(L{-}L)_2X_2]X_2$ does not occur [47,68]. All of these complexes appear to be *cis* octahedral complexes on the basis of their far IR and Mössbauer spectra. The tendency of the coordinated phosphine to oxidise in air to the ligand oxide is particularly marked with $SnBr_4(L{-}L)$ (L—L = *cis*-$Ph_2PCH{=}CHPPh_3$, $Ph_2PCH_2CH_2PPh_2$ ) and with $Ph_2AsCH_2AsPh_2$ and $Ph_2P(CH_2)_3PPh_2$ and $SnX_4$, only sticky partially oxidised species were obtained [68]. Harrison et al. [61] reported tin(IV) iodide adducts of *o*-$C_6H_4(PPh_2)_2$ and *o*-$C_6H_4(PPh_2)(NMe_2)$, but attempts to prepare $SnI_4(L{-}L)$ adducts of a range of bidentate ligands (above) produced dark red or brown solids which contained ligand oxide and probably some tin(II). Only one tridentate ligand PhP(*o*-$C_6H_4NMe_2)_2$ has been complexed [61] with $SnX_4$ to yield $SnLX_4$.

The ditertiary stibine $Ph_2SnCH_2SbPh_2$ is chlorinated by $SnCl_4$to $Ph_2Sb(Cl_2)$-$CH_2Sb(Cl_2)Ph_2$ [68].

Mössbauer spectra ($^{119}Sn$) have been recorded for a wide range of these complexes [59—63,68,71]. The interpretation of these data has been discussed in depth in several recent reviews [72—74]. The photoelectron spectrum of $SnCl_4(P^nBu_3)_2$ has been measured [75].

## J. LEAD

Surprisingly little effort has been devoted to the coordination chemistry of lead. The ligand 1,2-bis(diethylphosphino)ethane (dee) reacts with $PbBr_2$

dissolved in aqueous potassium bromide solution and with lead(II) perchlorate in ethanol, to form $Pb(dee)Br_2$ and $[Pb(dee)_2](ClO_4)_2$ respectively [76]. The ready formation of these complexes suggests that other lead(II)—phosphine complexes could be readily prepared.

Lead(IV) chloride reacts with $PPh_3$ at 0° C to form an uncharacterised yellow solid, which rapidly decomposes, probably by chlorination of the ligand [77]. Similarly $PbCl_4$ oxidises several tertiary arsines to $R_3AsCl_2$ [78].

## K. THE GROUP VB ELEMENTS

Although the group VB elements with the exception of bismuth cannot be described as metallic, the reactions of their halides with organo group VB donors is of interest in comparison with the studies reported above. It has been known for many years that the halides and organohalides of P, As and Sb react with triorganophosphines, triorganoarsines and triorganostibines [79—86], but the nature of the products has been clarified only recently. Thus Holmes and Bertaut [80] obtained compounds of composition corresponding to $ECl_3(PMe_3)_2$ ($E = P$, Sb) and $AsCl_3(PMe_3)$, $PCl_5 \cdot (PMe_3)_2$ and $SbCl_5(PMe_3)_n$ ($n = 1, 2$), but found that $SbMe_3$ reduced $PCl_5$ or $AsCl_3$ to the free element with formation of $Me_3SbCl_2$.

Summers and Sisler [82] have re-examined a wide variety of these systems and confirmed the formation of $PX_3 \cdot (PMe_3)_2$, ($X = Cl$, Br), $AsCl_3(PMe_3)_2$, $SbX_3(PMe_3)_2$ ($X = Cl$, I), $AsX_3(AsMe_3)$ ($X = Cl$, I), $SbX_3(AsMe_3)$ ($X = Cl$, I) and $SbI_3 \cdot SbMe_3$, in addition to numerous $REX_2$ and $R_2EX$ analogues. Proton NMR spectra and conductivity studies in solution suggested that varying degrees of ionic behaviour were exhibited. A number of the products seem to be best described as molecular adducts, whilst others can be formulated as phosphinophosphonium or phosphinoarsonium salts $[X_2EE'R'_3]X$ (E,E' = group VB element $X =$ halide, $R =$ organic group).

Sutton [87,88] prepared $PX_3(das)$ ($X = Br$, I), $AsX_3(das)$, $SbX_3(das)$ and $BiX_3(das)$ ($X = Cl$, Br, I), which appear to ionise partially in solution to $[MX_2das]X$, and $[AsdasI_2]ClO_4$ was isolated. A highly explosive $[Bi(das)_3](ClO_4)_3$ was also isolated. A re-examination of these complexes by vibrational spectroscopy or an X-ray study would be most interesting.

The work reviewed above shows that *p*-block elements have considerable affinity to group VB donors, and it is clear that there is much scope for further work. Only two papers have described the use of multidentate ligands, and the variation in the electronic and steric properties of such ligands opens up interesting possibilities in this area, which are as yet totally unexplored. It is also apparent that, whilst the chemistries of indium and tin(IV) have received considerable attention, those of tin(II), lead(II) and germanium seem to have considerable potential for much further work.

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