THE PREPARATION AND SPECTROSCOPIC STUDIES OF SOME CYCLIC
UREA ADDUCTS OF TRIPHENYL -TIN AND -LEAD HALIDES

by

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CYCLIC UREA ADDUCTS OF TRIPHENYL -TIN AND -LEAD HALIDES

*to my mother and father
with much gratitude for
their love and support*

ABSTRACT

1,3-Dimethyl-2-imidazolidinone (dimethylethylene urea, DMEU) and 1,3-dimethyl-3,4,5,6-tetrahydro 2(1H)-pyrimidinone (dimethylpropylene urea, DMPU) adducts of the type $\text{Ph}_3\text{SnX}\cdot\text{L}$ ($\text{X} = \text{Cl}, \text{Br}$ and I), $\text{Ph}_3\text{PbX}\cdot\text{L}$ ($\text{X} = \text{Br}, \text{I}$), $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$ and $2\text{Ph}_3\text{PbCl}\cdot\text{DMPU}$ have been prepared and characterized. Infrared and Raman spectra are reported and assignments made for $\nu(\text{CO})$ and $\nu(\text{CN})$ frequencies together with skeletal frequencies in the range 400 to 100 cm^{-1} . Infrared measurements show that the adducts are highly dissociated in dichloromethane solution. In addition, the complexes have been characterized by ^1H and ^{119}Sn or ^{207}Pb nmr measurements. The nmr studies confirm an equilibrium, fast on the nmr time scale, is present in solution. Coordination of the ligand causes a large upfield shift in the ^{119}Sn or ^{207}Pb resonances, with the exception of $\text{Ph}_3\text{MI}\cdot\text{L}$ which gave ^{119}Sn or ^{207}Pb chemical shifts similar to the parent iodides, indicating a particularly high degree of dissociation. The complexes $\text{Ph}_3\text{SnCl}\cdot\text{DMPU}$ and $\text{Ph}_3\text{SnBr}\cdot\text{DMPU}$ had percent dissociations of 66 and 74, respectively, for 0.25 M solutions at $20 \pm 3^\circ\text{C}$. The equilibrium constants were 0.32 and 0.53 for the chloride and the bromide.

RESUME

Les produits d'addition du type $\text{Ph}_3\text{SnX}\cdot\text{L}$ ($\text{X} = \text{Cl}$, Br et I), $\text{Ph}_3\text{PbX}\cdot\text{L}$ ($\text{X} = \text{Br}$, I), $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$ et $2\text{Ph}_3\text{PbCl}\cdot\text{DMPU}$ où $\text{L} = \text{diméthyle-1,3-imidazolidinone-2}$ (diméthyléthylène urée, DMEU) et diméthyl-1,3-tétrahydro-3,4,5,6 pyrimidinone-2(1H) (diméthylpropylène urée, DMPU) ont été caractérisés entre autres par spectroscopie infra-rouge et Raman. Les bandes $\nu(\text{CO})$ et $\nu(\text{CN})$ ainsi que les fréquences squelettiques dans la région de 400 à 100 cm^{-1} ont été attribuées. Les spectres infra-rouges en solution indiquent que ces produits d'addition se dissocient de façon important en solution dans le dichlorométhane. De plus, les complexes ont été caractérisés par $\text{rmn } ^1\text{H}$ et ^{119}Sn ou ^{207}Pb . Les études par rmn confirment que cet équilibre est présent en solution, et rapide sur l'échelle de temps de la rmn . Les résonances de l'étain et du plomb coordonnés sont déplacés vers les champs élevés sauf dans le cas de $\text{Ph}_3\text{MI}\cdot\text{L}$ où les déplacements chimiques des noyaux Sn et Pb sont similaires à ceux des iodures parents.

Pour des solutions 0.25 M à $20 \pm 3^\circ\text{C}$, les degrés de dissociation des complexes $\text{Ph}_3\text{SnCl}\cdot\text{DMPU}$ et $\text{Ph}_3\text{SnBr}\cdot\text{DMPU}$ sont de 66% ($K = 0.32$) et 74% ($K = 0.53$), respectivement.

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ABBREVIATIONS

iv

HMPA	hexamethylphosphoramide
DMF	dimethylformamide
DMSO	dimethylsulphoxide
PAN	1-(2-pyridylazo)-2-naphtholate
acac	acetylacetonate
terpy	2,2',2" terpyridyl
Py	pyridine
bipy	2,2' bipyridyl
TMU	tetramethylurea
TEU	tetraethylurea
DMEU	dimethylethylene urea (1,3-dimethyl-2-imidazolidinone)
DMPU	dimethylpropylene urea (1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)pyrimidinone)
EU	ethylene urea (2-imidazolidinone)
PU	propylene urea (2(1H)-tetrahydropyrimidinone)
vs	very strong
s	strong
m	medium
w	weak
sh	shoulder
DMAP	4-(dimethylamino)pyridine
TMS	tetramethylsilane
TMT	tetramethyltin
TMG	tetramethylgermane
TEL	tetraethyllead
TML	tetramethyllead
oxin	oxinate

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SECTION 1

INTRODUCTION

1.1 GENERAL INTRODUCTION TO GROUP IV ORGANOMETALLIC CHEMISTRY

Organic derivatives formed by the group IV elements silicon, germanium, tin and lead are one of the largest and most diversified groups of organometallic compounds. They are probably the most successful class of organometallics with widespread industrial uses. Silicone polymers and lead tetraalkyl compounds, for example, are particularly important. The latter has the largest industrial use of any organometallic in terms of bulk tonnage, being used extensively as an antiknock agent in petrol. Ever since this property was accidentally discovered in 1922 by Midgley and Boyd (1), a great variety of industrial applications have also been developed for organotin compounds within the last twenty years. They are used as fungicides in paints, wood preservatives and polymer stabilizers. Tributyltin and triphenyltin compounds, in particular, are incorporated into many woolen fabrics as protection against fungal attack and moths (2). On a broader aspect with regard to insect control, most trialkyltin compounds are very effective, but they also have a high mammalian toxicity. Hence, tricyclo-

hexyl- and triphenyl-tin derivatives are widely used instead since they are less poisonous to start with, and rapidly break down into harmless tin(II) inorganic compounds leaving no long lasting toxic residues in the ecosystem. Several dibutyltin compounds, notably dibutyltin diethanoate, dibutyltin di-(2-ethyl-hexanoate), and dibutyltin dilaurate have been used in the past to catalyze the addition of alcohols to isocyanates, to give polyurethanes (3). These are used in furniture manufacture and as cavity wall insulators. One particularly interesting study performed with triphenyltin acetate has indicated that this compound may inhibit tumour growth in mice (4).

Organolead compounds have been used as alkylating agents to produce organomercury fungicides through an exchange reaction:

This, however, is not used now as an industrial process, or even in the laboratory because tetraalkyllead compounds tend to be difficult to handle, being highly reactive with oxygen and water. Free radicals can be produced by the thermal decomposition of many organolead compounds. These may initiate chain reactions and hence are potential catalysts for a variety of reactions. Taylor and Jones (5)

in 1930 showed that the dissociation of tetraethyllead at 250-350°C catalyzed the polymerization of ethylene to a high boiling liquid. However, virtually no use is made at present of the catalytic polymerization properties of organolead compounds.

A number of organolead compounds have also been used as fungicides, pesticides and anti-marine fouling agents. However, these compounds are generally very toxic and leave poisonous residues in the environment. Thus, they are not used to the same extent as analogous organotin derivatives.

1.2 ORGANOTIN COMPOUNDS

Organotin compounds appear to be among the first class of organometallics to be discovered. The first reported compound to contain a Sn-C bond seems to have been diethyltin diiodide which was unambiguously characterized in 1853 by E. Frankland (6). He was also probably the first person to make tetraethyltin, by distilling "diethyl-ditin" (7).

The majority of organotin compounds are derivatives of the composition R_nSnX_{4-n} ($n = 1-4$) or $R_mX_{3-m}SnSnR_nX_{3-n}$ ($m, n = 1-3$) where R is the organic group and can be either substituted or non-substituted. In the cases where there are more than one R group, they need not be identical. R

may be an alkyl, alkenyl, alkynyl or aryl group. X may be halogen, pseudohalogen, or a group containing a wide variety of other elements. Theoretically, if there is more than one X group, they need not be identical, although this is more usually the case. On occasion, X may also be an electropositive group, as in the case of Me_3SnNa which was the first of this type of compound to be prepared (8). It can be obtained in high yield when sodium is added to trimethyltin bromide in liquid ammonia. It is, however, unstable at room temperature and decomposes rapidly at higher temperatures into hydrocarbons and a tin-sodium alloy (9). Other examples of organotin compounds include Me_3SnCl_2 , $\text{Ph}_2\text{HSnSnHPh}_2$, $(\text{Bu}_3^{\text{n}}\text{Sn})_2$ and $\text{Me}_3\text{SnMn}(\text{CO})_5$.

In the same way as carbon, the valence orbitals of tin contain four electrons, and these can undergo sp^3 hybridization to form four equivalent hybrids in a tetrahedral arrangement, as observed. The majority of organotin compounds have only one tin atom per molecule, usually with four substituents. The types of compounds possible of this nature include R_4Sn , R_3SnX , R_2SnX_2 and RSnX_3 .

Tetra-substituted organotin compounds, R_4Sn , are easily prepared by the action of a Grignard reagent, an organolithium compound, or an organoaluminium compound on tin(IV) chloride. By-products such as R_2SnCl_2 or R_3SnCl may be removed by shaking the ether solution with aqueous

ethanolic potassium fluoride. The precipitated fluorides can then be easily separated (10).

One of the most important classes of organotin compounds are the 4-coordinate organotin halides, R_3SnX , R_2SnX_2 and $RSnX_3$ and their 5- or 6-coordinate Lewis acid-base adducts $R_3SnX \cdot L$, $R_2SnX_2 \cdot L$ and $R_2SnX_2 \cdot 2L$ where L can be a negative ion or a neutral molecule having an electron pair donor atom. G.N. Lewis in 1918 was the first person to call those substances capable of acting as ligands, or electron pair donors, bases. The substances with which these react, or electron pair acceptors, he called acids (11). Hence, the reaction between an acid and a base of this kind, would give rise to a donor-acceptor complex (adduct) with a coordinate or dative bond.

The behavior of organotin halide compounds as Lewis acids has been explored for a long time, and many of the adducts formed are very stable for a large variety of Lewis bases. The reason why tin is able to increase its coordination number is the presence of low lying d-orbitals which are free to accept electron density, and thus participate in bonding. Neither the tetraaryl nor tetraalkyl derivatives form stable compounds with a coordination number greater than four. Five coordinate tin compounds may be formed only when the tin atom is made more electrophilic by the attachment of at least one electronegative ligand such

as chloride, as in the case of R_3SnCl . The inductive effect present here from the tin atom to the halogen atom favours attack by a strong donor ligand to form a dative or coordinate bond which, once formed, becomes indistinguishable from a 'normal' covalent bond.

The organotin halides are intermediate in Lewis acidity between R_4Sn and SnX_4 . Stannic halides form thermodynamically stable adducts of the type $SnX_4 \cdot 2L$ (12). The acceptor strength of tin in these compounds has been found to be proportional to the electronegativity of the halide substituents bound to tin. The greater the electron attracting power of the substituents, the less the electron density around the metal and the greater the acceptor strength. These have been found to decrease as follows (13): $SnCl_4 > SnBr_4 > SnI_4$. Farhangi and Graddon (14) have obtained thermodynamic data by the calorimetric titration of various organotin compounds with Lewis bases. From this work, they were able to establish that adduct stabilities increase with increasing chloride substitution and also in the order $Bu < Me < Ph$. It should, however, be pointed out that the apparent acceptor strength of a compound also depends on the nature of the donor (15). A strong donor such as hexamethylphosphoramide (HMPPA) would form a greater range of molecular adducts than would dimethylformamide (DMF).

Organotin halides of the type R_3SnX , R_2SnX_2 and $RSnX_3$ may all be prepared by the halogenation of the fully

substituted tetraorganotin compound. One particularly useful preparative reaction is the rearrangement between tin(IV) halides and R_4Sn compounds (16).

High yields have been obtained from the first two reactions above 180°C. The third reaction was found to be useful only for aryl compounds (17). However, the trihalides may be prepared more easily at a lower temperature as follows (18):

The mono-, di- and tri-halides all act as strong Lewis acids, forming a large range of much studied complexes, especially with nitrogen and oxygen donors. These seem to form more stable adducts than phosphorus or sulphur donors. The former are 'hard' bases, with a high electronegativity, low polarisability and high resistance to oxidation. Di-

methylsulphoxide (DMSO) for example, gives stable adducts with a wide variety of organotin compounds of the type $\text{RSnCl}_3 \cdot 2\text{DMSO}$, $\text{R}_2\text{SnCl}_2 \cdot 2\text{DMSO}$ and $\text{R}_3\text{SnCl} \cdot \text{DMSO}$. The adduct $\text{PhSnCl}_3 \cdot \text{DMSO}$ has also been obtained by using excess PhSnCl_3 (19). Various organotin adducts with HMPA have been made, including $\text{Ph}_3\text{SnCl} \cdot \text{HMPA}$, $\text{Ph}_3\text{SnBr} \cdot \text{HMPA}$ (20) and $\text{Ph}_3\text{SnI} \cdot \text{HMPA}$ (21). Wharf *et al.* (22) in 1979 studied the infrared and Raman spectra of these HMPA adducts together with $\text{Ph}_2\text{SnX}_2 \cdot 2\text{HMPA}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ and NCS) and $\text{Ph}_2\text{SnX}_2 \cdot \text{HMPA}$ ($\text{X} = \text{Cl}$ and Br). In all these cases, the R_3Sn or R_2Sn (or RSn) centres act as typical hard acid species with their acceptor power increasing in that order. Another interesting result of the electrophilic nature of the tin centre is that many of the organotin halides are self-associated in the solid state. This is particularly the case where both R and X are small, and X is electronegative. Thus, the structure of Me_3SnCN is a linear chain (23):

Organotin adducts are usually 5- or 6-coordinate. There are some 7-coordinate adducts known with various chelating ligands, as in the case of $(\text{Me})_2\text{Sn}(\text{PAN})(\text{acac})$, where PAN = 1-(2-pyridylazo)-2-naphtholate, and acac = acetylacetonate (24). Coordination numbers and stereochemistries of organotin compounds have been extensively studied using a variety of techniques. These include vibrational, nmr (^1H and ^{119}Sn) and Mössbauer spectroscopy. Numerous X-ray structural determinations have been reported (25,26), the stereochemistries of which are given in Figure 1.

In the case of organotin halides, the trihalides R_3SnX_3 and the dihalides R_2SnX_2 , like tin(IV) halides, form 1:2 complexes with monodentate ligands (27). Examples of these include $\text{MeSnCl}_3 \cdot 2\text{Py}$ and $\text{Me}_2\text{SnCl}_2 \cdot 2\text{Py}$ (Py = pyridine) (28). Monohalides, R_3SnX , form 1:1 (or occasionally 1:2) complexes (29), for example $\text{Ph}_3\text{SnX} \cdot \text{HMPA}$ (X = Cl and Br) (20) and $\text{Ph}_3\text{SnI} \cdot \text{HMPA}$ (21). The undissociated di- and tri-halide adducts are usually stable hexacovalent complexes, whilst the monohalide adducts are usually pentacovalent. Exceptions to this rule have been reported, and some monohalide adducts with hexacoordinate tin exist. One example of this is $\text{Me}_3\text{SnX} \cdot \text{bipy}$ (X = Cl, Br, I) (bipy = 2,2'-bipyridyl) (30). Similarly, there exist di- and tri-halide complexes which may be pentacovalent, for example $\text{Me}_2\text{SnCl}_2 \cdot \text{TMU}$, $\text{Ph}_2\text{SnCl}_2 \cdot \text{TMU}$, $\text{Ph}_2\text{SnBr}_2 \cdot \text{TMU}$ and $\text{PhSnCl}_3 \cdot \text{TMU}$ (TMU = tetramethyl urea) (31).

COORDINATION NO. 4 - TETRAHEDRAL

COORDINATION NO. 5 - TRIGONAL BIPYRAMID

COORDINATION NO. 6 - OCTAHEDRAL

COORDINATION NO. 7 - PENTAGONAL BIPYRAMID

Figure 1: Organotin(IV) Compound Stereochemistries
Established by X-Ray Crystallography.

In strongly electron donating solvents such as DMF, DMSO and HMPA, organotin halide adducts can ionize with cleavage of the tin-halogen bond. Some possible equilibria (32) are shown as follows:

R = ORGANIC GROUP

X = HALIDE

L = MONODENTATE LIGAND

Five and six coordinate anionic complexes have also been reported. Compounds of the type R_3SnX usually give rise to $R_3SnX_2^-$ species, one example of this being $[Mo_3(n-C_5H_5)_3S_4]^+[Me_3SnCl_2]^-$. The crystal structure of this revealed a trigonal bipyramidal anion with three Sn-C bonds in a plane (33).

Upon addition of halide ion, some $RSnX_3$ species produce hexacoordinate $RSnX_5^{2-}$ and $RSnX_6^-$ anions such as $MeSnCl_4^-$ and $MeSnCl_5^{2-}$. These are thought to be trigonal bipyramidal and octahedral, respectively, from the analysis

of their infrared spectra (34). R_2SnX_2 species can give rise to $R_2SnX_3^-$ and $R_2SnX_4^{2-}$ anions, for example the complex salt $[(\text{terpy})\text{SnMe}_2\text{Cl}]^+[\text{Me}_2\text{SnCl}_3]^-$, which contains a 6-coordinate cation and a 5-coordinate anion as confirmed by an X-ray structural determination (35).

An example of an $R_2SnX_4^{2-}$ anion is the pyridinium salt of $\text{Me}_2\text{SnCl}_4^{2-}$. The R groups were found to be *trans* in the crystal structure (36).

In conclusion, the organotin halides occupy a key

position in the chemistry of the organic compounds of tin. There is a large amount of information available on these compounds with regards to physical-chemical properties. Complex formation between the halides and various bases is of particular interest, and studies done on adducts of this type are an important part of organotin chemistry (37).

1.3 ORGANOLEAD COMPOUNDS

The first compound to contain a lead-carbon bond is thought to have been synthesized in 1853 by Löwig (38,39) who reacted a sodium-lead alloy and ethyl iodide, although it is unclear whether in fact he obtained tetraethyllead or hexaethyldilead. At about the same time, Cahours (40) had reported the formation of an organolead product resulting from the reaction between lead and ethyl iodide.

Lead is the final atom in group IV, and so is the largest. This is reflected in its chemistry. The bonds it forms are weaker than those of tin, and chain or ring compounds with several metal-metal links (catenation) appear to be unknown.

In a similar manner to carbon and tin, lead forms tetrahedral covalent compounds through sp^3 hybridization of its valence electrons. An interesting feature of lead chemistry is that its inorganic lead(II) compounds tend to be the most stable, whereas in the organometallic chemistry of

lead, the tetravalent derivatives are more stable, both thermodynamically and hydrolytically (41). Organolead (II) compounds are virtually unknown, one exception being dicyclopentadienyllead, $(C_5H_5)_2Pb$ (41).

The most stable class of organolead compounds are the tetrahedral R_4Pb species, where R may be alkyl, aryl, cycloalkyl, aralkyl, thienyl, furyl, or any of their substituted derivatives. The most commonly used preparative method for these compounds in the laboratory is the action of Grignard, organolithium or organoaluminium reagent on $PbCl_2$ (Equation 6), or on a lead(IV) compound such as R_2PbX_2 , R_3PbX or K_2PbCl_6 (42).

One disadvantage of this method seems to be the large amount of elemental lead that results ($\geq 50\%$). Tetraalkyllead compounds are highly refractive liquids, usually colourless and miscible with most organic solvents. Tetraaryllead compounds are white crystalline solids, usually soluble in non-polar solvents (42). In the presence of light and air, decomposition tends to occur, giving elemental lead, although to a lesser extent with the tetraaryl than the tetraalkyl compounds.

There have been far fewer studies of organolead halides

than of the analogous tin compounds. Where only one lead atom is involved, they have the general composition R_nPbX_{4-n} ($n = 1-4$). R is the organic group as described earlier, and X is usually the anion of an acid such as I^- , Br^- or Cl^- . The largest number of organolead derivatives are those of the type R_3PbX or R_2PbX_2 . $RPbX_3$ compounds tend to be thermally unstable and little is known about them. The aryllead carboxylates are, however, known (43), and have been well characterized since they are reasonably stable. Where R is aryl and X halide, or where R is alkyl, the resultant $RPbX_3$ compound is unstable and disproportionates into RX and PbX_2 (44).

Organolead halides (and other derivatives) of the type R_3PbX or R_2PbX_2 are best prepared by controlled cleavage reactions of tetraorganolead compounds R_4Pb , using halogens or acids (45).

or

Cleavage of a third R group gives PbX_2 and RX rather than the inherently unstable RPbX_3 .

Compounds of the type R_3PbX and R_2PbX_2 vary from being highly crystalline, high melting, ionic-type compounds, to low melting, covalent-like solids or liquids. For the compounds Ph_3PbX , the melting points decrease as X is varied in the order $\text{F} > \text{Cl} > \text{Br} > \text{I}$ ($\text{X} = \text{F}$, decomposition occurs at 319°C without melting). Melting points are 206°C , 166°C and 138°C for $\text{X} = \text{Cl}$, Br and I , respectively (46). The compounds R_2PbX_2 are thermally less stable than those of the type R_3PbX .

The structure of Ph_2PbCl_2 has been found to be a linear chain with hexacoordinate lead atoms and bridging chlorines (47).

It is reasonable to expect the solid compounds Ph_2PbX_2 ($\text{X} = \text{Br}$ and I) to have analogous structures. X-ray structures have been done on Ph_3PbCl and Ph_3PbBr . They are 5-coordinate

with bridging halogens and planar Ph_3Pb groups (48).

In benzene solution, however, the monohalides ($\text{X} = \text{Cl}, \text{Br}$ and I) and Ph_2PbI_2 are monomeric (49).

The ability of lead to expand its coordination sphere to form molecular adducts has been recognized for a long time. Polis (50-52) reported hydrates of diaryllead dinitrates and dicarboxylates in 1887. The coordination chemistry of the organolead halides seems to parallel that of the organotin halides, which was discussed in the previous section. However, a much smaller range of examples is known for lead.

Diphenyllead dihalides were shown by Pfeiffer *et al.* (51) to form adducts with pyridine, such as $\text{Ph}_2\text{PbX}_2 \cdot \text{Py}$. They reported that pyridine was liberated from this complex on exposure to air. Some of the first adducts of Ph_3PbCl were those formed with NH_3 reported by Foster *et al.* in 1939 (52). These were formulated as $\text{Ph}_3\text{PbCl} \cdot x\text{NH}_3$, where $x = 1.3$,

1.8, 2.7 and 9.65. Subsequently, little more was reported until the early 1960's.

Adducts of organolead compounds show a variety of stoichiometries depending on the number of R and X groups, and the type of ligands involved. For example, Ph_2PbCl_2 and Ph_2PbBr_2 form complexes with DMSO of the type $\text{Ph}_2\text{PbX}_2 \cdot 2\text{DMSO}$ (53). Other neutral complexes of dihalides such as $\text{Ph}_2\text{PbX}_2 \cdot \text{bipyridyl}$ (54) and $\text{Ph}_2\text{PbCl}_2 \cdot \text{Ph}_3\text{PO}$ (55), amongst others, have been reported, the former having an octahedral structure. Six coordinate adducts tend to predominate although 1:1 complexes of dihalides with monodentate ligands are also seen as in the latter case. Monohalides, R_3PbX , usually form pentacoordinate adducts of the type $\text{R}_3\text{PbX} \cdot \text{L}$. Hexamethylphosphoramide adducts of the type $\text{Ph}_3\text{PbX} \cdot \text{HMPA}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$ and NCS), $\text{Ph}_2\text{PbX}_2 \cdot 2\text{HMPA}$ ($\text{X} = \text{Cl}, \text{Br}$ and I) and $\text{Ph}_2\text{PbX}_2 \cdot \text{HMPA}$ ($\text{X} = \text{Br}$ and I) were synthesized and studied in some depth by Wharf *et al.* (56) in 1980. They examined the infrared, Raman, mass and ^{31}P nmr spectra of these compounds. All $\text{Ph}_3\text{PbX} \cdot \text{HMPA}$ complexes were reported to be 5-coordinate monomers, soluble in benzene, with similar melting points. The diadducts with Ph_2PbX_2 were found to have monomeric 6-coordinate structures. The ^{31}P resonance in HMPA was found to shift upfield by approximately 2 ppm on coordination, referenced to 85% H_3PO_4 . They explained this in terms of a compensation at the phosphorus atom from

the -NMe_2 groups after electron density loss *via* the oxygen atom.

Cationic complexes of organolead compounds appear to be present in solution when the easily ionizable perchlorate group is attached to lead, as in $[\text{Me}_3\text{Pb}\cdot\text{NC}_5\text{H}_5]^+ [\text{ClO}_4]^-$ (57). If, however, halide ions are added to organolead halides, anionic species such as $[\text{Ph}_3\text{PbCl}_2]^-$ and $[\text{Et}_2\text{PbCl}_3]^-$ can result (58).

One interesting technique that is being increasingly used to study organometallic lead compounds is that of ^{207}Pb nmr. Amongst the four naturally occurring isotopes of lead, ^{207}Pb ($I = 1/2$, abundance = 22.6%) has suitable nuclear magnetic properties for direct observation of its nmr spectra. Experiments using pulsed Fourier transform methods have shown the presence of very large chemical shifts (59). Also, heteronuclear double resonance techniques applied to ^1H nmr spectra have provided values of ^{207}Pb chemical shifts and $^{207}\text{Pb}\text{-C-}^1\text{H}$ coupling constants (60). The trends observed parallel those for ^{119}Sn resonances. Generally speaking, it is apparent that the chemistry of organolead compounds has been largely neglected until fairly recently. This is probably due to a number of reasons. They are less stable and more difficult to make than the corresponding organotin compounds. Their greater insolubility in common organic solvents makes them more difficult to study. The problem of insolubility is important to consider when measuring nmr

spectra, and it is only now with the advent of high field, super-conducting nuclear magnetic resonance spectrometers that advances are being made in this area (61).

1.4 CYCLIC UREAS

Liquid ureas have been used commercially for a variety of applications including lubrication (62), detergent production (63), slow acting fertilizers (64) and in the pretreatment of catalysts (65) and textiles, especially in 'permanent press' finishing (66-68). The acyclic ureas have been utilized as industrial solvents (69) to a much greater extent than the corresponding cyclic ones.

One of the most comprehensive articles on the use of an urea as a solvent and a reagent concerns tetramethylurea, written by Luttringhaus and Dirkson (69) in 1963.

TETRAMETHYLUREA (TMU)

The three electronegative heteroatoms in this compound are symmetrically arranged around the sp^2 carbon atom. Since

this article, more publications (70,71) have appeared which report the behavior of this and other liquid ureas as non-aqueous reaction media. Other solvents which have received increasing attention include tetraethylurea (TEU), the cyclic ureas 1,3-dimethyl-2-imidazolidinone ("dimethylethylene urea", DMEU) and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone ("dimethylpropylene urea", DMPU) (70).

Acyclic ureas of which TMU and TEU are two examples, have been prepared from carbon monoxide and alkylamines at elevated temperatures and pressures (64). The cyclic ureas DMEU and DMPU may be synthesized by a variety of established methods, and are also commercially available. Mulvaney and Evans (72) developed a procedure which utilizes cyclization at elevated temperature and pressure of the respective carbamate prepared by the addition of carbon dioxide to the appropriate alkylamine:

These reactions have been found to be suitable for industrial preparations of the compounds.

Alkyl substitution on the nitrogen atoms prevents hydrogen bonding, and ureas of this type are liquids at room temperature. Their physical properties have been carefully studied (73). These stable materials are being increasingly used as industrial solvents due to their considerable solvent power, favourable dielectric constants and dipole moments as summarized in Table 1.

Liquid ureas are usually purified by drying over anhydrous barium oxide, followed by distillation from calcium hydride; however, all tend to be very hygroscopic and absorb water readily. Lien and Kumber (77) have reported they were unable to obtain any of the N,N'-dimethylated cyclic ureas free of an O-H band in the $3200-3600 \text{ cm}^{-1}$ region of the infrared spectrum, despite rigorous drying procedures. They noted that this band had grown equal in size to the C-H band after only 15 minutes exposure to air. This was thought to

TABLE 1: DIELECTRIC CONSTANTS AND DIPOLE MOMENTS OF VARIOUS SOLVENTS.

SOLVENT	DIELECTRIC CONSTANT (ϵ at 25°C)	DIPOLE MOMENT (μ in Debyes)
TMU ^a	23.45	3.37
TEU ^a	14.39	3.45
DMEU ^a	37.60	4.09
DMPU ^a	36.12	4.23
HMPA ^b	30.00	4.31
DMSO ^b	49.00	4.03
H ₂ O	80.40 ^c	1.85 ^d

^aRef. 70; ^bRef. 74; ^cRef. 75; ^dRef. 76.

be an indication of the great tendency of the carbonyl oxygen to hydrogen bond with water.

Table 1 shows that the dielectric constants and dipole moments of the cyclic ureas are greater than those of the acyclic ones. This was reported by Rosenfarb *et al.* (73) in 1976. An increase in the size of the heterocyclic ring was also shown to decrease the dielectric constant. Thus DMEU has a dielectric constant, ϵ , of 37.6, and DMPU has a value of 36.12. Similar trends are also evident with homologous series of amides (78). There are other consider-

ations which are also important in their application as solvents; for example, the viscosity of DMPU is greater than that of DMEU, which may limit the former's usefulness.

Chemists have been paying increasing attention to the role of solvents in chemical reactions, especially dipolar aprotic solvents (71). Among the latter, one of the most interesting is HMPA. It has an impressive solvating power for a large number of organic and inorganic substances. However, its recently recognized considerable carcinogenicity makes it a serious risk to man (79). Mukhopadhyay and Seebach (71) have recently suggested that HMPA be substituted by the cyclic urea DMPU as a cosolvent for highly reactive nucleophiles and bases. They reported the carbonyl group of DMPU to be remarkably unreactive. This is an obvious requirement for its use as a solvent. The dielectric constant of cyclic ureas is somewhat greater than the value of 30 found for HMPA (Table 1).

Several ^1H -, ^{13}C -, and ^{23}Na -nmr studies have been undertaken on compounds dissolved in liquid ureas (60,80,81), although very little has been done on the actual ureas themselves. ^{23}Na -nmr studies have shown that salts dissolved in TMU are in the form of freely solvated ions (81). It was also found that the donor ability of TMU is greater than that of pyridine. Other studies, performed on cyclic ureas, include ultraviolet (77) and infrared (82) spectroscopy. In

the latter study, the ir spectra of some cyclic ureas, cyclic thioureas, and their N,N'-dialkyl derivatives were compared. The presence of hydrogen bonding of the type $C=S \cdots H-N \lt$ and $C=O \cdots H-N \lt$ led to a decrease in the C=S and C=O stretching frequencies in the unalkylated compounds. This was not present in the N,N'-dialkyl derivatives, and their C=S and C=O frequencies were correspondingly higher.

The presence of oxygen and nitrogen atoms in the urea molecules means that they are potential ligands. Little has been reported in the literature on cyclic urea-metal complexes, however. This is probably due in part to the ureas themselves not being readily commercially available. Complexes of 2-imidazolidinone (ethylene urea, EU) were reported by Berni *et al.* (83) in 1963 for Zn(II), Cd(II), Cu(II), Fe(III) and Co(II). They postulated on the basis of the C=O stretching frequency, that EU coordinates to the metal ion through the oxygen atom in $ZnCl_2 \cdot 2EU$, $CuCl_2 \cdot 2EU$, $CoCl_2 \cdot 3EU$ and $FeCl_3 \cdot 2EU$. They also postulated that the ligand in $CdCl_2 \cdot 2EU$ was coordinated through the nitrogen atom. Additional coordination compounds of these metals were prepared by Costamagna and Levitus (84) in 1966 using a variety of N-substituted ureas. In 1969, Berni *et al.* (85) reported a series of complexes of 2(1H)-tetrahydropyrimidinone (propylene urea, PU). They reported the preparation, spectral and magnetic properties of $ZnCl_2 \cdot 2PU$, $FeCl_3 \cdot 2PU$,

$3\text{CdCl}_2 \cdot 2\text{PU}$, $\text{NiCl}_2 \cdot \text{PU}$, $\text{CuCl}_2 \cdot \text{PU}$, $\text{CoCl}_2 \cdot 3\text{PU}$, $\text{HgCl}_2 \cdot \text{PU}$,
 $3\text{CdBr}_2 \cdot 2\text{PU}$ and $\text{Cu}(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot \text{PU}$.

EU

PU

In this series of compounds, coordination *via* the oxygen atom was assigned in all of the complexes with the exception of Hg(II). Complexation *via* the oxygen atom decreases the double bond character between the carbon and the oxygen by concentrating electron density on the latter. This causes a shift to lower frequencies in the $\text{C}=\text{O}$ stretching frequency (85). Berni *et al.* (83,85) proposed resonance hybrids of the canonical structures depicted in the following scheme for both EU and PU.

They suggested that on coordination in the complexes already described, the π -clouds of EU and PU are delocalized over the oxygen, carbon and nitrogen atoms, as indicated by:

Hence, on coordination to the metal ion, the π -cloud could spread over four atoms. Thus, the amount of electron delocalization in the π -system would be different if the nitrogen atom were coordinated as opposed to coordination by the oxygen atom. The criterion used to determine the atom through which coordination occurs was the shift in the C=O stretching frequency. If this was lowered in the complex relative to the free ligand, complexation through the oxygen atom was assigned.

The carbonyl stretching bands in $ZnCl_2 \cdot 2PU$, $CoCl_2 \cdot 3PU$ and $HgCl_2 \cdot PU$ are doublets. In the first two complexes, it was assumed to be due to asymmetry in the complex. A similar splitting has been observed by Cotton *et al.* (86) for the P=O band in the spectra of analogous complexes where the

ligands were trimethylphosphine oxide and triphenylphosphine oxide. They attributed the splitting to: a) coupling of the metal-oxygen vibrations through the metal ion, b) the existence of separate symmetrical and asymmetrical carbonyl stretching modes, and c) the existence in the crystal of non-equivalent ligand environments. Berni *et al.* (85) reported a small but significant shift (9 cm^{-1}) to higher frequency for one of the bands in $\text{HgCl}_2 \cdot \text{PU}$. This was interpreted as evidence of nitrogen to metal bonding, although the presence of another carbonyl stretching band at lower frequency led to the conclusion that some involvement of the carbonyl oxygen must be occurring also. It was suggested that the magnitude of the shift of the carbonyl frequency relative to the free urea was an indication of the strength or stability of the complex. They also suggested that an increase in the size of the ring from 5 atoms to 6 atoms on going from EU to PU, would lead to a change in ring strain and a change in bond angle between the C and N atoms of the amide group. They postulated that this would make PU a weaker π -acid than EU.

The complexes formed by a variety of N-substituted ureas with thorium and uranium tetrachloride and tetrabromide were investigated by Bagnall *et al.* (87). They found a difference in stoichiometry between the thorium and the uranium analogues similar to that seen in the analogous HMPA

complexes (88). Although UCl_4 and UBr_4 both form complexes of the type $\text{UX}_4 \cdot 2\text{TMU}$, the corresponding thorium complexes possess the stoichiometry $\text{ThX}_4 \cdot 3\text{TMU}$.

Prior to this, Penland and coworkers (89) had proposed oxygen coordination by urea to all metals of the first transition series, but nitrogen coordination to Pt(III) / Pd(III) . Apparently, unalkylated cyclic ureas may bind to a metal *via* the nitrogen or the oxygen atom. The presence of alkyl groups on the nitrogen atoms as in DMEU or DMPU would be expected to sterically hinder nitrogen coordination to the metal.

In summary, it appears that DMEU and DMPU together with other ureas will be useful solvents for future chemical investigations. The cyclic ureas are good dissociating media, and have higher dielectric constants and dipole moments compared to analogous acyclic ureas. The potential of DMEU and DMPU as ligands may be rather substantial considering their high μ and ϵ values.

1.5 STATEMENT OF THE RESEARCH

Hexamethylphosphoramide, with a donor number of 38.8, is the strongest O-donor ligand listed by Gutmann (90). He defined the "donor number" (DN) as a measure of the basicity or donor ability of a solvent in terms of the negative enthalpy of reaction, ΔH_R , of a base with the Lewis

acid antimony pentachloride, SbCl_5 .

$$\text{DN}_{\text{SbCl}_5} \equiv - \Delta H_R$$

These donor numbers compare the relative donor abilities of various solvents, typical values of which are given in Table 2:

TABLE 2: DONOR NUMBER, $\text{DN}_{\text{SbCl}_5}$, AND DIELECTRIC CONSTANTS (ϵ) OF CERTAIN SOLVENTS (90).

SOLVENT	$\text{DN}_{\text{SbCl}_5}$	ϵ
Sulphuryl Chloride	0.1	10.0
Acetonitrile	14.1	38.0
Acetone	17.0	20.7
Water	18.0	81.0
Diethyl Ether	19.2	4.3
THF (tetrahydrofuran)	20.0	7.6
DMF (dimethylformamide)	26.6	36.1
Pyridine	33.1	12.3
HMPA	38.8	30.0

This table does not give a correlation between donor

number and dielectric constant. The best donors, *e.g.*, pyridine do not always have high dielectric constants - in this case $\epsilon = 12.3$. Similarly, solvents with relatively high dielectric constants such as acetonitrile do not always have a high donor-number value (DN = 14.1, $\epsilon = 38.0$). HMPA with its high dielectric constant, dipole moment and donor number has been shown to form a number of complexes with Ph_3MX compounds (22,56). Recently (71), it was suggested that DMPU might, on account of its similar dielectric constant and dipole moment, be a good non-aqueous reaction medium, and might even replace the more carcinogenic HMPA. We decided to attempt the preparation of a series of complexes analogous to the HMPA adducts, only using DMPU and the similar DMEU as ligands. Our purpose was to obtain series of complexes of the type $\text{Ph}_3\text{MX} \cdot \text{L}$ where $\text{M} = \text{Sn/Pb}$, $\text{X} = \text{Cl, Br}$ and I and $\text{L} = \text{DMEU}$ and DMPU . In this way it was hoped to be able to draw conclusions from possible trends observed in the various spectra. Of particular interest was the measurement of ^{119}Sn and ^{207}Pb nmr spectra on a Varian XL-200 multinuclear spectrometer. This was thought to be important as the chemical shift ranges involved are very large and we hoped to draw conclusions as to the possible coordination number around the metal as the halide and ligand were varied. The presence of the ligand on the metal might be expected to make the parent triphenyl metal halide more soluble thereby facilitating spectroscopic measurements.

SECTION 2

EXPERIMENTAL

2.1 INSTRUMENTATION

Infrared spectra ($4000-400\text{ cm}^{-1}$) were recorded as nujol mulls between KBr plates on a Nicolet 6000 FTIR spectrometer. Far ir spectra ($400-100\text{ cm}^{-1}$) were recorded as nujol mulls between polyethylene plates on the same instrument. The numbers of scans employed were 32 and 400, respectively. A mylar beam splitter was used in the far ir together with purging times of approximately 1 hour at a fast rate between samples to remove as much H_2O vapour as possible. Solution ir were recorded in dry CH_2Cl_2 as dilute solutions on a Perkin Elmer 297. The resolution was 4 cm^{-1} and the accuracy $\pm 1\text{ cm}^{-1}$.

The Laser-Raman spectra of all the adducts in glass melting point tubes were measured on a Jarrell-Ash 25-300 Laser-Raman spectrometer in the region $1700-50\text{ cm}^{-1}$. An argon⁺ excitation wavelength of 488 nm was used with power at the sample of 50 mW. All lines were calibrated with a neon lamp, the resolution was 4 cm^{-1} and an accuracy of $\pm 1\text{ cm}^{-1}$ was obtained.

Nuclear magnetic resonance spectra were recorded on a Varian XL-200 spectrometer operating in the pulsed Fourier

transform mode. ^1H nmr spectra were measured in CD_2Cl_2 with TMS as internal standard. Chemical shifts obtained were accurate to ± 0.05 ppm unless otherwise indicated. Sweep widths of 2000 Hz were used, and 16K free induction decays (F.I.D.S.) obtained. ^{119}Sn and ^{207}Pb nmr spectra were run in dry CH_2Cl_2 at concentrations of 0.25 M, unless saturated, and were measured at 74.6 and 41.8 MHz, respectively. The chemical shifts are reported relative to Me_4Sn and Et_4Pb , respectively, as standards. These were contained in an external reference tube and were dissolved in C_6D_6 (50%) which acted as the external lock for field-frequency control. Negative chemical shift values indicate upfield shifts from the references and were found to be reproducible to within ± 1 ppm. Sweep widths were 50,000 Hz and F.I.D.S. of 32 K data points were collected. To measure the ^{207}Pb spectra, complete proton noise decoupling was employed. The decoupler was 'gated' in the case of the ^{119}Sn spectra and a delay time of 5 s was used. This led to much longer spectra collection times for this nucleus. All spectra were measured at room temperature ($20^\circ\text{C} \pm 3^\circ\text{C}$).

Elemental analyses for C, H and N were determined in duplicate by Guelph Chemical Laboratories, Guelph, Ontario. Melting points are uncorrected and were measured on a Thomas Hoover melting point apparatus.

2.2 PURIFICATION OF MATERIALS

Table 3 lists the commercial sources and the steps taken to purify the solvents and the ligands used, DMEU and DMPU.

2.3 PREPARATION OF Ph_3MX COMPOUNDS

The compounds Ph_3SnCl and Ph_3PbCl were obtained from Alfa and were used without further purification. The compounds Ph_3PbBr and Ph_3PbI were kindly supplied by Rosanda Cuenca of our laboratory and were used as obtained.

2.3.1 Preparation of Ph_3SnBr

The compound Ph_3SnCl (2 g) was treated with an excess of NaBr in methanol (25 ml). The mixture was refluxed overnight, allowed to cool and the solvent removed on a rotary evaporator under vacuum. The resulting solid was extracted with toluene (50 ml), and the resulting solution filtered. The filtrate was evaporated to dryness to give crude Ph_3SnBr . This was recrystallized from hot toluene to give the product (0.85 g) in 38% yield. The melting point was 118-120°C.

TABLE 3: PURIFICATION OF SOLVENTS

MATERIAL	SOURCE	PURIFICATION METHOD
d ₂ -Dichloromethane	Merck, Sharp and Dohme	Used as received
d ₆ -Benzene	"	"
Dichloromethane	American Chemicals Ltd. (spectrograde)	Distilled twice from phosphorus pentoxide. Stored over molecular sieves.
DMEU	Fluka Chemicals	Stirred with BaO for 1 day. Filtered and distilled under reduced pressure from CaH ₂ . Stored over molecular sieves.
DMPU	"	"
Toluene	American Chemicals Ltd. (spectrograde)	Stored over sodium
Pentane	"	"
Methanol	"	Stored over molecular sieves
Acetone	"	"

2.3.2 Preparation of Ph_3SnI

The compound Ph_3SnCl (2 g) was treated with an excess of NaI in acetone (25 ml). The mixture was refluxed for 3 days, allowed to cool and the solvent again removed under vacuum. The resulting solid was extracted with toluene (50 ml), and the resulting solution filtered. The filtrate was evaporated to dryness to give crude Ph_3SnI . This was recrystallized from hot toluene to give the product (1.55 g) in 63% yield. The melting point was 119-121°C.

2.4 PREPARATIONS OF $\text{Ph}_3\text{MX}\cdot\text{L}$

The adducts were prepared in the same way for L = DMEU and DMPU. The parent compound, Ph_3MX (2 g), was suspended in toluene (5 ml) together with the appropriate liquid ligand (3 ml, excess). Upon addition of the ligand, the parent compound dissolved. The adducts tended to crystallize out upon cooling at 0°C for 1 hr. In some cases a few drops of pentane was added to initiate crystallization. All the complexes were recrystallized from hot toluene and dried in air. The DMEU adducts appeared to be 'wet' and so were pumped in a vacuum overnight at room temperature.

SECTION 3

RESULTS AND DISCUSSION

3.1 ANALYTICAL DATA

The analytical data obtained for all the adducts prepared are summarized in Table 4. These adducts are air stable, crystalline solids which are soluble in solvents such as chloroform and dichloromethane but insoluble in pentane.

Ten of the twelve complexes made, that is 1 to 3, 5 to 9 and 11 to 12, have analyses corresponding to 1:1 molecular adducts of the type $R_3MX \cdot L$. Of these ten, $Ph_3SnCl \cdot DMEU$ and $Ph_3SnBr \cdot DMEU$ (complexes 1 and 2) gave values that did not agree with the percentages calculated for 1:1 adducts. It was calculated that for both adducts, the presence of approximately 0.9 mole of H_2O per mole of 1:1 adduct gives the observed percentages. This is consistent with the ir results, which despite repeated attempts at drying both complexes, continually showed the presence of water at approximately $\delta = 1.5$ ppm in the 1H nmr. A broad $\nu(OH)$ stretching frequency was seen at 3260 cm^{-1} in both complexes. If the attempts to dry the complexes were very vigorous, that is, if the samples were heated under vacuum at $65^\circ C$, ligand was lost. Hence, they were pumped on at room temperature for

TABLE 4: ANALYTICAL DATA FOR $\text{Ph}_3\text{MX} \cdot \text{L}$

Compound	Number	Yield ^a (%)	Colour	MP (°C)	% C Found (Calculated) ^b	% H Found (Calculated) ^b	% N Found (Calculated) ^b
$\text{Ph}_3\text{SnCl} \cdot \text{DMBU}^c$	1	71	White	113	53.37 (53.56)	5.24 (5.24)	5.30 (5.43)
$\text{Ph}_3\text{SnBr} \cdot \text{DMBU}^c$	2	47	Cream	95-97	49.14 (49.31)	4.82 (4.82)	4.52 (5.00)
$\text{Ph}_3\text{SnI} \cdot \text{DMBU}$	3	59	Yellow	106-108	46.80 (46.70)	4.27 (4.26)	4.76 (4.74)
$3\text{Ph}_3\text{PbCl} \cdot 2\text{DMBU}$	4	80	White	121-123 ^d	46.87 (46.61)	4.33 (3.97)	3.71 (3.40)
$\text{Ph}_3\text{PbBr} \cdot \text{DMBU}$	5	54	White	108-110	43.63 (43.67)	4.15 (3.99)	4.44 (4.43)
$\text{Ph}_3\text{PbI} \cdot \text{DMBU}$	6	63	Pale Yellow	96 ^d	40.60 (40.68)	3.78 (3.71)	4.03 (4.12)
$\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$	7	45	White	121-122	56.03 (56.12)	5.41 (5.30)	5.62 (5.45)
$\text{Ph}_3\text{SnBr} \cdot \text{DMPU}$	8	76	Pale Yellow	137-139	51.63 (51.65)	4.90 (4.88)	5.09 (5.02)
$\text{Ph}_3\text{SnI} \cdot \text{DMPU}$	9	82	Dark Yellow	146-148	47.55 (47.64)	4.46 (4.50)	4.61 (4.63)
$2\text{Ph}_3\text{PbCl} \cdot \text{DMPU}$	10	67	White	123 ^d	46.70 (46.89)	3.52 (3.94)	2.77 (2.60)
$\text{Ph}_3\text{PbBr} \cdot \text{DMPU}$	11	56	White	126	44.39 (44.62)	4.25 (4.21)	4.39 (4.34)
$\text{Ph}_3\text{PbI} \cdot \text{DMPU}$	12	45	Cream	136-137	41.57 (41.56)	3.96 (3.92)	4.07 (4.04)

^aAfter recrystallisation from toluene^bValues in brackets are calculated values.^cThe analysis was calculated by assuming 0.9 moles H_2O of crystallization was present per mole of complex.^dDecomposition.

several days only. This was found to be sufficient for the other complexes 3 to 12. Finally, complexes 1 and 2 were crushed in a pestle and mortar. They were then pumped on again at room temperature for 3 h. The ir finally showed a reduction in the amount of water present by a decrease of the intensity of the peak at 3260 cm^{-1} . The ^1H nmr confirmed this observation. In Figure 2, the two ^1H nmr spectra are shown of $\text{Ph}_3\text{SnBr}\cdot\text{DMEU}$ before and after the final pumping. In the first spectrum it can be seen that the integrated intensities are in a ratio of 14:3.5:5:1.7 which approximates to 15:4:6:1.8 which is the theoretical value for this complex if 0.9 mole H_2O is present. After pumping, as shown in the second spectrum of Figure 2, the ratio became 25:7:11:2 or 15:4.2:6.6:1.2. The water, although not completely removed, has obviously been depleted. Similar ratios were observed for the complex $\text{Ph}_3\text{SnCl}\cdot\text{DMEU}$. The fact that the H_2O was removed finally after crushing the samples suggests it was trapped in the crystal lattice as water of crystallization. The ir confirms this, as will be discussed later in Section 3.2.

The remaining complexes 4 and 10 are not 1:1 molecular adducts. Complex 4 has a 3:2 ratio of Lewis acid to Lewis base and complex 10 a ratio of 2:1.

Nine of the twelve adducts melt sharply. The complexes 4, 6 and 10 decompose. In the case of adduct 6, it is likely that decomposition occurs through a mere loss of ligand. The

Figure 2: ^1H nmr spectrum of $\text{Ph}_3\text{SnBr} \cdot \text{DMEU}$ before and after the final pumping.

evidence for this suggestion comes from the fact that a liquid was seen condensing half-way up the melting point tube.

All adducts were recrystallized from toluene with no decomposition. The colours of the solid complexes were varying shades of white to yellow. In complexes 1 to 3, 4 to 6, 7 to 9 and 10 to 12, or as the halogen atom changed within one series, from Cl to I, the colours observed changed from white to varying shades of yellow.

3.2 VIBRATIONAL SPECTROSCOPY

The main value of both ir and Raman spectroscopy in the study and characterization of complexes 1-12 was the determination of the mode of attachment of the urea ligands DMEU and DMPU to the metal centres, as the possibility exists that coordination could occur through one of the nitrogen atoms or through the carbonyl oxygen atom.

3.2.1 Results

The carbonyl and CN stretching frequencies of the free ligands together with those of their complexes 1 to 12 are given in Table 5. The $\nu(\text{CO})$ frequencies of the N,N'-dialkyl cyclic ureas appear in the $1700\text{--}1630\text{ cm}^{-1}$ region. In the case of the DMEU adducts, the carbonyl stretching frequency decreased by $60\text{ to }62\text{ cm}^{-1}$ for the tin adducts,

TABLE 5: INFRARED GROUP FREQUENCIES (cm^{-1}) FOR THE LIGANDS DNEU AND DNEU AND THEIR ADDUCTS $\text{Ph}_3\text{MX} \cdot \text{L}^a$

Compound	$\nu(\text{CO})$		$\nu(\text{CN})^b$	
	Frequency (cm^{-1})	$\Delta(\text{cm}^{-1})^c$	Frequency (cm^{-1})	$\Delta_1(\text{cm}^{-1})^d$
DNEU	1697s	-	1293s	-
$\text{Ph}_3\text{SnCl} \cdot \text{DNEU}$	1635s	-62	1296m	+3
$\text{Ph}_3\text{SnBr} \cdot \text{DNEU}$	1635s	-62	1294m	+1
$\text{Ph}_3\text{SnI} \cdot \text{DNEU}$	1637s	-60	1294m	+1
$3\text{Ph}_3\text{PbCl} \cdot 2\text{DNEU}$	1647s	-50	1298m	+5
$\text{Ph}_3\text{PbBr} \cdot \text{DNEU}$	1656s	-41	1296m	+3
$\text{Ph}_3\text{PbI} \cdot \text{DNEU}$	1653s	-44	1298m	+5
DNEU	1637s	-	1315s	-
$\text{Ph}_3\text{SnCl} \cdot \text{DNEU}$	1574s	-63	1323m	+8
$\text{Ph}_3\text{SnBr} \cdot \text{DNEU}$	1572s	-65	1320m	+5
$\text{Ph}_3\text{SnI} \cdot \text{DNEU}$	1575s	-62	1320s	+5
$2\text{Ph}_3\text{PbBr} \cdot \text{DNEU}$	1583m	-54	1321m	+6
$\text{Ph}_3\text{PbBr} \cdot \text{DNEU}$	1579s	-58	1316m	+1
$\text{Ph}_3\text{PbI} \cdot \text{DNEU}$	1589m	-48	1318m	+3

^aAs Nujol mulls except for DNEU and DNEU (neat liquids).

^bCarbonyl carbon.

^c $\Delta = \nu(\text{CO})_{\text{bound ligand}} - \nu(\text{CO})_{\text{free ligand}}$

^d $\Delta_1 = \nu(\text{CN})_{\text{bound ligand}} - \nu(\text{CN})_{\text{free ligand}}$

and by 41 to 50 cm^{-1} for the lead adducts. The $\nu(\text{CN})$ frequencies increased on coordination by only 1 to 3 cm^{-1} for the tin adducts and by 3 to 5 cm^{-1} for the lead adducts. In the DMPU adducts, the carbonyl stretching frequency decreased by 62 to 65 cm^{-1} for the tin adducts, and by 48 to 58 cm^{-1} for the lead adducts. The $\nu(\text{CN})$ frequencies increased by 5 to 8 cm^{-1} for the tin adducts, and by 1 to 6 cm^{-1} for the lead adducts.

Infrared spectral measurements (2000-1100 cm^{-1}) of complexes 1 to 12 in dilute CH_2Cl_2 solution showed $\nu(\text{CO})$ frequencies consistent with a high degree of dissociation. This is assuming the integrated molar absorptivities remain constant for the bound and the free carbonyl peaks. The $\nu(\text{CO})$ frequencies assigned to the free ligand were observed as strong peaks, while those assigned to the bound ligand were weak. The positions and intensities of the peaks assigned to $\nu(\text{CO})_{\text{free}}$, $\nu(\text{CO})_{\text{bound}}$ and $\nu(\text{CN})$ are given in Table 6. Only one peak is seen for $\nu(\text{CN})$, the difference between the free and bound frequencies being so small as to prevent resolution.

To aid in the characterization of the complexes, assignments of the skeletal frequencies both in the ir and the Raman were made. These absorption frequencies occurred in the far ir region (400-100 cm^{-1}). They are given in Tables 7 and 8 and the assignments are based on those made

TABLE 6: INFRARED ABSORPTION FREQUENCIES (cm^{-1}) OF ADDUCTS
 $\text{Ph}_3\text{MX} \cdot \text{L}$ IN CH_2Cl_2 SOLUTION

Complex	$\nu(\text{CO})^{\text{a}}_{\text{free}}$	$\nu(\text{CO})_{\text{bound}}$	$\nu(\text{CN})^{\text{b}}$
$\text{Ph}_3\text{SnCl} \cdot \text{DMEU}$	1694s	1656w	c
$\text{Ph}_3\text{SnBr} \cdot \text{DMEU}$	1694s	1656w	c
$\text{Ph}_3\text{SnI} \cdot \text{DMEU}$	1685s	1658w	c
$3\text{Ph}_3\text{PbCl} \cdot 2\text{DMEU}$	1696s	1666w	c
$\text{Ph}_3\text{PbBr} \cdot \text{DMEU}$	1691s	1661w	c
$\text{Ph}_3\text{PbI} \cdot \text{DMEU}$	1691s	1658w	c
$\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$	1629s	1581w	1316m
$\text{Ph}_3\text{SnBr} \cdot \text{DMPU}$	1631s	1580w	1318m
$\text{Ph}_3\text{SnI} \cdot \text{DMPU}$	1628s	1579w	1310m
$2\text{Ph}_3\text{PbCl} \cdot \text{DMPU}$	1630s	1594w	1310m
$\text{Ph}_3\text{PbBr} \cdot \text{DMPU}$	1631s	1596w	1310m
$\text{Ph}_3\text{PbI} \cdot \text{DMPU}$	1636s	1598w	1313m

^a $\nu(\text{CO})$ for DMEU in $\text{CH}_2\text{Cl}_2 = 1696 \text{ cm}^{-1}$.

$\nu(\text{CO})$ for DMPU in $\text{CH}_2\text{Cl}_2 = 1631 \text{ cm}^{-1}$.

^b $\nu(\text{CN})$ for DMEU in $\text{CH}_2\text{Cl}_2 = 1287 \text{ cm}^{-1}$.

$\nu(\text{CN})$ for DMPU in $\text{CH}_2\text{Cl}_2 = 1318 \text{ cm}^{-1}$.

^cPeak not resolved - present as a diffuse, broad band.

TABLE 7: SKELETAL VIBRATIONS (cm^{-1}) FOR $\text{Ph}_3\text{SnX} \cdot \text{L}$ ADDUCTS^a.

Assignment	COMPLEX											
	$\text{Ph}_3\text{SnCl} \cdot \text{DMEU}$		$\text{Ph}_3\text{SnBr} \cdot \text{DMEU}$		$\text{Ph}_3\text{SnI} \cdot \text{DMEU}$		$\text{Ph}_3\text{SnCl} \cdot \text{DNPU}$		$\text{Ph}_3\text{SnBr} \cdot \text{DNPU}$		$\text{Ph}_3\text{SnI} \cdot \text{DNPU}$	
	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R
$\nu_{\text{as}}(\text{Sn-Ph})$ (τ) ^b	274s		274s	274w	276s		274s ^c		278s	275w	276s	274w
$\nu(\text{Sn-Cl})$	267sh	264w					274s ^c	267m				
$\nu(\text{Sn-O})$	238m 230sh	237w	233sh 228m	232w	232s	228w	236m	233w	235s	229w	230s	225sh
ν^b	210m	218vs	214w	215m	213sh	212m ^d	212m	217vs	206w	211vs	199s	213m
$\nu_{\text{s}}(\text{Sn-Ph})$ (τ_1) ^b	203w	205s	204w	205s	208w	212m ^d	202m	202s	190sh	e	193sh	e
$\nu(\text{Sn-Br})$			172s	171m					172s	167ws		
$\nu(\text{Sn-I})$					134s	132vs					131s	127vs
ν^b	195sh		80w 155w			152m		193sh		158sh		155w
$\delta(\text{Sn-Cl})$	153m							146m				
Deformations										105sh		101sh
$\delta(\text{Sn-Br})$										71sh		

^aAs Nujol mulls between polyethylene plates.^bWhiffen's notation (91).^cSuperimposed.^dSuperimposed.^eHidden under u.

TABLE 8: SKELETAL VIBRATIONS (cm^{-1}) FOR $\text{Ph}_3\text{PbX}\cdot\text{L}$ ADDUCTS^a.

Assignment	C O M P L E X											
	$3\text{Ph}_3\text{PbCl}\cdot\text{ZnDMEU}$		$\text{Ph}_3\text{PbBr}\cdot\text{DMFPU}$		$\text{Ph}_3\text{PbI}\cdot\text{DMFPU}$		$2\text{Ph}_3\text{PbCl}\cdot\text{DMFPU}$		$\text{Ph}_3\text{PbBr}\cdot\text{DMFPU}$		$\text{Ph}_3\text{PbI}\cdot\text{DMFPU}$	
	IR	R	IR	R	IR	R	IR	R	IR	R	IR	R
$\nu_{\text{as}}(\text{Pb-Ph})$ (ϵ) ^b	235sh 229s	234w	228s	229w	227s		230s	234w	229s	229w	230sh 220s	
$\nu(\text{Pb-Cl})$	222sh	218w					212m	220w				
$\nu(\text{Pb-O})$	203m		203m		201m		205m		206m		195w	
ν^b	182m	186w 173w		179sh			184m				172w	170sh
$\nu_{\text{s}}(\text{Pb-Ph})$ (ϵ_1) ^b	206sh	198vs		194vs	206w	197m		200vs	199m	201vs	207m	202s
$\nu(\text{Pb-Br})$			152s	151w					149s	151m		
$\nu(\text{Pb-I})$					122s	121vs					119s	117vs
χ^b		151w						155w				155w
Deformations		101sh 69sh 55sh		94sh 62sh 42sh		150w 60sh		108sh				96sh 58sh

^aAs Nujol mulls between polyethylene plates.^bWhiffen's notation (91).

for the parent lead halides (49) and those made by Wharf
et al. (22,56) for the analogous HMPA adducts.

3.2.2 Discussion of Infrared Spectra (2000-600 cm^{-1})

$\nu(\text{CO})$ frequencies should decrease while the $\nu(\text{CN})$ frequency should increase. In this case, the carbonyl carbon to nitrogen bond order increases. Coordination through a nitrogen atom should increase the carbonyl stretching frequency. Simultaneously, the $\nu(\text{CN})$ frequency should decrease because of a decrease in the double bond character of the C-N bond.

As shown in Table 5, for all complexes 1 to 12, the carbonyl stretching frequency decreased relative to the free ligand. The $\nu(\text{CN})$ frequency increased as expected, although the magnitude of the change was not comparable to the decrease observed for $\nu(\text{CO})$, as evident from a comparison of Figure 4, which shows the ir spectrum (2000-600 cm^{-1}) of $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$, with Figure 3, which shows the ir spectrum (2000-600 cm^{-1}) of the free ligand DMPU. On the basis of such observations for complexes 1 to 12, it is reasonable to postulate that coordination of the cyclic ureas to the metal atoms occurs through the carbonyl oxygen atom. Moreover, the presence of an alkyl group on each nitrogen would be expected to hinder sterically coordination *via* nitrogen.

Berni *et al.* (85) have suggested that, for those complexes where coordination occurs through the carbonyl oxygen, the amount by which the $\nu(\text{CO})$ frequency decreased on coordination of propylene or ethylene urea to various

Figure 3: The IR Spectrum of DMPU ($2000-600\text{ cm}^{-1}$).

Figure 4: The Solid State IR Spectrum of $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$ (2000-600 cm^{-1}).

metal chlorides might indicate the relative stability of the complex thus formed. Carbonyl stretching frequencies of some of the complexes prepared, and those of the free ligands are given in Table 9.

TABLE 9: $\nu(\text{CO})$ FREQUENCIES OF THE CYCLIC UREAS EU
AND PU AND SOME OF THEIR COMPLEXES^a
(83,85).

COMPOUND	$\nu(\text{CO})$	
	FREQUENCY (cm^{-1})	$\Delta(\text{cm}^{-1})^b$
EU ^c	1660s	-
CuCl ₂ ·2EU ^c	1639s	-21
FeCl ₃ ·2EU ^c	1629s	-31
ZnCl ₂ ·2EU ^c	1626s	-34
CoCl ₂ ·3EU ^c	1658s	- 2
PU ^d	1686s	-
CuCl ₂ ·PU ^d	1625s	-61
FeCl ₃ ·2PU ^d	1610s	-76
ZnCl ₂ ·2PU ^d	1634s	-52
CoCl ₂ ·3PU ^d	1639s	-47

^aAs KBr discs.

^b $\Delta = \nu(\text{CO})_{\text{bound ligand}} - \nu(\text{CO})_{\text{free ligand}}$

^cReference (83).

^dReference (85).

The ir absorption frequencies, especially of $\nu(\text{CO})$, obtained for these complexes, relative to the free cyclic ureas, were thought to indicate that the mode of coordination is through the carbonyl oxygen. Frequency shifts in $\nu(\text{CO})$ were greater in the PU complexes. Based on the changes observed in the carbonyl stretching frequencies, Berni *et al.* (83) assigned a relative stability order of: $\text{Zn(II)} \approx \text{Fe(III)} > \text{Cu(II)} > \text{Co(II)}$ to the ethylene urea complexes, and for the propylene urea complexes (85): $\text{Fe(III)} > \text{Cu(II)} \geq \text{Zn(II)} > \text{Co(II)}$. The fact that shifts in the propylene urea complexes were greater, was attributed to increased stability of these complexes compared with those of EU. This was thought to be due to the increased size of the ring from 5 to 6, the change in ring strain, and corresponding change in bond angles between the C and N atoms of the amide group of PU. The increase in ring size appears to increase the amount by which the carbonyl band shifts on coordination for the dimethylated complexes 1 to 12 also. Berni *et al.* (83,85) justified their stability assignments on the basis of measurements made by Bellamy and Branch (92). The carbonyl stretching frequency was used by Bellamy and Branch to measure relative stabilities of salicylaldehyde-metal ion complexes, and these corresponded well to stability values obtained by electrochemical measurements. The correspondence was thought sufficient proof that $\nu(\text{CO})$ values could be used as an

indication of stability. Berni *et al.* made no further measurements to substantiate their stability assignments. If the correlation of frequency shifts with stability is valid for complexes 1 to 12, one might expect tin complexes to be more stable than the lead adducts. In addition, complexes with DMPU are slightly more stable than complexes with DMEU, reinforcing the idea given earlier by Berni *et al.*, that the increase in ring size of the cyclic urea causes an increase in the stability of the complexes formed. The $\nu(\text{CN})$ frequency of DMPU changed little on going from free to bound ligand for all complexes 1 to 12, and the shifts observed were comparable to those for the DMEU adducts.

It has been suggested that the $\nu(\text{CO})$ frequencies of the N,N'-dialkyl cyclic ureas occur at higher frequencies than those of the corresponding unalkylated ureas. This might be expected if hydrogen bonding is greater in the latter, as they suggest. However, the data for DMEU and DMPU (Table 5) and for EU and PU (Table 9) does not agree with this. In fact, the data of Hussein and Lein (82) does not support their statement. From Tables 5 and 9, EU has a lower $\nu(\text{CO})$ frequency than its dimethyl analogue DMEU, but PU has a larger $\nu(\text{CO})$ than DMPU.

As already pointed out in the section on the analytical results, the analyses of the two complexes $\text{Ph}_3\text{SnCl} \cdot \text{DMEU}$ and $\text{Ph}_3\text{SnBr} \cdot \text{DMEU}$ were both consistent with the

presence of approximately 0.9 moles of water per mole of complex. The free ligands, although dried over BaO and CaH_2 as indicated in the experimental section, always contained a small amount of H_2O , as indicated by the observation of an OH stretching frequency at 3495 cm^{-1} . These results are in agreement with the observation of Lien and Kumler (77) who were frustrated in their attempts at drying a variety of dimethyl cyclic ureas. They consistently obtained a $\nu(\text{OH})$ bond in the range $3200\text{--}3600\text{ cm}^{-1}$ for all the N,N'-dimethylated cyclic ureas they studied, an observation attributed to the great tendency of the carbonyl oxygen to participate in hydrogen bonding. The two adducts always showed broad $\nu(\text{OH})$ frequencies at 3260 cm^{-1} despite rigorous drying procedures. Generally, water that is trapped within the crystal lattice absorbs at $3550\text{--}3200\text{ cm}^{-1}$ (antisymmetric and symmetric OH stretching frequencies), and at $1630\text{--}1600\text{ cm}^{-1}$ (HOH bending frequency) (93). The latter was not observed, being hidden under the strong $\nu(\text{CO})$ frequencies. The broadness of the peaks is consistent with the H_2O not being bound as a ligand to the metal. In addition to this, OH bound to the metal, as in Ph_3SnOH , was ruled out because this compound gives a sharp peak at 3620 cm^{-1} . The water observed in these two complexes is probably due to water of crystallization, and $\nu(\text{OH})$ occurs at a lower frequency than the "free" water observed in the neat liquid ligands.

As mentioned previously, this water was finally decreased after samples of the complexes were ground up and pumped on *in vacuo* for 3 hours. Solid state ir measurements confirmed this as a reduction in intensity of the peak at 3260 cm^{-1} . Equally, the ^1H nmr peak assigned to H_2O at approximately $\delta = 1.5$ ppm decreased in intensity as discussed earlier. The fact that prolonged pumping on crushed crystals finally depleted the water indicating that it is water of crystallization that is present.

The ir solution data given in Table 6 is consistent with highly dissociated complexes. This is obvious from a comparison of Figure 5 with Figure 3. The largest peak in each solution ir spectrum was assigned to the $\nu(\text{CO})$ frequency of the free ligand. In most cases, only a small peak was observed where the $\nu(\text{CO})$ frequency of the bound ligand should occur.

The observation of free and bound carbonyl stretching peaks in the spectra of complexes 1 to 12 (that of $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$ is given as an example in Figure 5) suggests that the following type of equilibrium occurs in solution:

Furthermore, provided the integrated molar absorptivities remain constant, band intensities indicate that the

Figure 5: IR Solution Spectrum of $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$ (2000-1100 cm^{-1}).

equilibrium lies well to the right. As the predominant species in solution is the free cyclic urea, presumably the predominant metal species present is the 4-coordinate parent metal halide. No solution ir measurements were made below 400 cm^{-1} to confirm the presence of Ph_3MX . It has been shown that the analogous HMPA complexes dissociate in benzene solution (22,56).

3.2.3 Discussion of Skeletal Frequencies

From Tables 7 and 8 no clear trends are obvious in the lead-phenyl stretching frequencies. There are two fundamental vibrations: the asymmetric stretching vibration should be strongly infrared active, whilst the symmetric one should be strongly Raman active. Generally, the observed relative intensities of the peaks are correct, but some asymmetric bands are seen in the Raman spectra, and some symmetric bands in the infrared spectra. They are, however, weak. This is the most convincing evidence for the existence of 5-coordination in complexes 1 to 12.

The phenyl group, when σ -bonded to a metal, exhibits bands characteristic of monosubstituted benzenes (91). Four of these weak, broad peaks were observed in the region of $2200\text{--}1800\text{ cm}^{-1}$. The $\text{M-C}_6\text{H}_5$ type of system exhibits 30 fundamentals, only six of these, the t, x and u modes, are sensitive to a change in the metal (49):

Lead-oxygen stretching bands were assigned in the region $195-220\text{ cm}^{-1}$, slightly lower than in the corresponding tin complexes whose tin-oxygen stretching bands ranged from $225-240\text{ cm}^{-1}$. These ranges compare favourably with those obtained for the corresponding HMPA complexes (56,22).

Halogen atoms or ions are among the most common ligands in coordination chemistry. Many studies have been done, and it is generally agreed that terminal M-X stretching bands appear in the regions of: $750-500\text{ cm}^{-1}$ for X = F; $400-200\text{ cm}^{-1}$ for X = Cl; $300-200\text{ cm}^{-1}$ for X = Br and $200-100\text{ cm}^{-1}$ for X = I (94). Clark and Williams (95) have suggested that for terminal halides the ratio $\nu(\text{MBr})/\nu(\text{MCl})$ is approximately 0.77 and $\nu(\text{MI})/\nu(\text{MCl})$ is 0.65. The ratios obtained for complexes 1 to 12 are listed in Table 10:

TABLE 10: RATIOS OF TERMINAL HALIDE STRETCHING FREQUENCIES FOR $\text{Ph}_3\text{MX} \cdot \text{L}$.

RATIO	$\text{Ph}_3\text{MX} \cdot \text{DMEU}$		$\text{Ph}_3\text{MX} \cdot \text{DMPU}$	
	M = Sn	M = Pb	M = Sn	M = Pb
$\frac{\nu(\text{MBr})}{\nu(\text{MCl})}$	0.65	0.68	0.64	0.69
$\frac{\nu(\text{MI})}{\nu(\text{MCl})}$	0.50	0.55	0.48	0.55

These values do not correspond closely to those suggested by Clark and Williams. However, the ratios observed for complexes 1 to 12 are quite independent of the metal or the cyclic urea present.

The parent compounds Ph_3PbX ($\text{X} = \text{Cl}, \text{Br}$) are polymeric (48) with bridging halogen atoms. The possibility also exists that some of the PbX stretching frequencies in complexes 4 to 6 and 10 to 12 are not, in fact, terminal. This would be particularly true for the triphenyllead chloride adducts which, from elemental analyses results, are probably associated to some degree. These adducts gave analyses corresponding to $3\text{Ph}_3\text{PbCl} \cdot 2\text{DMEU}$ for complex 4, and $2\text{Ph}_3\text{PbCl} \cdot \text{DMPU}$ for complex 10. However, the bromide complexes gave analyses corresponding to 1:1 adducts and are probably

monomeric from melting point and solubility criteria. If this is true, coordination of the cyclic urea probably breaks the bromine atom bridges completely. The lead-bromine bonds are slightly longer than the lead-chlorine bonds. This might give rise to a weaker polymer structure which breaks down to give the observed 1:1 adducts. One other possibility is that lead increases its coordination number from 5 to 6, maintains its polymeric structure, and still gives rise to a repeating unit of 1:1 stoichiometry. This possibility exists for both $\text{Ph}_3\text{PbBr}\cdot\text{L}$ complexes. The structure postulated for these would be:

The evidence against a structure such as this is the sharp melting point observed for both bromide adducts. A decomposition point might be expected for a polymeric structure of this type. The range found for the $\nu(\text{MBr})$ frequencies, $172\text{--}149\text{ cm}^{-1}$, does not correspond to the range quoted earlier for terminal MBr stretching bands. Wharf *et al.*

((22,56) obtained similar values, $148-140\text{ cm}^{-1}$, for the analogous HMPA complexes. No explanation was offered for the discrepancies in $\nu(\text{MBr})$ frequencies.

The $\nu(\text{MCl})$ and $\nu(\text{MI})$ frequencies appear within the ranges given earlier for terminal halides. In the case of the $\nu(\text{PbCl})$ frequencies, this is contrary to what might be expected because of the probable association. In general, bridging $\nu(\text{MX})$ stretching frequencies are lower than terminal ones. Clark et al. (49) have assigned values of 180 and 121 cm^{-1} to the $\nu(\text{PbCl})$ and $\nu(\text{PbBr})$ frequencies, respectively, in the 5-coordinate associated compounds Ph_3PbCl and Ph_3PbBr . The lead adducts $\text{Ph}_3\text{PbX}\cdot\text{L}$, where $\text{X} = \text{Cl}$ and Br , show $\nu(\text{PbX})$ frequencies greater than the values obtained for the Ph_3PbX species. Generally, $\nu(\text{MX})$ decreases as the coordination numbers increase, provided oxidation numbers remain constant (94). In other words, on going from the monomeric 4-coordinate parent triphenylmetal halides to the 5-coordinate 1:1 molecular adducts, the terminal $\nu(\text{MX})$ stretching frequency should decrease. The decrease could be an indication of the relative stabilities of the complexes. Certainly by comparing complexes 1 to 12 with their HMPA analogues (22,56), the latter have lower $\nu(\text{MX})$ frequencies, suggesting more stable complexes. For the adducts 1 to 12, the differences between the corresponding sets of complexes is too small to enable any firm conclusions to be drawn,

although the $\nu(\text{MX})$ frequencies of the DMPU adducts are slightly smaller.

As mentioned in the analytical section, the only two complexes that emerged other than as 1:1 molecular adducts were the complexes $3\text{Ph}_3\text{PbCl} \cdot 2\text{DMEU}$ and $2\text{Ph}_3\text{PbCl} \cdot \text{DMPU}$. Two possible structures of the latter which differ in the mode of bridging are shown below:

In the case where the urea ligand is bridging the metal atoms, the $\nu(\text{CO})$ frequency would be expected to be lower than that where the ligand is terminal, as in the 1:1 adducts of Ph_3PbBr and Ph_3PbI . As evident from Table 5, this was not observed. Thus, the structure with a bridging chlorine atom would seem to be more reasonable. A $\nu(\text{PbCl})$ peak was observed at 212 cm^{-1} , consistent with a terminal chlorine

atom. A band due to a bridging chlorine atom would be expected in the range below 200 cm^{-1} (94). The presence of internal ligand modes prevented any bridging PbCl stretching frequencies from being assigned. One thing which was observed in both the ir spectrum of this complex and that of $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$, was a lowered baseline compared to that observed in the bromide and iodide complexes below approximately 200 cm^{-1} . This might suggest the presence of a superimposed peak (or peaks) in the bridging halide region. This may be seen in the comparison of the far ir spectrum of $2\text{Ph}_3\text{PbCl}\cdot \text{DMPU}$ (Figure 6) with that of $\text{Ph}_3\text{PbBr}\cdot \text{DMPU}$ (Figure 7).

The nature of the $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$ complex is less obvious. The $\nu(\text{CO})$ frequency, 1647 cm^{-1} , is consistent with a terminal bonding mode. No peaks could be assigned to bridging $\nu(\text{PbCl})$ frequencies. The band which was assigned to a terminal $\nu(\text{PbCl})$ vibration, 222 cm^{-1} , agreed with that, 217 cm^{-1} , found for $\text{Ph}_3\text{PbCl}\cdot \text{HMPA}$ (56), a 1:1 molecular complex. In addition, for the complexes $\text{Ph}_3\text{MX}\cdot \text{DMEU}$ ($\text{M} = \text{Sn}$ or Pb), values of the ratios $\nu(\text{PbX})/\nu(\text{SnX})$ are 0.84 ($\text{X} = \text{Cl}$), 0.88 ($\text{X} = \text{Br}$) and 0.91 ($\text{X} = \text{I}$). For the DMPU adducts, the values of the ratios are 0.81 ($\text{X} = \text{Cl}$), 0.88 ($\text{X} = \text{Br}$) and 0.92 ($\text{X} = \text{I}$). These correspond to the values obtained by Wharf *et al.* (56) for their 1:1 HMPA adducts. The only 3:2 adduct known by the author is $3\text{CdI}_2\cdot 2\text{HMPA}$ (96). This is not

Figure 6: Infrared Spectrum of $2\text{Ph}_3\text{PbCl} \cdot \text{DMF}$ ($400\text{--}100\text{ cm}^{-1}$).

Figure 7: Infrared Spectrum of $\text{Ph}_3\text{PbBr} \cdot \text{DMPU}$ ($400\text{--}100\text{ cm}^{-1}$).

an organometallic complex and no structure has been postulated for it. Two highly speculative structures for $3\text{Ph}_3\text{PbCl} \cdot 2\text{DMEU}$ are:

The second structure would appear to be unlikely because cyclic urea molecules are unlikely to be bridging in the presence of chloride ions. As already mentioned, the $\nu(\text{CO})$ frequency in a complex such as this should be lowered relative to those values obtained for the 1:1 adducts formed with DMEU. Neutral complexes involving a stoichiometry of 3:2 are only possible if two lead atoms are 5-coordinate and one 6-coordinate as in the following structure:

3.3 ^1H NMR SPECTRA

3.3.1 Results

The ^1H nmr data of the free cyclic urea ligands is given in Table 11, and that of complexes 1 to 12 in Table 12.

TABLE 11: ^1H NMR DATA FOR THE CYCLIC UREAS DMEU AND DMPU^a.

UREA	$\delta(\text{CH}_3)^b$	$\delta(\text{CH}_2)^b$
DMEU	2.71	3.23
DMPU	2.63	1.73 ^c 3.04 ^d

^aMeasured in CD_2Cl_2 .

^bChemical shifts measured in ppm.

^cMiddle CH_2 -quintet $^3J(\text{H-H}) = 6 \text{ Hz}$.

^d CH_2 's bonded to N.

The spectrum of $\text{Ph}_3\text{SnBr} \cdot \text{DMEU}$ may be seen as an example in Figure 2. There are basically two regions of interest in these spectra. One is the high field region where the peaks associated with the protons of the ligands appear, in the region $\delta = 1.5\text{--}3.5 \text{ ppm}$. The other is the low field region where the phenyl protons appear, at about $\delta = 7\text{--}8 \text{ ppm}$.

Relative to the respective free ligand, the urea

TABLE 12: ^1H NMR DATA FOR COMPLEXES $\text{Ph}_3\text{MX}\cdot\text{L}^{\text{a,b,c}}$ WHERE $\text{M} = \text{Sn}$ AND Pb , $\text{X} = \text{Cl}$, Br AND I , AND $\text{L} = \text{DMKU}$ AND DMPU .

Complex	Number	$\delta(\text{CH}_3)$	$\delta(\text{CH}_2)$	$^3\text{J}(\text{H-H})$	$\delta(\text{ortho})^{\text{d}}$	$\delta(\text{meta/para})^{\text{e}}$	Δ^{f}	$^3\text{J}(^{207}\text{Pb-H})$
$\text{Ph}_3\text{SnCl}\cdot\text{DMKU}$	1	2.67	3.20		7.69	7.49	0.20	
$\text{Ph}_3\text{SnBr}\cdot\text{DMKU}$	2	2.71	3.22		7.66	7.47	0.19	
$\text{Ph}_3\text{SnI}\cdot\text{DMKU}$	3	2.72	3.22		7.66	7.46	0.20	
$3\text{Ph}_3\text{PbCl}\cdot 2\text{DMKU}$	4	2.53	3.14		7.75	7.44	0.31	128
$\text{Ph}_3\text{PbBr}\cdot\text{DMKU}$	5	2.63	3.18		7.75	7.47	0.28	112
$\text{Ph}_3\text{PbI}\cdot\text{DMKU}$	6	2.69	3.21		7.73	7.46	0.27	104
$\text{Ph}_3\text{SnCl}\cdot\text{DMPU}$	7	2.77	1.89^{g} 3.16^{h}	6	7.71	7.45	0.26	
$\text{Ph}_3\text{SnBr}\cdot\text{DMPU}$	8	2.81	1.91^{g} 3.19^{h}	6	7.68	7.47	0.21	
$\text{Ph}_3\text{SnI}\cdot\text{DMPU}$	9	2.82	1.92^{g} 3.19^{h}	6	7.64	7.45	0.19	
$2\text{Ph}_3\text{PbCl}\cdot\text{DMPU}$	10	2.67	1.82^{g} 3.11^{h}	6	7.76	7.51	0.25	111
$\text{Ph}_3\text{PbBr}\cdot\text{DMPU}$	11	2.73	1.84^{g} 3.14^{h}	6	7.78	7.53	0.25	111
$\text{Ph}_3\text{PbI}\cdot\text{DMPU}$	12	2.81	1.92^{g} 3.18^{h}	6	7.72	7.47	0.25	104

^aMeasured in CD_2Cl_2 .

^bChemical shifts measured in ppm relative to internal TMS - accurate to ± 0.05 ppm.

^cCoupling constants measured in Hz. Digital resolution = 0.25 Hz.

^dOrtho protons of phenyl rings.

^eMeta/para protons of phenyl rings.

^f $\Delta = \delta(\text{ortho multiplet}) - \delta(\text{meta/para multiplet})$ in ppm.

^gMiddle CH_2 -quintet.

^h CH_2 's bonded to H.

proton peaks for all the complexes 1 through 12 have shifted little. In the case of the DMEU adducts, 1 to 6, the shifts due to complexation are of the order of 0.01-0.18 ppm for the methyl protons, and 0.01-0.09 ppm for the methylene protons. With the exception of the methyl protons in $\text{Ph}_3\text{SnI}\cdot\text{DMEU}$, all shifts are to high field, being somewhat larger in the lead series for both types of ligand proton. For the DMPU adducts, shifts on complexation are also very small, 0.04-0.19 ppm for the methyl protons, 0.09-0.19 ppm for the middle methylene protons, and 0.07-0.15 ppm for the terminal methylene protons. However, these shifts are to low field of those obtained for free DMPU. There is no significant difference between the tin and lead series for this ligand. For both series of complexes, however, chemical shift differences noted between free and bound ligand are too small to merit further discussion.

The pattern observed for the aromatic protons was the same in all cases. Two clearly distinct sets of multiplets were observed. In the case of the lead complexes 4 to 6 and 10 to 12, increased resolution over the tin complexes gave rise to what may be three multiplets. The aromatic proton regions for complexes $\text{Ph}_3\text{SnCl}\cdot\text{DMPU}$, $\text{Ph}_3\text{SnCl}\cdot\text{DMEU}$ and $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$ are shown in Figure 8. From the spectra in this figure, the high field multiplet in the aromatic proton region of the lead complex is further split

into a triplet and a doublet. The tin complexes rarely show a complex multiplet. The triplet, which is first order, may be due to the meta protons while the second-order doublet would be due to the para protons. It was not possible to obtain the ratio of the meta to para protons in the lead complexes by integration, the two multiplets being too close together.

In all the complexes studied the ortho proton resonances of the phenyl rings are downfield relative to the meta/para protons. The ^1H nmr spectrum of Ph_3SnCl in CD_2Cl_2 (97) revealed two groups of closely spaced, partially overlapping multiplets. The ^1H nmr spectra of Ph_3SnCl , Ph_3PbCl and Ph_3PbI , obtained in this work, gave multiplet separations of 0.196, 0.238 and 0.257 ppm, respectively, which are similar within the limits of the experimental error, estimated to be 0.0025 ppm. The multiplet separations (Δ in Table 12) for the series of complexes 1 to 12 varied from approximately 0.20 to 0.30 ppm. These were obtained from the weighted centres of the two main multiplets.

Coupling constants obtained include $^3J(^{207}\text{Pb-H})$ values for all lead adducts, and these are given in Table 12, although only the low field satellite was observed. This will be discussed later. $^3J(^{117/119}\text{Sn-H})$ coupling constants could not be absolutely assigned, although the low field satellites were observed.

Figure 8: Aromatic Proton Region of Some Adducts $\text{Ph}_3\text{MX} \cdot \text{L}$.

3.3.2 Discussion

Sau *et al.* (97) have reported a splitting pattern for the aromatic proton resonances in several phenyl substituted pentacoordinated derivatives of tin (IV) identical to that observed in this work. The complexes they studied included both neutral and cationic-anionic ones, some of these were Ph_3SnCl , $\text{Ph}_3\text{SnCl} \cdot \text{HMPA}$, $\text{Ph}_3\text{SnCl} \cdot \text{Py}$, $\text{Ph}_3\text{SnCl} \cdot \text{DMAP}$ (DMAP = 4-(dimethylamino)pyridine), $\text{Ph}_3\text{SnF} \cdot \text{HMPA}$, $[\text{Et}_4\text{N}]^+ [\text{Ph}_3\text{SnCl}_2]^-$ and $[\text{Ph}_4\text{As}]^+ [\text{Ph}_3\text{SnCl}_2]^-$. Subsequently, this work was extended (98) to complexes of some phenyl substituted pentacoordinate derivatives of Si, Pb, P, As, Sb, S, Te and I, some of which were Ph_3SbCl_2 , $(\text{Ph}_3\text{TeCl})_2$, $[\text{Et}_4\text{N}]^+ [\text{Ph}_3\text{PbCl}_2]^-$ and $\text{Ph}_3\text{PbCl} \cdot \text{HMPA}$. All showed the same characteristic splitting pattern.

The complexes $[\text{Me}_4\text{N}]^+ [\text{Ph}_3\text{SnCl}_2]^-$ (97) and $[\text{Ph}_3\text{AsCH}_2\text{COPh}]^+ [\text{Ph}_3\text{SnCl}_2]^-$ (99) have been shown by X-ray crystallography to have trigonal bipyramidal environments around the tin, with the chlorine atoms occupying axial sites. The crystal and molecular structures of Ph_3SbCl_2 (100), $\text{Ph}_3\text{Sb}(\text{O}_2\text{CCH}_3)_2$ (101) and $(\text{Ph}_3\text{TeCl})_2$ (102) all show that the phenyl groups are equatorial. Therefore, the three phenyl rings are chemically equivalent. Presumably, either an A_2B_3 or $\text{A}_2\text{B}_2\text{C}$ spin system exists for the phenyl protons. Either one would give a complex multiplet, and so the observed pattern of two main multiplets for adducts 1 to 12 and the complexes

studied by Sau *et al.* (97,98) is unexpected. It was also noticed (97) that the diphenyl derivative $[\text{Et}_4\text{N}]^+[\text{Ph}_2\text{SnCl}_3]^-$ and the monophenyl derivative $[\text{n-Bu}_4\text{N}]_2^+[\text{PhSnCl}_5]^{2-}$ had similar aromatic proton splitting patterns. From these results it was suggested that the two sets of multiplets could not be due to nonequivalent phenyl groups, but were probably caused by some differential effect on the ortho, meta and para protons within the phenyl rings in the complexes. For all the complexes studied by these workers the lower field multiplet was assigned to the ortho protons, and the higher field multiplet to the meta and para protons, on the basis of the integrated intensities which were found to have ratios of approximately 1:1.8 instead of the calculated 1:1.5. The discrepancy was thought to be due to the overlap of the high field tin or lead satellites, which arise from coupling between ^{117}Sn , ^{119}Sn and ^{207}Pb (natural abundances of 7.54%, 8.62% and 23%, respectively) with the ortho protons, and the multiplet arising from the meta and para protons. Hence, the satellite intensities must be taken into account when interpreting the integration of the spectra. The spectra measured for complexes 1 to 12 maintained this relative intensity of the two sets of peaks.

Sau *et al.* (97,98) have suggested that pentacoordinate complexes might be expected to show larger differences in separation between the two multiplets. They also suggested

that the neutral molecular adducts $\text{Ph}_3\text{SnF}\cdot\text{HMPA}$, $\text{Ph}_3\text{SnCl}\cdot\text{HMPA}$, $\text{Ph}_3\text{SnCl}\cdot\text{DMPA}$ and $\text{Ph}_3\text{PbCl}\cdot\text{HMPA}$ all contain relatively weak dative bonds. Their multiplet separations are 0.55, 0.42, 0.35 and 0.58 ppm, respectively, which are larger than typical 4-coordinate values, but smaller than those obtained for complexes of the type $[\text{Et}_4\text{N}]^+[\text{Ph}_3\text{SnX}_2]^-$ in CH_2Cl_2 where $\text{X} = \text{Br}$, Cl and F . The ionic complexes are more likely to remain 5-coordinate in solution, and as X increases in electronegativity the multiplet separations increase from 0.62 to 0.75 to 0.82 ppm, respectively. The complex $[\text{Et}_4\text{N}]^+[\text{Ph}_3\text{PbCl}_2]^-$ shows a multiplet separation of 1.2 ppm which is also larger than the value obtained for the neutral molecular adduct $\text{Ph}_3\text{PbCl}\cdot\text{HMPA}$. The multiplet separations given in the results section for the 4-coordinate parent compounds Ph_3SnCl and Ph_3PbI , and the 5-coordinate associated parent compound Ph_3PbCl , are not appreciably different from those observed for complexes 1 to 12. The multiplet separations in Table 12 do, however, appear to verify some of the conclusions drawn by Sau *et al.* (97,98), namely that Δ tends to become larger if the electronegativity of the central atom is lowered. In this work, on going from the tin to the lead complexes Δ increased slightly, although the differences in electronegativities between these two elements is negligible. In fact, as mentioned previously, the possibility exists that for the lead complexes prepared

(in this work there are in fact three multiplets. The high field multiplet is split into what appears to be a triplet and a doublet. The triplet appears to be first-order and from its position would seem to be due to the meta protons. The doublet appears to be second-order and, being to higher field, would presumably be due to the para protons. Thus, for the lead complexes, in addition to the ortho protons being to low field of the meta/para multiplet, the meta protons are probably the triplet. This is a tentative but reasonable suggestion. The lead complexes do, however, appear to have their aromatic proton regions better resolved with greater separations between the three types of aromatic proton. Sau *et al.* (98) did not observe a similar pattern in their ^1H nmr spectra of complexes such as $\text{Ph}_3\text{PbCl}\cdot\text{HMPA}$, presumably because of the low field strength used by them, 60 MHz as opposed to 200 MHz used in this work. Sau *et al.* (97,98) also suggested Δ increases if the electronegativity of the ligands, and the number of such ligands bonded to the central atom, is increased. The lead-DMEU and tin-DMPU adducts (complexes 4 to 6 and 7 to 9), showed the greatest range in Δ values, and as the halide varied from iodide to chloride, Δ increased although only slightly.

The observation of the high field tin satellites for $\text{Ph}_3\text{SnCl}\cdot\text{DMPU}$, as shown in Figure 8, may be a result of

(the larger multiplet separation observed for this complex compared to the other tin adducts. Apparently the coupling constants remain approximately similar whilst the separations increase. In the case of $\text{Ph}_3\text{SnCl} \cdot \text{DMEU}$, also shown in Figure 8, the high field $^{117/119}\text{Sn}$ satellites of the ortho protons appear as a shoulder on the meta/para multiplet.

Sau *et al.* (97) have suggested that the enhanced downfield shifts of the ortho protons relative to the meta/para protons for pentacoordinated species, in comparison with those of 4-coordinate complexes such as Ph_3SnCl , may be evidence of π -electron density transfer from the phenyl rings to the vacant 5d orbitals of the central tin on pentacoordination. They suggested this might be an indication of pentacoordination in adducts of triphenyl tin halides. They have also suggested that the extent of the multiplet separation is proportional to the basicity of the newly added ligand, but there is no thermochemical data to support the suggestion.

It is necessary to mention briefly the spin-spin coupling between the $^{117/119}\text{Sn}$ and ^{207}Pb isotopes and the ortho protons of the three phenyl rings. These couplings produce satellite peaks centered about the main ortho proton multiplet, originating from molecules containing non-magnetic nuclei. Values of about 60 Hz were obtained by Verdonck *et al.* (103) for 3J ($^{117/119}\text{Sn}-\text{C}-\text{C}-\text{H}$) in Ph_3SnCl . Sau *et al.*

((98) obtained values of about 120 Hz for $^3J(^{207}\text{Pb-C-C-H})$ in $\text{Ph}_3\text{PbCl}\cdot\text{HMPA}$. The magnitudes of three-bond coupling constants of this type depend on factors similar to those which determine one-bond coupling constants, such as effective nuclear charge and 's' character of the orbitals on the metal atom. The ratio of the two coupling constants obtained from the $^{117/119}\text{Sn}$ satellites in complexes 1 to 3 and 7 to 9 should be directly proportional to the magnetogyric ratios of the nuclei according to equation 15 (104).

$$\frac{{}^3J(^{117}\text{Sn-C-C-H})}{{}^3J(^{119}\text{Sn-C-C-H})} = \frac{\gamma_{^{117}\text{Sn}}}{\gamma_{^{119}\text{Sn}}} = 0.95 \quad [15]$$

It is not clear how valid this equation is, since isotopic substitution can alter the vibrational states of the molecule, affecting the values of J. However, isotopic effects on spin-spin coupling constants are normally negligible (104), and this equation should hold true. The values of $^3J(^{207}\text{Pb-C-C-H})$, given in Table 12, are similar to that observed by Sau *et al.* (98) for $\text{Ph}_3\text{PbCl}\cdot\text{HMPA}$. Only the low field satellite is seen in the spectra of complexes 4-6 and 10-12. It is split into a multiplet similar to that observed for the ortho protons attached to the non-magnetic lead nuclei. The pattern of the aromatic region for $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$ is shown in Figure 8. The high field satellites

are not visible, being buried under the large meta/para multiplet. Hence, in order to obtain values for the coupling constants, measurements were made from the centre of the satellite multiplet to the centre of the ortho proton multiplet and doubled. It is possible for large discrepancies to occur in the measurement of J values, usually when proton couplings render spectra very complex, making it more difficult to determine the coupling constants with precision. This is evident in the appearance of the tin satellites for complexes 1-3 and 7-9. Figure 8 shows the low field satellites observed for $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$ and $\text{Ph}_3\text{SnCl} \cdot \text{DMEU}$. In the case of the former complex, the high field satellites also appear. In the latter, the high field satellites may be present as a shoulder on the meta/para multiplet. None of these satellites can be resolved, although they show a similar pattern to that observed for the lead satellites in the ^1H nmr of the lead complexes. The ^{207}Pb low field satellites of the ortho protons for $3\text{Ph}_3\text{PbCl} \cdot 2\text{DMEU}$ are also evident in Figure 8. In all complexes the ortho protons which are split, either by tin or lead, are also split by the protons meta to the metal. The splitting observed in this case should be identical to that observed for the ortho protons attached to non-magnetic nuclei. The associated three-bond coupling constants, 3J (H-C-C-H), should be similar in all spectra. Values of approximately 8 Hz were

obtained, whether measured using the tin or the lead satellites, and this agrees well with the value for C_6H_6 of 7.6 Hz (105). There is considerable broadness of the tin satellites compared to the lead ones. This is due to the presence of two magnetic tin nuclei, ^{117}Sn and ^{119}Sn , of approximately equal natural abundances at 7.54 and 8.62%, respectively, as opposed to only one for the lead nuclei, ^{207}Pb :

REPRESENTATION OF THE SPIN-SPIN

SPLITTING OF THE ORTHO PROTONS:

IN THE TIN COMPLEXES
1-3 AND 7-9

$$a = {}^3J(H-H)$$

IN THE LEAD COMPLEXES
4-6 AND 10-12

$$a = {}^3J(H-H)$$

To confirm the assignment of the 3J ($^{207}\text{Pb-C-C-H}$) satellites, a series of homonuclear decoupling experiments were done on $3\text{Ph}_3\text{PbCl} \cdot 2\text{DMEU}$. These are shown in Figure 9. Spectrum 1 of Figure 9 shows the coupled aromatic proton region of $3\text{Ph}_3\text{PbCl} \cdot 2\text{DMEU}$. It is evident that the high field multiplet may in fact be two multiplets, a triplet with a doublet to higher field. The latter is probably due to the para protons, while the triplet is assigned to the meta protons, as previously discussed. The peaks labelled 'a' may be due to the 4J ($^{207}\text{Pb-C-C-C-H}$) low field satellite. This would assume a triplet structure in the same way as the meta protons in the molecule with a non-magnetic lead nucleus due to proton-proton couplings. The high field portion of this triplet is buried under the large meta multiplet. The value of 4J ($^{207}\text{Pb-C-C-C-H}$) is 40 Hz in this complex. Values of 15.8 ± 0.1 Hz and 18.3 ± 0.1 Hz have been obtained for 4J (Pb, H_a) and 4J (Pb, H_b) coupling constants in the following molecule (106):

Spectrum 2 shows the results when the decoupler is

SPECTRUM 1 SPECTRUM 2 SPECTRUM 3 SPECTRUM 4

Figure 9: Homonuclear Decoupling Experiments on $3\text{Ph}_3\text{PbCl} \cdot 2\text{DMEU}$.

x = POSITION OF DECOUPLER

placed on the low field meta lead satellite. This perturbs and collapses the ortho lead satellite as expected. The low field ortho lead satellite now presumably shows only the very small coupling to the para protons. In addition to this, the ortho and meta protons in the non-magnetic lead molecules are also perturbed. This perturbation is probably due to the position of the decoupler being too near the main ortho and meta multiplets.

Spectrum 3 shows that when the decoupler is set on the low field lead satellite of the ortho protons, the low field lead satellite of the meta protons labelled 'a' in the spectrum is perturbed, although the rest of the spectrum remained intact.

Spectrum 4 in Figure 9 shows that when the decoupler is placed where the low field lead satellite of the para protons should be, assuming as mentioned earlier that the doublet is in fact due to the para protons, the lead satellites of the meta protons are perturbed. At the same time the lead satellites of the ortho protons appear slightly simplified, as would be expected if the coupling to the para protons was removed.

It has already been suggested from the solution ir results that all the adducts 1 to 12 are highly dissociated in CH_2Cl_2 solution. The most reasonable type of equilibrium to postulate was given earlier in equation 14. The ^1H nmr

spectrum of $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$ was remeasured in the same solvent (CD_2Cl_2) after a couple of drops of neat DMPU had been added. The proton peaks associated with the ligand shifted by an amount less than the estimated error of 0.05 ppm. The shifts involved are so small, perhaps because the complexes $\text{Ph}_3\text{MX} \cdot \text{L}$ are almost completely dissociated in CH_2Cl_2 and the main species seen is free ligand. This suggests the equilibrium lies to the right hand side. On addition of excess free ligand, the peak positions of the ligand protons shift to a negligible extent. Very little 5-coordinate complex therefore, exists in solution. This agrees with the solution ir spectral results which indicated that little bound ligand was present in CH_2Cl_2 .

On addition of excess free ligand, the phenyl proton region also changed only slightly. The separation between the multiplets increased from 0.26 ppm for the complex $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$ to 0.34 and 0.44 ppm as 0.01 and 0.03 ml of DMPU was added to the solution. The increase in separation was due to the ortho proton multiplet shifting to lower field while the meta/para multiplet stayed constant. This change in shift caused the high field $^{117/119}\text{Sn}$ satellites to become more visible, although still not well resolved, as shown in Figure 10.

If an equilibrium of the type mentioned earlier (equation 14) exists in solution, then addition of excess

Figure 10: Aromatic Proton Region of $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$ and
Excess DMPU (.01 ml).

ligand would tend to push the equilibrium to the left, increasing the concentration of 5-coordinate species in solution. The greater splitting between the two aromatic proton multiplets is consistent with this expectation. The neutral complexes examined by Sau *et al.* (97,98) were assumed to remain pentacoordinate in solution with no obvious dissociation. This is known to be untrue in at least two of the complexes they studied; $\text{Ph}_3\text{SnCl}\cdot\text{HMPA}$ (22) and $\text{Ph}_3\text{PbCl}\cdot\text{HMPA}$ (56) have been shown to dissociate in benzene solution. Therefore, in a more polar solvent such as CH_2Cl_2 , dissociation would also be extensive.

3.4 METAL NUCLEI NMR SPECTRA

There are several factors that affect the ease with which nmr signals may be observed. One of these factors is the nuclear spin angular momentum which is indicated by the quantum number I . All nuclei may be categorized as possessing $I = 0$, $I = 1/2$ or $I > 1/2$. The latter class of nuclei are said to possess nuclear electric quadrupole moments, Q , which tend to shorten relaxation times and broaden lines. Nuclei with no spin, $I = 0$, do not possess angular momentum and therefore show no nmr properties. The values I are quantized in terms of $h/2\pi$, *i.e.* $\hbar$, where h is Planck's constant. Associated with the nuclear spin is the nuclear magnetic moment, μ , given by the following equation (107):

$$\mu = \gamma \hbar \quad [16]$$

where γ = magnetogyric ratio. γ may be positive or negative, and is a function only of the nucleus under study. The strength of the signal and the sensitivity of the nmr measurement is related to μ . Large magnetic moments lead to easier detection of nuclear magnetic resonance. The values of the magnetic moments for the group IV elements, with the exception of germanium, make them suitable for study. The nuclear properties of these elements are given in Table 13.

Four out of the five elements of group IV possess isotopes with spin 1/2, suitable for nmr measurements. As indicated earlier, quadrupolar nuclei such as ^{73}Ge give rise to broad lines. With $I = 9/2$, natural abundance = 7.8%, and a lower receptivity than carbon, germanium is unsuitable for nmr study. Although there are 3 tin isotopes with $I = 1/2$, the ^{119}Sn nucleus is usually examined because it is superior to ^{115}Sn and ^{117}Sn with regard to abundance and receptivity. In fact, the former is very seldom used.

As a particular group in the periodic table is descended, changes in trends of nuclear behaviour might be expected with different degrees of chemical shielding. This is, however, difficult to confirm due to the inadequate distribution of sufficiently abundant nuclei with the required magnetic properties throughout the periodic table. Group IV

TABLE 13: NMR PROPERTIES OF GROUP IV NUCLEI RELATIVE TO $^1\text{H}^a$.

ISOTOPE	SPIN	NATURAL ABUNDANCE (%)	RELATIVE RECEPTIVITY ^b	γ^c	REFERENCED ^d COMPOUND	USUAL CHEMICAL SHIFT RANGE (ppm)
^1H	1/2	99.98	1.00	26.751	TMS	10
^{13}C	1/2	1.11	1.76×10^{-4}	6.7263	TMS	350
^{29}Si	1/2	4.70	3.69×10^{-4}	-5.3141	TMS	400
^{73}Ge	9/2	7.76	1.09×10^{-4}	-0.9332	TMG	1200
^{115}Sn	1/2	0.35	1.22×10^{-4}	-8.7475		
^{117}Sn	1/2	7.61	3.44×10^{-3}	-9.5301	TMT	
^{119}Sn	1/2	8.58	4.44×10^{-3}	-9.9707		2000
^{207}Pb	1/2	22.6	2.07×10^{-3}	5.5968	TML	16000

^aReference (61,107).

^bRelative to ^1H .

^cMagnetogyric ratio, $\gamma/10^7$ rad T⁻¹s⁻¹.

^dTMS = tetramethylsilane; TMG = tetramethylgermane; TMT = tetramethyltin;
TML = tetramethyllead.

is thus unique in that all its elements possess a spin. The order of importance of nmr work on the four spin 1/2 nuclei is as follows: $^{13}\text{C} > ^{29}\text{Si} > ^{119}\text{Sn} > ^{207}\text{Pb}$. This order also reflects the chemical interest in these elements.

One important comparison of the properties of the spin 1/2 group IV nuclei must be mentioned. The sign of the magnetic moment of the nuclei has an important practical consequence. Spectra may be obtained under conditions of complete heteronuclear proton decoupling. The decoupling, allied with pulsed Fourier transform methods, gives dramatic improvements in sensitivity such that complex multiplets are collapsed to single peaks. In this work, the removal of the couplings is especially significant since the presence of phenyl groups attached to the metal atoms considerably complicate the coupled spectra. When a second radiofrequency is employed, as in the decoupling experiment, the nuclear Overhauser effect (NOE) must be taken into consideration. If ^{207}Pb is observed while ^1H is irradiated, the integrated intensity of the ^{207}Pb spectrum will differ from its value from the simple coupled ^{207}Pb spectrum. The NOE is the ratio of the double-resonance intensity relative to the single resonance intensity (108). The application of the second radiofrequency during complete proton decoupling experiments not only removes the associated multiplicity, but it can also induce intensity changes. The nuclear

Overhauser enhancement has its maximum value when dipole/dipole relaxation is the dominant relaxation mechanism (108). Hence, different peaks within the same spectrum may have their intensities altered to different extents. In the case of isotopes such as ^{13}C or ^{207}Pb , where the magnetogyric ratio, γ , is positive, peak intensities can increase although integrals must be treated with caution, as not all nuclei will relax by the same mechanism. In the case of nuclei such as ^{119}Sn , the negative value of γ can cause signals to be reduced considerably, again depending on the extent of the dipolar contribution to the relaxation mechanism. Nuclear Overhauser enhancement factors of 0 to -1.34 have been observed in $^{119}\text{Sn}\text{-}\{^1\text{H}\}^*$ experiments (61). Hence, this effect for tin is never beneficial with regards to signal intensities. The problem of decreasing signal intensities is outweighed by the obvious advantage of collapsing a multiplet (due to proton couplings). Reduction in signal intensities may be overcome by removing the nuclear Overhauser effect. This can be done in a number of ways: a) use of a paramagnetic relaxation time reagent such as $[\text{Cr}(\text{acac})_3]$ (108), which does not react chemically with either the compound under study, or the solvent in which the measurements are being made; b) the use of gated decoupling which exploits the difference in time scales between the decoupling

* This symbol indicates that the resonance of ^{119}Sn is observed whilst ^1H is irradiated.

and the nuclear Overhauser effects (108). On application of a second radiofrequency pulse to decouple the protons, the decoupling occurs immediately, but the NOE only builds up slowly. The growth is exponential with a time constant in the order of the spin lattice time T_1 . The second radiofrequency may thus be switched on or off immediately before data collection, when either decoupled or coupled spectra will be obtained, respectively. The NOE, however, depends on the state of the decoupler in the time before the exciting pulse. If the proton irradiation power (the decoupler) is switched on just before data acquisition, as seen in region 3 of the pulse sequence below, the spectrum will be decoupled but the NOE will not have become established. The basic two pulse sequence, which is the standard one for the XL-200 nmr spectrometer used in this work, is given below (109):

PAD = Pre-acquisition delay	D_1 and D_2 = Delay times
AT = Acquisition time	P_1 = Perturbing pulse before the observation pulse
NT = Number of transients	
N = No (decoupler off)	P_w = width of the transmitter observe pulse
Y = Yes (decoupler on)	

P_1 and D_2 are set to zero for recording normal spectra. If experiments to measure T_1 are performed, P_1 and D_2 are assigned values.

There are a number of practical points that must be taken into consideration when doing nmr work on metal nuclei. One problem is the lack of uniformity in the chemical literature as to the reference compound used for a particular nucleus. In the case of group IV, the tetramethyl analogues of TMS are generally used where available. In this work, TMT (tetramethyltin) was used for ^{119}Sn measurements, but for ^{207}Pb spectra, TEL (tetraethyllead) was used instead of TML (tetramethyllead) because of the unavailability of the latter. Maciel and Dallas (59) have measured the chemical shift of neat TEL with TML as reference and so their values may be used, if required, to convert the chemical shifts obtained in this work to values referenced in TML. Multi-nuclear nmr reference compounds very often have resonances somewhere in the middle of the chemical shift range for the nucleus under study. This makes the sign convention assigned

to chemical shift values very important. Chemical shifts to high field of the reference are now indicated as negative whilst those to low field of the reference material are positive. This convention is usually, but not always, adopted in the chemical literature. Consequently, care must be taken in comparisons of various literature references.

If the reference is to be used as an internal one, in the same way as TMS is used in routine proton work, the reference compound must be stable and soluble in the solvent, and provide a sharp signal, detectable at low concentrations. An internal reference must not react with either the solute or the solvent, and should be insensitive to the inevitable experimental variations in temperature and concentration. Due to the reactivity of most metal complexes, an external referencing technique is usually preferable. This technique usually takes the form of an additional tube within the normal sample nmr tube. It has the advantage that there can be no displacement of the reference peak due to inter-molecular effects between the reference and the solute or solvent. In addition to this, the reference material can be sealed in the inner tube and used repeatedly. External reference tubes may contain either neat reference material or a mixture of the reference and a deuterated solvent when the spectrometer has an internal field-frequency locking system. The most commonly used locking frequency for pulsed

nmr spectrometers is the deuterium lock. The main characteristics required of the locking signal are that: it be a single sharp line, and that it must not be near another strong line in the spectrum. The deuterium ($I = 1$) in common deuterated solvents satisfies these requirements, and is high enough in concentration to overcome its low sensitivity. In this work, a 50% v/v solution of the reference compound in hexadeuterobenzene was employed. This mixture was contained in an internal tube which snugly fitted the external nmr sample tube and which had a screw cap:

In all external referencing techniques, a correction should be applied for the difference in the bulk magnetic susceptibility of the reference and the sample since the solution under study and the reference material do not experience the same magnetic field. This correction may be calculated from the following equation (110):

$$\delta_{\text{corr}} = \delta_{\text{obs}} + \frac{2\pi}{3}(\kappa_r - \kappa_s) \quad [17]$$

κ_r and κ_s are the bulk magnetic susceptibilities of the reference and the sample, respectively. For concentric spherical samples, the correction is zero, similar to when an internal reference is used. In the ^{119}Sn and ^{207}Pb experiments performed here, the bulk susceptibility correction was ignored. This is usual for nuclei other than the proton because the magnitude of this correction is usually less than 1 ppm and the chemical shift ranges (Table 13) are 2000 ppm for ^{119}Sn and 16000 ppm for ^{207}Pb . The estimated error itself is 1 ppm.

3.4.1 Results

The ^{119}Sn chemical shifts of the parent triphenyltin halides and complexes 1 to 3 and 7 to 9, relative to TMT, are given in Table 14. The ^{13}C satellites of the reference, TMT, were detected: $^1J(^{119}\text{Sn}-^{13}\text{C}) = 346 \text{ Hz}$. McFarlane (112) obtained a value of $340 \pm 2 \text{ Hz}$ for $^1J(^{119}\text{Sn}-^{13}\text{C})$, for the same compound, but this was measured with 10% dioxan in the sample as a reference signal for the field-frequency locking circuit of the spectrometer. The nmr spectra in this work were obtained using 50% v/v TMT in C_6D_6 and the digital resolution was 3.1 Hz.

The complexes $\text{Ph}_3\text{SnI} \cdot \text{DMEU}$ and $\text{Ph}_3\text{SnI} \cdot \text{DMPU}$ both showed ^{13}C satellites and the $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constants were 574.8 Hz for the former complex and 578.3 Hz for the latter.

TABLE 14: ^{119}Sn CHEMICAL SHIFTS (ppm)^a.

COMPOUND	$\delta(^{119}\text{Sn})$	
Ph_3SnCl	- 48	- 44.7 ^b
Ph_3SnBr	- 62	- 59.8 ^b
Ph_3SnI	-113	-112.8 ^b
$\text{Ph}_3\text{SnCl} \cdot \text{DMEU}$	- 85	
$\text{Ph}_3\text{SnBr} \cdot \text{DMEU}$	- 84	
$\text{Ph}_3\text{SnI} \cdot \text{DMEU}$	-118	
$\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$	-108	-103 ^c
$\text{Ph}_3\text{SnBr} \cdot \text{DMPU}$	-105	-
$\text{Ph}_3\text{SnI} \cdot \text{DMPU}$	-128	-123 ^c

^aMeasured for 0.25 M solutions in CH_2Cl_2 at 20°C relative to TMT.

^bReference (111): measured in CDCl_3 .

^cSaturated solution in C_6H_6 .

The ^{207}Pb chemical shifts of the parent triphenyllead halides and complexes 4 to 6 and 10 to 12, relative to TEL in C_6D_6 (50% v/v) are given in Table 15. The ^{13}C satellites of the reference, TEL, were observed and $^1J(\text{Pb}-\text{C})$ was 196 Hz. Michell *et al.* (113) reported a value of 202 Hz for the same compound, neat and at 40°C. In this work, the digital resolution was 3.3 Hz compared to 3 Hz in reference 113.

Figure 11 shows the ^{207}Pb spectrum of $2\text{Ph}_3\text{PbCl} \cdot \text{DMPU}$,

TABLE 15: ^{207}Pb CHEMICAL SHIFTS (ppm)^a.

COMPOUND	$\delta(^{207}\text{Pb})$
Ph_3PbCl^b	- 42 - 38 ^c
Ph_3PbBr^b	- 74 - 68 ^c
Ph_3PbI^b	-195 -202 ^c
$3\text{Ph}_3\text{PbCl} \cdot 2\text{DMEU}^b$	-144
$\text{Ph}_3\text{PbBr} \cdot \text{DMEU}$	-123
$\text{Ph}_3\text{PbI} \cdot \text{DMEU}$	-196
$2\text{Ph}_3\text{PbCl} \cdot \text{DMPU}^b$	-124
$\text{Ph}_3\text{PbBr} \cdot \text{DMPU}$	-141
$\text{Ph}_3\text{PbI} \cdot \text{DMPU}$	-201

^aMeasured as 0.25 M solutions in CH_2Cl_2 at $20 \pm 3^\circ\text{C}$ unless otherwise indicated, relative to TEL.

^bSaturated solution (< 0.25 M).

^cReference (113). Saturated solutions in CDCl_3 . Measured relative to TML but corrected relative to TEL for comparison purposes.

and the ^{119}Sn spectra of $\text{Ph}_3\text{SnI} \cdot \text{DMEU}$ and $\text{Ph}_3\text{SnI} \cdot \text{DMPU}$. The parameters used to obtain these spectra are given in Fig. 12.

3.4.2 Discussion

The chemical shift ranges observed for the ^{119}Sn and

a)

b)

c)

Figure 11: ^{207}Pb and ^{119}Sn NMR Spectra of some Adducts $\text{Ph}_3\text{MX}\cdot\text{L}$:
 a) ^{207}Pb spectrum of $2\text{Ph}_3\text{PbCl}\cdot\text{DMPU}$; b) ^{119}Sn spectrum of $\text{Ph}_3\text{SnI}\cdot\text{DMEU}$; c) ^{119}Sn spectrum of $\text{Ph}_3\text{SnI}\cdot\text{DMPU}$.

2Ph₃PbCl·DMPU^b

EXP4	PULSE SEQUENCE	S2PUL	°
ACQUISITION			
TN	207 000	DN	1.200
SW	50000 0	DO	0
AT	0 300	DM	YYY
NP	30000	DMM	E
PW	10 0	DMF	100
P1	0	DHP	Y
D1	1 000	DLP	20
D2	0	VTC	25.0
TO	19000		
NT	1 00E 9	PROCESSING	
CT	11200	SE	0 318
FB	27500	LB	1.000
BS	200	FN	32768
SS	0	MATH	I
QP	Y		
CP	Y	DISPLAY	
IL	N	SP	-5916.4
IN	N	WP	7323.5
DP	N	VS	1000
HS	NN	SC	0
FAD	2 000	WC	25
		IS	100
		RFL	33136.0
		RFP	0
		TH	50
		INS	1 000

Ph₃SnI·DMEU and Ph₃SnI·DMPU

EXP4	PULSE SEQUENCE	S2PUL	
ACQUISITION			
TN	119 000	DN	1.700
SW	50000 0	DO	0
AT	0 320	DM	NNY
NP	32000	DMM	E
PW	10.0	DMF	200
P1	0	DHP	Y
D1	5.000	DLP	20
D2	0	VTC	25 0
TO	-17500		
NT	1.00E 9	PROCESSING	
CT	6977	SE	0.159
PAD	1.000	LB	2.000
FB	27500	FN	32768
BS	50	MATH	I
SS	0		
QP	Y	DISPLAY	
CP	Y	SP	-10072.5
IL	N	WP	12065.8
IN	N	VS	1500
DP	N	SC	0
HS	NN	WC	420
		IS	3142
		RFL	36294.6
		RFP	0
		TH	65
		INS	1.000
		AI	DC

^aInstrument parameters given in this figure are explained in Appendix 1.

^bDue to locking problems encountered, reference compound was put in d₆-acetone as 50% v/v solution instead of d₆-benzene.

Figure 12: ¹¹⁹Sn and ²⁰⁷Pb XL-200 Instrument Parameters used to obtain the Spectra in Figure 11^a.

^{207}Pb nuclei are given in Table 13. The wide ranges of 2000 ppm for tin, and 16000 for lead, enable clearer resolution of peaks compared to the resolution of proton peaks in ^1H nmr where a usual shift range of only 10 ppm is observed. However, these wide ranges encountered for tin and lead can result in large solvent and temperature variations of the chemical shifts, which can thereby mask chemically significant interactions. The wide range of chemical shifts usually observed for metal nuclei arise from a paramagnetic contribution to the shielding. This is absent for hydrogen nuclei and arises for those nuclei which possess valence electrons other than 's' electrons. The shielding of ^{119}Sn and ^{207}Pb nuclei may be divided into three parts (114):

$$\sigma = \sigma_d + \sigma_p + \sigma_n \quad [18]$$

σ_d is the diamagnetic contribution to the shielding;
 σ_n is the contribution arising from the magnetic effects due to electronic circulation from other atoms in the molecule;
 σ_p is the paramagnetic contribution.

σ_d and σ_n are important for protons but may be ignored in metal nuclei nmr because the overall chemical shift range is so large that σ_d and σ_n become negligible. σ_p is given as follows (115):

$$\sigma_p = - \frac{\mu_o e^2 \hbar^2}{6\pi m^2 \Delta E} (\langle r^{-3} \rangle_{np} P_u + \langle r^{-3} \rangle_{md} D_u) \quad [19]$$

ΔE = mean electronic excitation energy;

P_u = electronic imbalance associated with the metal atom's valence 'p' orbitals;

D_u = electronic imbalance associated with the metal atom's valence 'd' orbitals;

np, md = appropriate valence 'p' and 'd' electrons under consideration;

$\langle r^{-3} \rangle_{np}$ = average value of r^{-3} , where r is the separation between the metal nucleus and the valence 'p' electrons;

$\langle r^{-3} \rangle_{md}$ = average value of r^{-3} , where r is the separation between the metal nucleus and the valence 'd' electrons.

ΔE is usually constant for a closely related series of compounds, for a particular metal nucleus. The values of P_u and D_u are zero for the case of spherically symmetrical electron shells, while large values of P_u and D_u correspond to highly imbalanced 'p' and 'd' electron distributions. The values depend on the coordination number, hybridization of atomic orbitals in bonding, and ionicity of the bonds. An increase in electronegativity of a group (e.g. halide) attached to the metal atom will increase P_u , and σ_p will

decrease. The resultant decrease in shielding causes the chemical shift to move to lower field. Any participation of the metal 'd' orbitals in bonding would offset this effect. The 'd' orbitals may be populated in two ways: 1) $(p+d)\pi$ bonding, 2) $(d+d)\pi$ bonding. $(p+d)\pi$ bonding would decrease in a metal-halogen bond over the series $F \rightarrow Cl \rightarrow Br \rightarrow I$ as the 'p' electrons in I are more distant. As the bond distance between the metal atom and halide increases, the overlap integral decreases, i.e., from $F \rightarrow I$. This would result in decreased 'd' orbital participation for compounds containing I relative to analogous compounds containing F, and the latter would be to higher field. The term $\langle r^{-3} \rangle_{md}^{D_u}$ would now no longer be 0, as either the 5d orbitals (of tin) or 6d orbitals (of lead) would now be at least partially occupied. As the term $\langle r^{-3} \rangle_{md}^{D_u}$ becomes larger, the shielding becomes smaller and the chemical shift moves to low field. This rationalizes why a fluoride compound would be to lower field than an analogous iodide compound, using the concept of 'd' orbital participation.

Holecak *et al.* (111) have shown that for ^{119}Sn chemical shifts, 5-coordinate complexes are upfield from those of 4-coordinate complexes. Otera (116) has reported that the ^{119}Sn chemical shift of 5-coordinate chelates such as $\text{Bu}_2\text{SnCl}(\text{oxin})$, (oxin = oxinate), which retain their coordination in solution, appear at lower field than

6-coordinate compounds of the type $\text{Bu}_2\text{Sn}(\text{oxin})_2$. The tin resonance of $\text{Bu}_2\text{SnCl}(\text{oxin})$ appears at -112 ppm, relative to TMT (CHCl_3 solution), and of $\text{Bu}_2\text{Sn}(\text{oxin})_2$ at -262 ppm. Otera *et al.* (117) also studied the ^{119}Sn nmr of some 7-coordinate chelates. They obtained a ^{119}Sn chemical shift value of -561 ppm for $\text{BuSn}(\text{oxin})_3$. Cox (118) has shown that ^{207}Pb chemical shifts of 4-coordinate lead complexes such as Me_3PbCl in CHCl_3 , increase dramatically when placed in highly coordinating solvents such as HMPA. Thus, by comparing the observed chemical shifts with published data, structural information may be obtained in a similar way to proton information from ^1H nmr.

When comparing ^{119}Sn or ^{207}Pb chemical shifts of similar complexes, it is important to measure the tin or lead nmr spectra under identical conditions, *i.e.* the concentration, temperature and solvent should remain the same. Hunter and Reeves (119) have shown that the ^{119}Sn chemical shifts of Me_3SnCl and Me_3SnBr in non-coordinating solvents such as CCl_4 , C_6H_6 and CHCl_3 varied by less than 5 ppm. $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$ and $\text{Ph}_3\text{SnI} \cdot \text{DMPU}$ had their ^{119}Sn spectra measured in C_6H_6 (Table 14) and the chemical shift values differed by only 5 ppm in each case from the values in CH_2Cl_2 . Lack of large changes in chemical shift is indicative that no complexing is occurring between the compound and the solvent and also that no association between discrete Me_3SnX molecules is

occurring. Polar coordinating solvents such as DMSO, HMPA, DMEU or DMPU, can produce large variations in both ^{119}Sn and ^{207}Pb chemical shifts of compounds such as Me_3SnCl or Me_3PbCl .

Both the ^{119}Sn and ^{207}Pb chemical shifts obtained in this work were to high field of the reference compound. This is inconsistent with the greater electron withdrawing capability of the phenyl group relative to alkyl groups such as methyl. It is possible that overlap of the metal 5d or 6d orbitals with the π -orbitals of the phenyl groups occurs, to give an excited state of low energy, so reducing E in equation [19] as was suggested by Davies *et al.* (120) for $\text{Ph}_{4-n}\text{SnCl}_n$ compounds. However, they pointed out that this would shift the ^{119}Sn resonance to low field, opposite to what would be expected. They suggested that the high field chemical shifts observed for phenyltin compounds are due to an increase in $p\pi \rightarrow p\pi$ bonding between chlorine and tin by a synergic process, although they did point out that this could not account for the high field chemical shift observed for Ph_4Sn .

The chemical shifts obtained for the parent triphenyltin halides, (Table 14), showed the expected trend. The ^{119}Sn chemical shift change toward lower field correlates with the increase in electronegativity from I to Cl. This is consistent with removal of electron density from the central tin atom. A similar trend in the analogous lead compounds (Table 15) exists with the overall chemical shift range larger. The two pairs of adducts, $\text{Ph}_3\text{SnX} \cdot \text{DMEU}$ ($\text{X} = \text{Cl}, \text{Br}$) and $\text{Ph}_3\text{SnX} \cdot \text{DMPU}$ ($\text{X} = \text{Cl},$

Br), have very similar ^{119}Sn chemical shift values (Table 14). This might be due to similar species being present, for example:

Ionization is less likely for $\text{X} = \text{Cl}$ and Br than for $\text{X} = \text{I}$ because of the weaker Sn-I bond. Moreover, for both $\text{Ph}_3\text{SnI}\cdot\text{DMEU}$ and $\text{Ph}_3\text{SnI}\cdot\text{DMPU}$, the ^{119}Sn chemical shifts are to higher field by 20 ppm. Conductivity measurements are necessary to determine whether or not ionization occurs.

As solution ir results had suggested (Section 3.2), complexes 1 to 12 are thought to be highly dissociated in dilute solution, with both free and complexed ligand observed. From this, it can be inferred that in CH_2Cl_2 solution, both parent halide and complexed species should be present in equilibrium, as indicated in equation [14]. As only one sharp peak was observed in all ^{119}Sn and ^{207}Pb spectra, this equilibrium must be fast on the nmr time scale. The chemical shift of the observed peak in all spectra should be to higher field of the chemical shift of the parent halide, but to lower field of the fully complexed adduct, i.e., a weighted average of the individual species. The ^{119}Sn resonances of Ph_3SnCl and Ph_3SnBr , in neat DMPU were -225 and -230 ppm, respectively. The peaks appeared broad, probably due to the high viscosity of the solvent. An equilibrium of the type given in equation [14], for complexes 1 to 12 in CH_2Cl_2 solution, should favor the adduct in neat ligand and the chemical shifts should reflect

the complexed species. It should be possible to estimate the degree of dissociation for the complexes $\text{Ph}_3\text{SnCl}\cdot\text{DMPU}$ and $\text{Ph}_3\text{SnBr}\cdot\text{DMPU}$ using the above chemical shifts of the parent halides in neat ligand and the results in Table 14 (121):

$$\nu = \nu_A P_A + \nu_B P_B \quad [21]$$

ν_A = chemical shift (ppm) of Ph_3SnX ($\text{X} = \text{Cl}, \text{Br}$);

ν_B = chemical shift (ppm) of $\text{Ph}_3\text{SnX}\cdot\text{DMPU}$ ($\text{X} = \text{Cl}, \text{Br}$);

P_A = mole fraction of Ph_3SnX ($\text{X} = \text{Cl}, \text{Br}$);

P_B = mole fraction of $\text{Ph}_3\text{SnX}\cdot\text{DMPU}$ ($\text{X} = \text{Cl}, \text{Br}$).

In the case of $\text{Ph}_3\text{SnCl}\cdot\text{DMPU}$, the extent of dissociation was calculated as 66% for a 0.25 M solution at 20°C. $\text{Ph}_3\text{SnBr}\cdot\text{DMPU}$ gave a percent dissociation of 74% for the same concentration and temperature. It should be emphasized that in these calculations it is assumed that the species at -225 and -230 ppm are 100% $\text{Ph}_3\text{SnCl}\cdot\text{DMPU}$ and $\text{Ph}_3\text{SnBr}\cdot\text{DMPU}$, respectively. DMPU is an ionizing solvent and could lead to the production of the $\text{Ph}_3\text{SnDMPU}^+$ ion. The fact that similar ^{119}Sn chemical shifts were obtained for Ph_3SnCl and Ph_3SnBr in neat DMPU, suggests ionization has occurred. However, the ^{119}Sn shift is at rather high field for a 4-coordinate tin compound (Table 14), especially one

which carries a positive charge. (This would tend to contract the valence electron cloud, reducing the separation between the metal nucleus and the valence electrons, r , in equation [19]). A 4-coordinate, positively charged, tin complex might be expected to have a ^{119}Sn chemical shift to lower field than that of a 4-coordinate neutral complex, although there is no literature precedence for this. Conductivity studies are necessary in cases such as this to confirm or disprove the existence of ionic species.

Assuming equilibrium conditions, equilibrium constants may be obtained for the complexes $\text{Ph}_3\text{SnX} \cdot \text{DMPU}$ ($\text{X} = \text{Cl}, \text{Br}$):

$$K = \frac{\alpha^2 C}{1 - \alpha} \quad \begin{array}{l} \alpha = \text{degree of dissociation} \\ C = \text{concentration (mole l}^{-1}\text{)} = 0.25 \end{array} \quad [22]$$

For the complex $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$, $K = 0.32$ and for the complex $\text{Ph}_3\text{SnBr} \cdot \text{DMPU}$, $K = 0.53$.

The presence of an equilibrium in solution of complexes 1 to 12 gives rise to one peak in the ^{119}Sn and ^{207}Pb spectra of all adducts. It should theoretically be possible to slow down the fast exchange that is indicated by the single peak. Two peaks should be obtained as the temperature is lowered, giving the chemical shift of the parent halide and complexed species. In an attempt to observe these chemical shifts, the ^{119}Sn nmr spectra of

$\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$, $\text{Ph}_3\text{SnBr} \cdot \text{DMPU}$ and $\text{Ph}_3\text{SnI} \cdot \text{DMPU}$ were recorded in the temperature range of 20 to -80°C : the results are given in Table 16.

TABLE 16: LOW TEMPERATURE $\delta(^{119}\text{Sn})$ VALUES OF SOME ADDUCTS
 $\text{Ph}_3\text{SnX} \cdot \text{DMPU}$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$)^a.

COMPLEX	TEMPERATURE ($^\circ\text{C}$)	$\delta(^{119}\text{Sn})$
$\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$	20	-108
	-20	-174
	-50	-207
	-80	-227
$\text{Ph}_3\text{SnBr} \cdot \text{DMPU}$	20	-105
	-10	-157
	-20	-175
	-30	-190
	-50	-216
	-80	-239
$\text{Ph}_3\text{SnI} \cdot \text{DMPU}$	20	-128
	-20	-164
	-50	-207
	-80	-235

^aMeasured in ppm, referenced to 50% v/v TMT in d_6 -acetone, for 0.25 M solutions at 20°C .

As the temperature was lowered, the chemical shifts moved to high field. This is reasonable if an equilibrium exists, as suggested earlier. By lowering the temperature, more complexed material exists in solution. On no occasion was more than one peak observed. Interestingly, in the case of $\text{Ph}_3\text{SnCl} \cdot \text{DMPU}$ and $\text{Ph}_3\text{SnBr} \cdot \text{DMPU}$, at -80°C , the chemical shifts observed, -227 and -239 ppm, respectively, are to higher field of the values given earlier for Ph_3SnCl and Ph_3SnBr in neat DMPU, -225 and -230 ppm, respectively. Low temperature studies were not done on any of the lead complexes as these were thought less likely to remain in solution as the temperature was lowered.

The parent triphenyltin halides and Ph_3PbI are unassociated and should thus have their ^{119}Sn and ^{207}Pb chemical shifts remain invariant to temperature changes in solvents such as CH_2Cl_2 . Compounds such as Ph_3PbCl and Ph_3PbBr , however, are known to be 5-coordinate, polymeric structures in the solid state (48). The results of ^{207}Pb nmr measurements on a saturated solution (< 0.25 M) of Ph_3PbBr at several temperatures are given in Table 17.

It is assumed that the chemical shift value of the reference itself, TEL, remains constant regardless of temperature. Ph_3PbBr shows an increase in the ^{207}Pb chemical shift as the temperature is lowered. Temperature changes have been shown to affect the shielding through variations

TABLE 17: $\delta(^{207}\text{Pb})$ VALUES FOR Ph_3PbBr AT VARIOUS TEMPERATURES^a.

TEMPERATURE ($^{\circ}\text{C}$)	$\delta(^{207}\text{Pb})$ (ppm)
20	-74
-20	-76
-30	-76
-40	-77
-60	-78
-70	-84
-80	-91

^aReference compound 50% v/v TEL in d_6 -acetone.

in the mean electronic excitation energy (ΔE) in equation [19] (123), although this was for cobalt. Temperature variations should not affect ΔE in metals such as lead, and there are no other terms in equation [19] that are temperature dependent. The most probable explanation for the variation in chemical shift observed for Ph_3PbBr at lower temperatures is an increase in the amount of polymeric species present in solution. The chemical shift remains approximately constant over the range 20°C to -60°C . In solution, the possibility exists of monomers, dimers, trimers and polymers, all being in equilibrium, and it may be that at temperatures below -70°C polymeric species become prevalent with a

corresponding shift to high field of the ^{207}Pb resonance.

In both Tables 14 and 15 it is evident that ^{119}Sn and ^{207}Pb chemical shifts of the DMPU adducts are to higher field than those of the DMEU adducts which in turn are to higher field than those of the parent halides. One very important exception to this general trend is the compound Ph_3PbCl , and the complexes $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$ and $2\text{Ph}_3\text{PbCl}\cdot \text{DMPU}$, the ^{207}Pb chemical shifts of which are -42, -144 and -124 ppm, respectively. Since Ph_3PbCl is 5-coordinate and polymeric in the solid state (48), it might be thought that -42 ppm is to low field for a 5-coordinate species. However, it is not clear whether the structure of Ph_3PbCl remains intact in solution. It is possible that it breaks down in solution at low concentrations, and this may well be reflected in the ^{207}Pb chemical shift value of -42 ppm. The peak at -144 ppm in the ^{207}Pb nmr spectrum of a saturated solution of $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$ is to higher field than that given by a saturated solution of $2\text{Ph}_3\text{PbCl}\cdot \text{DMPU}$ (-124 ppm). This is confirmation of a higher average coordination number around each lead in the DMEU than in the DMPU system. One possible structure for $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$, assuming ionic species are not present, in the solid phase is:

This would mean one lead nucleus is 6-coordinate and two are 5-coordinate. The possible equilibria that might occur in solution for the above are numerous. However, the presence of a 6-coordinate lead atom might cause the single peak observed (which is really an average of all the lead nuclei) to move to high field relative to the complex $2\text{Ph}_3\text{PbCl}\cdot\text{DMPU}$, the structure of which might be:

In this case, both lead atoms are 5-coordinate, and despite the presence of the larger ligand on one lead atom, may well give rise to a single peak to lower field than that observed for $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$.

The ^{119}Sn and ^{207}Pb chemical shifts observed for $\text{Ph}_3\text{MI}\cdot\text{L}$ where $\text{M} = \text{Sn}$ and Pb , and $\text{L} = \text{DMEU}$ and DMPU , are similar to the parent iodides. This suggests that the iodides are highly dissociated. This is particularly true for $\text{Ph}_3\text{PbI}\cdot\text{DMEU}$ and $\text{Ph}_3\text{PbI}\cdot\text{DMPU}$ which have almost identical ^{207}Pb chemical shifts of -196 and -201 ppm, respectively, almost the same as the chemical shift of Ph_3PbI , -195 ppm.

Measured coupling constants included $^1J(^{119}\text{Sn}-^{13}\text{C}) = 574.8$ and 578.3 Hz for the complexes $\text{Ph}_3\text{SnI}\cdot\text{DMEU}$ and $\text{Ph}_3\text{SnI}\cdot\text{DMPU}$, respectively. The ^{13}C satellites of the former may be seen in Figure 13. Coupling constants are in the same range as those obtained by Holecek *et al.* (111) for Ph_3SnCl (614.3 Hz), Ph_3SnBr (595.0 Hz) and Ph_3SnI (567.6 Hz). The $^1J(^{119}\text{Sn}-^{13}\text{C})$ values for $\text{Ph}_3\text{SnI}\cdot\text{DMEU}$ and $\text{Ph}_3\text{SnI}\cdot\text{DMPU}$ correspond to those of 4-coordinate species, confirming the iodides to be the most dissociated in solution.

The complexes $\text{Ph}_3\text{PbI}\cdot\text{DMEU}$ and $\text{Ph}_3\text{PbI}\cdot\text{DMPU}$, also largely dissociated, did not yield any $^1J(^{207}\text{Pb}-^{13}\text{C})$ coupling constants. This may have been due to the increased noise hiding the weak ^{13}C satellites, the lead complexes being more insoluble than the analogous tin ones.

Holecek *et al.* (111) obtained a large number of coupling constants $^nJ(^{119}\text{Sn}-^{13}\text{C})$ where $n = 1, 2, 3$ and 4 for a variety of 4- and 5-coordinate tin compounds including the series $\text{Ph}_3\text{SnCl}\cdot\text{DMSO}$, $\text{Ph}_3\text{SnBr}\cdot\text{DMSO}$ and $\text{Ph}_3\text{SnI}\cdot\text{DMSO}$. $^1J(^{119}\text{Sn}-^{13}\text{C})$ coupling constants, obtained from the ^{119}Sn satellites in the ^{13}C spectra, were 810.6 , 793.0 and 775.4 Hz, respectively (111). Coupling constants $^1J(^{119}\text{Sn}-^{13}\text{C})$ for 4-coordinate compounds were in the range 550 - 660 Hz, and for 5-coordinate compounds in the range 750 - 850 Hz (111).

Couplings may involve a number of mechanisms (122):

- 1) Interaction between magnetic moments due to nuclear spin

Figure 13: ${}^{119}\text{Sn}$ Spectrum of $\text{Ph}_3\text{SnI} \cdot \text{DMEU}$ showing ${}^{13}\text{C}$ Satellites.

and electron orbital motion; 2) Dipolar interaction between electron and nuclear spins; 3) An interaction between the nuclear magnetic moment and the electron spins in 's' orbitals, as the electron wave function is not zero here. The last mechanism is known as the "fermi Contact Term", and it accounts for the possibility that the electron may be in the same region of space as the nucleus. It is generally thought to be the dominant term for coupling in neighboring atoms joined by a single bond (122).

The coupling constant across a single bond is related to the 's' character of the bond between the two coupled nuclei, and thereby to the type of hybridization (122). When considering the contact term, only atoms with 's' orbitals have electron density at the nucleus. Hence, only contributions from the valence atomic 's' orbitals need be considered (122):

$$J_{jk} \propto \frac{\gamma_j \gamma_k \alpha_j^2 \alpha_k^2 \langle S_j / \delta(r_j) / S_j \quad S_k / \delta(r_k) / S_k \rangle}{\Delta E} \quad [23]$$

j and k are two directly coupled nuclei;

γ_j and γ_k are the magnetogyric ratios of j and k;

S_j and S_k are the valence shell 's' functions for j and k, respectively;

$\langle S_j / \delta(r_j) / S_j \rangle$ is the 's' electron density at nucleus j;

$\langle S_k / \delta(r_k) / S_k \rangle$ is the 's' electron density at nucleus k;
 α_j^2 and α_k^2 are the 's' characters of the hybrid orbitals used
 by j and k in the j-k bond;
 ΔE is the energy of excitation from the bonding to the anti-
 bonding j, k molecular orbital.

Provided neither j nor k have a lone electron pair,
 the 1J values are directly proportional to the 's' character
 of their hybrid orbitals. Equation [23] suggests that 1J
 is always positive, although negative coupling constants
 are known. Changes in electronegativity of substituents
 might affect 's' electron density at a tin/lead atom in any
 of the 4-coordinate parent halides in a number of ways.
 Assuming the initial hybridization of the central metal atoms
 is 'sp³', the hybridization of the metal atom (α)² used in
 various bonds may be affected. Electronegative substituents
 (e.g. halides) prefer to make use of metal orbitals having
 'p' character since the electron density will be furthest
 from the metal nucleus than if it were in an 's' orbital.
 This will, of course, result in an increase in the 's'
 character to the remaining substituents on the metal (the
 three phenyl groups), and the coupling constants $^1J(^{119}\text{Sn}/$
 $^{207}\text{Pb}-^{13}\text{C})$ will, therefore, increase. Another way change in
 electronegativity of the substituents can affect 's' electron
 at a metal atom is by bond polarization. Reduced electron

density around the metal will increase the effective nuclear charge on the metal nucleus so that the radial distribution is modified and the metal electron cloud contracts; electron density is then drawn further into the nucleus and the terms $\langle 5S_{\text{Sn}}/\delta(r_{\text{Sn}})/5S_{\text{Sn}} \rangle$ (for tin) or $\langle 6S_{\text{Pb}}/\delta(r_{\text{Pb}})/6S_{\text{Pb}} \rangle$ (for lead) will increase if α^2 remains constant. Coupling constants, $^1J(^{119}\text{Sn}/^{207}\text{Pb}-^{13}\text{C})$, will increase in this case.

Although the bonding in tetrahedral Ph_3MX compounds may be interpreted in terms of four hybrid ' sp^3 ' orbitals, for the 5-coordinate complexes, it is necessary to use the "three-centre orbital" model (124) if d-orbital participation is to be avoided. Such molecular orbitals based on a combination of p or atomic orbitals have been invoked to interpret the coordination bonding (28,125) in 5-coordinate tin complexes, such as:

C = CARBON ATOM OF PHENYL RING

X = HALIDE

D = DONOR ATOM

Okawara and Wada (123) suggested that the use of the tin 'd' orbitals is unlikely. The tin atom may possess an

appreciable energy separation between the 'p' and 'd' orbitals. In addition to this, for compounds which do not possess a number of highly electronegative substituents, the 'd' orbitals may be rather diffuse. They suggested that for the above trigonal bipyramidal structures, the three Sn-C bonds may be represented as essentially 'sp²' hybridized. The remaining 'p' orbital could then participate in a linear 3-centre bond:

Since the tin orbitals bonded to the 3 carbon atoms are 'sp²' hybridized, they have a higher degree of 's' character than in 4-coordinate 'sp³' hybridized compounds, accounting for the increase observed by Holecek *et al.* (111) in $^1J(^{119}\text{Sn}-^{13}\text{C})$ of the 5-coordinate complexes $\text{Ph}_3\text{SnX} \cdot \text{DMSO}$, $\text{X} = \text{Cl}, \text{Br}$ and I , over the 4-coordinate compounds Ph_3SnX .

SECTION 4SUMMARY

A series of complexes $\text{Ph}_3\text{MX}\cdot\text{L}$ have been prepared where $\text{M} = \text{Sn}$ and Pb , $\text{X} = \text{Cl}$, Br and I , $\text{L} = \text{DMEU}$ and DMPU , by direct reaction of excess liquid ligand with the parent halides Ph_3MX in toluene. All adducts were air stable, crystalline solids, soluble in such solvents as dichloromethane and chloroform, but insoluble in pentane. Ten of the twelve complexes had elemental analyses corresponding to 1:1 molecular adducts. The two exceptions were $3\text{Ph}_3\text{PbCl}\cdot 2\text{DMEU}$ and $2\text{Ph}_3\text{PbCl}\cdot \text{DMPU}$, with stoichiometries as indicated. These complexes decomposed, as did $\text{Ph}_3\text{PbI}\cdot\text{DMEU}$, on gentle heating. The remaining adducts melted sharply.

Infrared and Raman spectra of the solid adducts, $\text{Ph}_3\text{MX}\cdot\text{L}$, were measured and assignments made for $\nu(\text{CO})$ and $\nu(\text{CN})$. For both ligands DMEU and DMPU , the coordination atom was the carbonyl oxygen, as evident from the decrease in the $\nu(\text{CO})$ frequency of the complexes relative to that of the free ligands. Skeletal frequencies have been reported and they aid in the characterization of the complexes. Infrared measurements indicated the adducts are highly dissociated in dichloromethane solution. In all solution ir spectra, two $\nu(\text{CO})$ frequencies occurred, one corresponding to the $\nu(\text{CO})$ of the free ligand, and one corresponding to

the $\nu(\text{CO})$ of the complexed ligand.

Complexes were characterized by ^1H and ^{119}Sn or ^{207}Pb magnetic resonance spectroscopy. The results suggested the complexes are in equilibrium with the parent halides, as only one set of peaks was observed in both proton and metal nuclei nmr, suggesting the exchange is fast on the nmr time scale. Chemical shifts $\delta(^{119}\text{Sn})$ and $\delta(^{207}\text{Pb})$ depend to a great extent on the coordination number of the tin or lead atom. The ^{119}Sn chemical shifts of the 4-coordinate tin compounds were in the range -48 to -113 ppm relative to TMT, whilst the ^{207}Pb chemical shifts of the 4-coordinate lead compounds were in the range -48 to -113 ppm referenced to TEL. ^{119}Sn chemical shifts of the prepared complexes were in the range -85 to -128 ppm, and ^{207}Pb chemical shifts in the range -144 to -201 ppm. These shifts were generally to higher field than those of the parent halides, although this depended on the extent of the dissociation. The iodides were the most dissociated and both ^{119}Sn and ^{207}Pb chemical shifts of $\text{Ph}_3\text{SnI}\cdot\text{L}$ and $\text{Ph}_3\text{PbI}\cdot\text{L}$, respectively, reflected this. The tin chemical shifts were to low field of the range given by Otera (116) for 5-coordinate complexes which, being chelates, remain intact in solution.

The complexes $\text{Ph}_3\text{SnX}\cdot\text{L}$ ($\text{X} = \text{Cl}, \text{Br}$ and I) and $\text{Ph}_3\text{PbX}\cdot\text{L}$ ($\text{X} = \text{Br}, \text{I}$) had elemental analyses corresponding to

1:1 molecular adducts. The sharp melting points confirmed the presence of molecular species. For the 1:1 adducts in the solid state, the structure is most likely trigonal bipyramidal:

X = HALIDE

M = Sn/Pb

L = DONOR LIGAND

Infrared and Raman spectra were consistent with this structure.

In the case of Ph_3PbCl adducts, elemental analyses for carbon, hydrogen and nitrogen gave stoichiometries of $3\text{Ph}_3\text{PbCl} \cdot 2\text{DMEU}$ and $2\text{Ph}_3\text{PbCl} \cdot \text{DMPU}$. The $\nu(\text{CO})$ frequency in the solid state ir spectra indicated terminal carbonyls as opposed to bridging ones. Assuming the complexes are neutral and not ionic, the following structures were postulated. However, with no X-ray crystal data, they could not be confirmed:

L = DMEU

APPENDIX 1: LIST OF XL-200 INSTRUMENT PARAMETERS

TN	<u>Transmitter nucleus.</u> This refers to the observed nucleus.
SW	<u>Sweep width.</u> This is the range in hertz where spectral lines may be observed.
AT	<u>Acquisition time.</u> Measured in seconds, this parameter refers to the length of time data is acquired during the pulse sequence.
NP	<u>Number of data points.</u> $NP = 2 \cdot SW \cdot AT$.
PW	<u>Pulse width.</u> This is the width of the transmitter observe pulse. It is measured in microseconds.
P ₁	<u>Perturbing pulse.</u> Used to modify the spin system before P _w .
D ₁ , D ₂	<u>Delay times.</u> Measured in seconds between pulses.
TO	<u>Transmitter offset.</u> Measured in hertz. When added to the transmitter base offset gives the exact frequency of the observe transmitter.
NT	<u>Number of transients.</u> (Scans) required.
CT	<u>Number of completed transients</u> before the acquisition was stopped.
FB	<u>Filter bandwidth.</u> It is automatically set to a value of 10% greater than SW/2 in quadrature phase detection.
BS	<u>Block size.</u> This refers to the number of transients to be processed before transfer of data to the disc. The spectrum observed is thus updated every block size.
SS	<u>Steady state.</u> This refers to the dummy transients that occur before an acquisition block.
QP	<u>Quadrature phase detection</u> exists when the flag is set to Y (for yes).
CP	<u>CAPS flag.</u> Computer Alternating Pulse Sequence. When this is set to Y, removes unwanted transient phenomena from the FID.

- IL Interleave. This indicates whether array cycling occurs in a multifid experiment.
- IN Interlock. If this is set to some value, the acquisition is aborted if the nmr lock level falls below the present value.
- DP Double precision. If this is set to N (no), single precision (16-bit word) is used for time averaging and if the Y (yes), double precision (32-bit word) is used.
- HS Homospoil. This refers to the homospoil pulse. It is activated for 8 ms at the start of D2 when it is included in the pulse sequence.
- PAD PreAcquisition delay. This refers to a delay prior to the beginning of the pulse sequence. It is often used to establish sample equilibrium in a variable temperature experiment.
- DN Decoupler nucleus. This determines the appropriate base offset for the decoupler offset synthesizer.
- DO Decoupler offset. This is in Hz and when added to the DBO (decoupler base offset), gives the exact frequency of the decouple transmitter.
- DM Decoupler mode. This controls the gating of the decoupler during a pulse sequence and was shown in the 2-pulse sequence given earlier as regions 1, 2 and 3. Y denotes the times the decoupler is on and N the times it is off. The gating sequence where the decoupler is only on during the acquisition time is entered as 'NNY' whereas if full decoupling conditions are required, the sequence is 'YYY'.
- DMM Decoupler modulation mode. This switches the modulation mode of the decoupler as follows:
 C = continuous wave
 S = square wave
 N = noise modulation
 E = external.
- DMF Decoupler modulation frequency. This sets the modulation frequency of the decoupler for the square wave and noise modulation modes.
- DHP Decoupler high power. This may be set to Y, in which case the decoupler is in the high power mode, or N when the decoupler is in the low power mode.

DLP Decoupler low power. This may be given a numerical value and becomes significant when DHP is set to N.

VTC Variable temperature cutoff. This is the temperature below which the liquid N₂ bucket is selected.

SE Sensitivity enhancement. This is an exponential time constant (measured in seconds). It is an exponential multiplier ($\exp-t/SE$) used to process the FID data after a WT (weight) command.

LB $LB = 1/(\pi SE).$ May be used instead of SE.

FN Fourier number. This determines the number of data points to be Fourier transformed. Permitted values are 2^n between 128 and 32,768. When FN is entered as 'N', then it will set automatically to the smallest permitted value greater than NP.

MATH Processing mathematics. When this is set to I, integer mathematics is used in the Fourier transform. If set to F, floating point transform is done.

SP Start of plot. This is given in hertz.

WP Width of plot. This is given in hertz.

VS Vertical scale.

SC Start of chart. This determines the start of the spectral display and plot.

WC Width of chart. This gives the width of the spectral display and plot.

IS Integral scale. This refers to the amplitude of the integral.

RFL Reference line. This is given in hertz and refers to the position of the reference line relative to the high field end of the data table.

RFP Reference position. This is the shift value in hertz (or ppm) assigned to a reference.

TH Threshold. This sets the minimum peak amplitude for the peak frequency printout routine.

INS Integral normalizing scale. This is used to allow normalizing of the integral printout to a convenient number.

Ph₃PbI · DMEU

^aThe peak positions given on the spectra were calibrated using standard polystyrene and may not correspond exactly to the scale.

Ph₃SnBr-DMPU

154

5×10^3 cps

10×10^3 cps

10×10^3 cps

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