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Tin-119 NMR Studies on Diorganoyltin(IV)dihalides and Triorganoyltin(IV)halides; Formation and Stereochemistry of Adducts

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Abstract

The reactions of R_2SnX_2 (R = Ph, Me; X = Cl, Br) with excess halide, tributylphosphine, tricyclohexylphosphine and tributylphosphine oxide have been investigated in dichloromethane solution by tin-119 and phosphorus-31 NMR techniques. R_2SnX_2 form five coordinate 1:1 adducts with halide and phosphine (phos) ligands whilst both 1:1 and 1:2 adducts are formed with tributylphosphine oxide (L). Tin-119 spectra imply that Ph_2SnX_2(phos) has the phosphine in the equatorial position of a trigonal bipyramid. At low temperature there is evidence for a slow intramolecular twist mechanism between octahedral isomers of $Ph_2SnCl_2L_2$. The stereochemistry of the complexes $Ph_2SnX_2L_2$ differ between chloro and bromo compounds and no mixed halide complex is observed. In the case of the bromo system only, the 1:3 adduct $[Ph_2SnBrL_3]^+Br^-$ is formed. Ph_3SnCl does not react with phosphines but it does give 1:1 adducts with Cl^-, L and pyridine. All the adducts have similar tin-119 chemical shifts which is consistent with the phenyl groups being equatorial in the five coordinate trigonal bipyramidal adducts. Ph_4Sn does not form adducts with X^-, L or phosphine.

Introduction

There have been numerous studies on the adduct formation by R_2SnX_2 and R_3SnX complexes with a variety of oxygen donor ligands but rather few studies using halide and phosphine as the Lewis base. R_2SnX_2 generally form both 1:1 and 1:2 adducts with monodentate donors such as Ph_3PO and dimethylsulphoxide and infrared and Mössbauer studies on the solids suggest five coordinate (trigonal bipyramidal) and octahedral structures respectively [1–5]. The five coordinate structure has been confirmed for $Me_3SnCl\cdot py$ by X-ray diffraction [6] which shows the organo-groups occupying the equatorial positions. More recently tin-119 NMR studies have been reported for a few systems which are relevant to this work. Ph_2SnCl_2 and Ph_3PO give a labile system in which only exchange average signals were observed [7], but with $(octyl)_3PO$ both 1:1 and 1:2 adducts were observed at low temperature [8]. Other reports of tin-119 NMR spectra of Bu_2SnCl_2, Bu_3SnX and Ph_3SnX adducts have appeared [9–11].

In previous papers in this series we have systematically examined the adducts of SnX_4 [12, 13] and $PhSnX_3$ [14] with halide, tributylphosphine oxide (L) and tributylphosphine. A feature of these systems is the labile halogen exchange leading to mixed halide species in solution which have been shown to provide considerable stereochemical information. In this paper similar data are presented for R_2SnX_2 and R_3SnX systems.

Results

Diorganoyltin(IV)dihalides

Each of the diorganoyltin(IV)dihalides gives rise to a sharp tin-119 NMR resonance at room temperature. Dichloromethane solutions containing equimolar mixtures of Ph_2SnCl_2 and Ph_2SnBr_2 give three resonances at room temperature which are due to the starting materials and the mixed halide species $Ph_2SnClBr$ (Table I). A similar mixture involving Me_2SnCl_2 and Me_2SnBr_2 requires cooling to −100 °C before halide exchange is slowed sufficiently to allow observation of all three species. Thus, in both systems the halides are labile on the preparative time scale but the methyl compounds require lower temperature than the phenyl compounds to slow the intermolecular exchange on the NMR time scale. Equimolar mixtures of Me_2SnCl_2 and Ph_2SnCl_2 or Me_2SnBr_2 and Ph_2SnBr_2 in each case show tin-119 resonances due only to the starting materials which indicates that organo group exchange is slow even on the preparative time scale.

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TABLE I. Tin-119 NMR Data for R_2SnX_2 and $[R_2SnX_3]^-$ Systems in Dichloromethane Solution at 30 °C

Compound	$\delta(^{119}Sn)$	Compound	$\delta(^{119}Sn)$	Compound	$\delta(^{119}Sn)$
Ph_2SnCl_2	−33	Me_2SnCl_2	137	Bu_2SnCl_2	126
$PhSnClBr^a$	−52	$Me_2SnClBr^b$	106		
Ph_2SnBr_2	−75	Me_2SnBr_2	72	Bu_2SnBr_2	93
$[Ph_2SnCl_3]^{-c}$	−258	$[Me_2SnCl_3]^{-d}$	−125	$[Bu_2SnCl_3]^-$	−113
$[Ph_2SnBr_3]^{-e}$	−293	$[Me_2SnBr_3]^-$	−148	$[Bu_2SnBr_3]^-$	−108

[a] Observed in a 1:1 mixture of Ph_2SnCl_2 and Ph_2SnBr_2. [b] Observed in a 1:1 mixture of Me_2SnCl_2 and Me_2SnBr_2 at −100 °C. [c] Chloride as $[Ph_4CH_2P]Cl$. [d] Bromide as $[Bu_4N]Br$. [e] $w_{1/2}$ 300 Hz at 30 °C. At −50 °C −302 ppm, $w_{1/2}$ 20 Hz.

Addition of one mole equivalent of halide ion to R_2SnX_2 compounds (R = Ph, Me; X = Cl, Br) results in a significant change in the position of the tin-119 resonance consistent with the formation of the five coordinate species $[R_2SnX_3]^-$ (Table I). The tin-119 spectrum of an equimolar mixture of $[Ph_2SnCl_3]^-$ and $[Ph_2SnBr_3]^-$ is a single resonance over the temperature range 30 to −110 °C indicating that halide exchange is fast on the NMR time scale. This rapid halide exchange is further demonstrated by addition of a mole equivalent of bromide ion to a solution of Ph_2SnCl_2 at room temperature which results in a single resonance (−276 ppm) at a position intermediate between the values for $[Ph_2SnCl_3]^-$ and $[Ph_2SnBr_3]^-$ and close to the calculated weighted exchange average position. Additions of further quantities of halide to solutions of $[R_2SnX_3]^-$ do not cause any further significant change in the position of the tin-119 resonances, implying that in solution, $[R_2SnX_3]^-$ species do not have sufficient Lewis acidity to allow expansion of the tin coordination from five to six with excess halide. In the solid state, however, six coordinate $[R_2SnX_4]^{2-}$ anions have been characterised [4]. Mixtures of $[Me_2SnX_3]^-$ and $[Ph_2SnX_3]^-$ show no evidence for R group exchange.

Diphenyltin(IV)dihalides Ph_2SnX_2 react with one mole of each of the phosphines tributylphosphine, PBu_3, and tricyclohexylphosphine, $Pcycl_3$, to give 1:1 adducts in dichloromethane solution. The adducts with PBu_3 require cooling to −30 °C before J(Sn–P) coupling is established, whereas J(Sn–P) is observed for the $Pcycl_3$ adducts at room temperature. For both types of phosphine adducts, the chemical shifts of the tin-119 doublets are similar to those of the singlets for $[Ph_2SnX_3]^-$ complexes. For each series of phosphine complex, the tin-119 chemical shifts of the dichloro and dibromo complexes differ by only a few ppm (Table II). That the 1:1 adducts are five coordinate is verified by the tin-119 spectra of mixtures of Ph_2SnCl_2, Ph_2SnBr_2 and either PBu_3 or $Pcycl_3$ (1:1:2) which show three doublets of total relative intensities approximately 1:2:1, corresponding to the adducts $Ph_2SnCl_2(phos)$, $Ph_2SnBrCl(phos)$ and $Ph_2SnBr_2(phos)$. If the adducts were in fact dimeric octahedral species, with halogen bridges, the mixture could be expected to give a more complex spectrum at low temperature. Cooling to −100 °C does not cause the signal of the mixed halide complex to split into two signals. The significance of these observations will be discussed later.

TABLE II. Tin-119 and Phosphorus-31 NMR Data for Adduct Formation of R_2SnX_2 with PBu_3 and $Pcycl_3$ in Dichloromethane Solution

Compound	$\delta(^{31}P)$	$\delta(^{119}Sn)$	$^2J(^{119}Sn-P)$	Temperature (°C)
$Ph_2SnCl_2PBu_3$	12.7	−282d	840	−30
$Ph_2SnBr_2PBu_3$	10.3	−289d	705	−30
$Ph_2SnClBrPBu_3$	11.6	−284d	775	−30
$Me_2SnCl_2PBu_3$	3.1	−172d	510	−40
$Me_2SnBr_2PBu_3$	−3.8	−186d	360	−40
$Bu_2SnCl_2PBu_3$	4.3	−185d	220	−80
$Bu_2SnBr_2PBu_3$	−1.1	−177d	55	−80
$Bu_2SnBrClPBu_3$	2.1	−179d	125	−80
$Ph_2SnCl_2Pcycl_3$	29.8	−283d	735	−100
$Ph_2SnBr_2Pcycl_3$	27.0	−276d	610	−100
$Ph_2SnClBrPcycl_3$	28.7	−277d	675	−100
$Me_2SnCl_2Pcycl_3$	17.4	−170d	385	−100
$Me_2SnBr_2Pcycl_3$	10.4	−180d	240	−100
$Me_2SnClBrPcycl_3$	14.0	−174d	310	−100

Addition of further quantities of PBu_3 to the 1:1 adduct of that phosphine induced exchange resulting in loss of J(Sn–P) coupling which could not be re-established within the accessible temperature range.

Dimethyltin(IV)dihalides Me_2SnX_2 also react with PBu_3 and $Pcycl_3$ to form 1:1 adducts in dichloromethane solution. Adducts with PBu_3 require lower temperatures than those with $Pcycl_3$ in order to observe J(Sn–P) coupling. A solution containing Me_2SnCl_2, Me_2SnBr_2 and $Pcycl_3$ (1:1:2) at −100 °C shows three doublet resonances, as did the analogous phenyl system. However, mixtures of Me_2SnCl_2, Me_2SnBr_2 and PBu_3 (1:1:2) give a single broad resonance at room temperature which is still not resolved at −110 °C, indicating greater lability of halides when R = Me compared to R = Ph. Inter-

TABLE III. NMR Data for Adduct Formation of R_2SnX_2 with Tributylphosphine Oxide (L)

Compound	$\delta(^{31}P)$	$\delta(^{119}Sn)$	$J(^{119}Sn-P)$	Temperature (°C)
Ph_2SnCl_2L[a]	62.8	-276d	156	-80
Ph_2SnBr_2L[a]	62.6	-319d	166	-80
$Ph_2SnBrCl$[a]		-282d	156	-100
		-312d	163	-100
$Ph_2SnCl_2L_2$	62.9, 60.1	-472t	170	-85
		-477t	170	
$Ph_2SnBr_2L_2$	63.3	-467t	190	-85
	61.4	-479t	185	-85
$[Ph_2SnBrL_3]Br$	64.9	-523q	205	-85

[a] From ref. 15.

estingly, a mixture of Bu_2SnCl_2, Bu_2SnBr_2, and PBu_3 (1:1:2) does show the presence of three tin-119 doublet resonances at -80 °C (Table II).

The $[R_2SnX_3]^-$ anions react with PBu_3 to give spectra which are the same as those observed for reactions of R_2SnX_2 and one mole equivalent of PBu_3, indicating that one halide ion has been replaced by the phosphine. The only significant difference between the two systems is that lower temperatures are required to slow phosphine exchange in the $[R_2SnX_3]^-$ reaction. The presence of additional halide labilises the tin–phosphorus bond, presumably via formation of a six coordinate intermediate

$$[R_2SnX_3PBu_3]^- \longleftrightarrow R_2SnX_2PBu_3 + X^-$$

but the equilibrium clearly lies to the right. This result is consistent with the high lability of the $[R_2SnX_3]^-$ anions themselves, described earlier.

The reactions of Ph_2SnCl_2 or Ph_2SnBr_2 with one mole equivalent of tributylphosphine oxide and the observation of a slow Berry pseudorotation in the mixed species $Ph_2SnClBr(OPBu_3)$ have already been reported [15]. However, it may be noted that the tin-119 chemical shifts of $Ph_2SnCl_2(OPBu_3)$ and $Ph_2SnBr_2(OPBu_3)$ differ by more than 40 ppm (Table III) in contrast to the differences of only 6–7 ppm between those of the corresponding PBu_3 and $Pcycl_3$ complexes, thereby suggesting different stereochemical arrangements of ligands in the five coordinate phosphine and phosphine oxide adducts which will be discussed later.

Dimethyltin(IV)dihalides also react with one mole equivalent of tributylphosphine oxide as evidenced by changes in positions of the phosphorus-31 and tin-119 resonances. Although the tin-119 resonance is at a position consistent with the formation of a five coordinate 1:1 adduct, it is a singlet at temperatures down to -90 °C, indicating that the tributylphosphine oxide is still undergoing appreciable intermolecular exchange. Thus the general trend of the dimethyl systems being more labile than the diphenyl systems is continued.

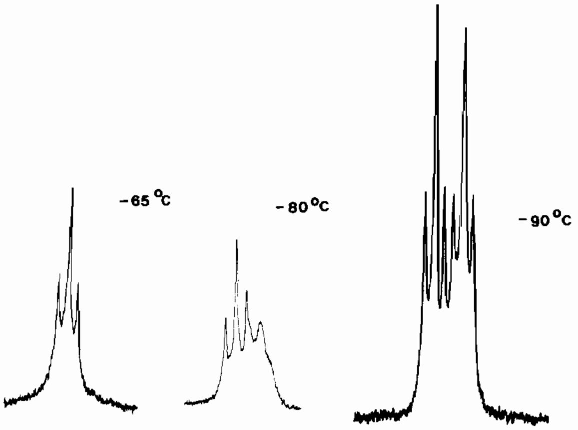


Fig. 1. Tin-119 spectra, at various temperatures, of a dichloromethane solution containing Ph_2SnCl_2 and $OPBu_3$ (molar ratio 1:2).

Diphenyltin(IV)dichloride reacts with further tributylphosphine oxide and the tin-119 spectrum of a solution of Ph_2SnCl_2 with $OPBu_3$ (1:2) at -65 °C shows a triplet at -472 ppm with J(Sn–P) 170 Hz (Fig. 1). At -80 °C the triplet broadens and there are signs of a second signal. At -90 °C there is clear resolution into two sharp triplets of equal intensity separated by 5 ppm. The tin-119 chemical shifts of these triplets are consistent with the formation of isomers of the six coordinate 1:2 adduct, $Ph_2SnCl_2(OPBu_3)_2$. We interpret the spectral changes with changes in temperature in terms of stereochemical non-rigidity. At -65 °C the molecule $Ph_2SnCl_2(OPBu_3)_2$ is six coordinate but fluxional between the possible octahedral isomers. At -95 °C intramolecular exchange is slow but only two of the five possible isomers are observed.

Diphenyltin(IV)dibromide reacts with additional tributylphosphine oxide. The tin-119 spectrum at -85 °C of a solution containing Ph_2SnBr_2 and $OPBu_3$, in the molar ratio 2:3, shows two triplets and a quartet (total relative intensities approximately 1:5:5) in the region expected for the six coordinate adduct $Ph_2SnBr_2(OPBu_3)_2$. The tin-119 spectrum also contains a doublet resonance due to the 1:1 adduct $Ph_2SnBr_2OPBu_3$. Addition of more $OPBu_3$ causes the phosphorus-31 resonance at 64.9 ppm to increase in intensity whilst the tin-119 doublet resonance decreases and the quartet increases in intensity. The relative intensities of the two triplets remain at about 1:5. That the quartet was genuine and not two overlapping triplets was confirmed by recording the NMR spectrum at a lower magnetic field. It is proposed that the quartet results from a six coordinate 1:3 adduct, where ionisation of a bromide ion has occurred such that the species in solution is the cation $[Ph_2SnBr(OPBu_3)_3]^+$. The quartet indicates that all three tributylphosphine oxide molecules are equivalent, a situation which can only arise if the molecule is still fluxional at −85 °C. Thus it is suggested that there is an equilibrium in solution

$$Ph_2SnBr_2L \xleftrightarrow{L} Ph_2SnBr_2L_2 \xleftrightarrow{L} [Ph_2SnBrL_3]^+Br^-$$

This equilibrium does not occur for the chloride system; addition of an excess of $OPBu_3$ to a solution containing $Ph_2SnCl_2(OPBu_3)_2$ causes no change in the tin-119 spectrum.

Conductivity measurements were made on Ph_2SnBr_2, $OPBu_3$ and mixtures thereof in dichloromethane solution at room temperature. Although the probability of ion pairing makes dichloromethane a poor solvent for conductance measurements, some general observations can nevertheless still be made. The conductance of a 10^{-2} M solution of Ph_2SnBr_2 and $OPBu_3$ (1:1 mole ratio) is about one tenth that of a solution of 10^{-2} M solution of Bu_4NI. On addition of a further two mole equivalents of $OPBu_3$ the conductance rises by a factor of five and confirms the liberation of bromide ion. It is not to be expected that the conductivity of the solution would approach that of Bu_4NI because the NMR measurements show the presence of the above equilibrium. A similar experiment with Ph_2SnCl_2 shows no increase in conductivity on addition of four mole equivalents of $OPBu_3$, confirming the conclusion from the NMR studies that no further reaction occurs after formation of $Ph_2SnCl_2L_2$.

The tin-119 spectrum at −90 °C of a mixture of Ph_2SnCl_2, Ph_2SnBr_2 and $OPBu_3$ (in the molar ratio 1:1:4) shows only the resonances seen in the original solutions of the chloro and bromo compounds. There are no additional resonances due to mixed halide species. In all previous studies, mixed halide species have been observed and this represents the first occasion where halide exchange is not observed.

Triorganoyltin(IV)halides

The tin-119 chemical shifts for Ph_3SnCl and Ph_3SnBr are very similar. Addition of the appropriate halide ion gives a shift in the tin resonances consistent with the formation of a five coordinate complex $[Ph_3SnX_2]^-$ which again have very similar chemical shifts (Table IV). In addition, a solution of Ph_3SnCl in pyridine also gives a very similar chemical shift, consistent with the formation of a five coordinate 1:1 adduct.

Addition of PBu_3 to solutions of Ph_3SnX gives no indication of any interaction: the tin-119 NMR spectra are identical to those of Ph_3SnX themselves and the phosphorus-31 NMR spectra show only a resonance due to free PBu_3. However, Ph_3SnCl reacts with $OPBu_3$ and the tin-119 spectrum of a solution containing 1:1 ratio Ph_3SnCl at −65 °C shows a doublet with J(Sn–P) 112 Hz. Addition of further quantities of $OPBu_3$ causes no change in the spectra apart from the appearance of an additional peak in the phosphorus-31 spectrum, due to uncoordinated $OPBu_3$.

TABLE IV. NMR Data for Triorganoyltin(IV)halide Systems at 30 °C

Compound	$\delta(^{119}Sn)$
Ph_3SnCl	−47
$[Ph_3SnCl_2]^-$ [a]	−220
$Ph_3SnCl{\cdot}C_6H_5N$ [b]	−219
Ph_3SnBr	−40
$[Ph_3SnBr_2]^-$	−233
Bu_3SnCl	154
$[Bu_3SnCl_2]^-$	−4
$Ph_3SnCl + L$ [c]	−258

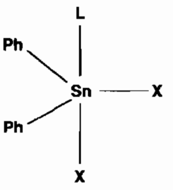
[a] −251 ppm at −90 °C. [b] In pyridine. [c] $\delta(^{31}P)$ 58.2 ppm, $^2J(^{119}Sn–P)$ 112 Hz at −65 °C.

Tetraphenyltin

On the basis of tin-119 and phosphorus-31 NMR studies, Ph_4Sn does not form adducts with halide ions, PBu_3 or $OPBu_3$.

Discussion

The compounds R_2SnX_2 form only 1:1 adducts with excess halide and with PBu_3, but form both 1:1 and 1:2 adducts with $OPBu_3$. The five coordinate $Ph_2SnX_2(PBu_3)$ adducts display a tin-119 chemical shift difference of only 7 ppm between the chloro and bromo derivatives and the mixed halo complex $Ph_2SnClBr(PBu_3)$ remains as a single doublet at very low temperature. In contrast, the 1:1 adducts $Ph_2SnCl_2(OPBu_3)$ and $Ph_2SnBr_2(OPBu_3)$ differ by 43 ppm in their tin-119 chemical shifts and the mixed halo complex $Ph_2SnClBr(OPBu_3)$ gives two doublets at low temperature [15]. It has been shown that the $OPBu_3$ adducts have the structure I and that the two doublets at low temperature are due to the two isomers with the Cl and Br interchanged. It has also been shown [15] that the tin-119 chemical shifts of five coordinate complexes are dominated by the contribution from the equatorial ligands, so that the observed insensitivity of chemical shifts of the phosphine adducts Ph_2SnX_2(phos) to the identity of the halide strongly suggests that the halides are not



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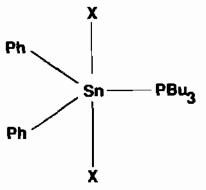

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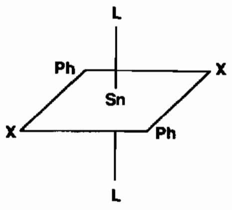

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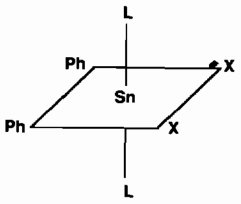

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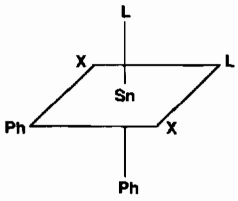

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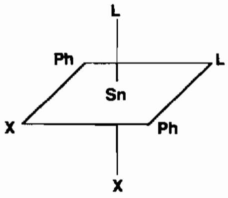

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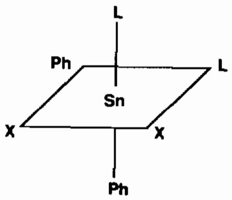

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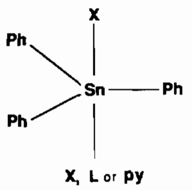

VIII

equatorial in these adducts so that the structure must be **II**. This is also consistent with the observation that the mixed halo complex gives only one doublet at low temperature.

Tributylphosphine oxide clearly has the higher Lewis basicity in this system as it is the only ligand to give 1:2 adducts. Quite different behaviours are shown for the chloro and bromo derivatives and in both cases only two of the possible five isomers $Ph_2SnX_2(OPBu_3)_2$ are found. This non-statistical distribution of isomers, which is unusual in these tin systems, suggests that steric effects are important in these systems. Assignment of these two isomers is based on the fact that the relative intensities of the two triplets is equal. The *trans* isomers **III** and **IV** have unequal statistical probabilities (6:12) whereas the probability of formation of the two *cis* isomers **V** and **VI** have equal statistical probability (12:12) and isomer **VII** has statistical probability of 24. Furthermore the two *cis* isomers, which are of equal probability, can be interconverted by a simple twist mechanism involving only one octahedral face. Therefore we deduce that at low temperature the two tin-119 triplets arise from the *cis* isomers **V** and **VI**. At higher temperature we are unable to differentiate whether the adduct is fluxional only between the structure **V** and **VI** or whether the other isomers also are involved to a significant degree. Two observations which are unique in our studies of these tin systems are noted. The first is that no mixed halide derivatives are seen in mixtures of $Ph_2SnCl_2(OPBu_3)_2$ and $Ph_2SnBr_2(OPBu_3)_2$. The absence of mixed halide species for the 1:2 adducts $Ph_2SnX_2(OPBu_3)_2$ implies substantially different structures for the chloro and bromo derivatives. Since we earlier deduced that the chloro derivatives probably have *cis* tributylphosphine oxide ligands, it now seems reasonable to assign the *trans* geometry to the bromo derivatives. Although the isomers **III** and **IV** might be expected to occur in their statistical distribution (6:12), the ratio of relative abundances observed is actually somewhat different. We cannot differentiate structures **III** and **IV** from the NMR data. The other unusual feature of this system is the displacement of a bromo group by a third $OPBu_3$ to give $[Ph_2SnBr(OPBu_3)_3]^+Br^-$. This displacement does not occur in the corresponding chloro system and must be a reflection of the steric pressures in $Ph_2SnBr_2(OPBu_3)_2$ itself. It is significant that only the strongest Lewis base of the ligands investigated in this series achieves this displacement.

The triorganoyltin(IV) halides do not form adducts with PBu_3 and only 1:1 adducts with excess halide ion and $OPBu_3$ and pyridine and all the adducts have similar chemical shifts (Table IV). On the basis of the arguments given above concerning the effects of axial and equatorial ligands in five coordinate structures, we propose that the phenyl groups are equatorial as shown in Structure **VIII**. This agrees with earlier conclusions in similar systems [4, 6, 10, 11].

The results reported in this paper complete the investigation of the series Ph_nSnX_{4-n} ($X = Cl, Br$; $n = 0$–4) with the three types of additive ligand (halide, phosphine, phosphine oxide) and it is appropriate at this point to make some general observations. The Lewis acidity of the tin compounds towards these ligands falls steadily from SnX_4 to Ph_4Sn so that Ph_4Sn does not interact with any of these ligands. Towards the organo rich end of this series it is possible to show that phosphines are the weakest Lewis base since they do not react with Ph_3SnCl, but halide and $OPBu_3$ do form 1:1 adducts with this Lewis acid. The evidence also indicates that $OPBu_3$ is a better Lewis base than halide since $OPBu_3$ forms 1:2 adducts with Ph_2SnX_2 whereas halides form only 1:1 adducts.

These studies have also shown the frequent presence of stereochemical non-rigidity within many of these systems. By systematically making use of mixing experiments involving several ligand or halide combinations, we have been able to show in many instances that this stereochemical non-rigidity is frequently intramolecular in nature. Furthermore, these mixing experiments have yielded far more stereochemical information than is available from study of the individual compounds themselves.

Experimental

NMR spectra were recorded on JEOL FX100 or JEOL GX270 spectrometers using external ^{7}Li lock. Phosphorus-31 spectra were referenced against 85% H_3PO_4 and tin-119 against external Me_4Sn.

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