Tin-119 NMR Studies on Adduct Formation and Stereochemistry of Organoyltin(IV)trihalides

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Abstract

Tin-119 and phosphorus-31 NMR spectra have been recorded for a series of adducts of $RSnX_3$ (R = Me, Ph; X = Cl, Br) with halide, tributylphosphine (P) and tributylphosphine oxide (L). The adducts were either 1:1 five coordinate or 1:2 six coordinate complexes. The tin-119 NMR spectra of mixtures of corresponding chloro and bromo complexes reveal, in most cases, all possible mixed halide species but much additional structural information is obtained from these spectra which could not be extracted from the spectra of individual compounds themselves. Thus in some cases, in the five coordinate species the Berry pseudorotation between isomers within a particular stoichiometry could be slowed on the NMR timescale which allowed a determination of the molecular structure. An equimolar mixture of $[PhSnCl_5]^{2-}$ and $[PhSnBr_5]^{2-}$ shows eleven of the twelve geometries possible for $[PhSnCl_xBr_{5-x}]^{2-}$. In the six coordinate series $[RSnX_4P]^-$ the tin-119 NMR spectra of the mixtures of $[RSnCl_4P]^-$ and $[RSnBr_4P]^-$ allow the geometry to be determined as *trans*. Application of the pairwise additivity model for calculation of the tin-119 chemical shift positions for the mixed halide systems are discussed.

Introduction

The utility of tin-119 NMR spectroscopy to the study of both inorganic and organometallic tin chemistry continues to expand rapidly and has recently been reviewed by Wrackmeyer [1]. We have been interested in the Lewis acid behaviour of tin(IV) compounds and recently reported tin-119 NMR studies on adduct formation of tin(IV) tetrahalides with neutral and anionic Lewis bases [2, 3]. It was shown that the pairwise additivity model for calculating tin-119 chemical shifts was very useful in permitting identification of geometric isomers in solution. Introduction of organoyl groups at the tin atom reduces the Lewis acidity of the tin(IV) centre [4] as well as increasing the number of structural possibilities of adducts in solution. We now report data for the interaction, in dichloromethane solution, of organoyltin(IV)trihalides with halide, tributylphosphine and tributylphosphine oxide.

Experimental

NMR spectra were recorded on a JEOL FX100 spectrometer, tin-119 at 37.06–37.08 MHz and phosphorus-31 at 40.26 MHz using external ^7Li lock. Tin-119 NMR spectra were referenced against external Me_4Sn and phosphorus-31 spectra against external 85% H_3PO_4. Spectra were generally recorded with complete proton decoupling. Temperatures were maintained using a JEOL NM 5471 controller.

Phenyltin(IV)trihalides were prepared by reaction between tetraphenyltin(IV) and the appropriate tin(IV) tetrahalide and purified by distillation under reduced pressure. Other compounds were obtained from commercial sources.

Results

Organoyltin(IV)trihalides

The compounds $RSnX_3$ (R = Ph, Me; X = Cl, Br) all give sharp tin-119 proton decoupled NMR spectra in dichloromethane solution at room temperature. Most of these spectra have been observed before and the chemical shifts given in Table I agree well with literature values [5–7]. A normal halogen dependence [8] is observed in all systems, that is, the resonances for the chloro compounds are at a higher frequency than those of the bromo analogues.

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TABLE I. Tin-119 NMR Data for $RSnX_3$ Systems in Dichloromethane Solution

Compound	$\delta(^{119}Sn)$[a]	Temperature (°C)	Compound	$\delta(^{119}Sn)$[a]	Temperature (°C)
$PhSnCl_3$	−65	30	$MeSnCl_3$	+6	30
$PhSnCl_2Br$[b]	−114	−30	$MeSnCl_2Br$[b]	−45	−100
$PhSnClBr_2$[b]	−168	−30	$MeSnClBr_2$[b]	−99	−100
$PhSnBr_3$	−225	30	$MeSnBr_3$	−167	30

[a] Reference $SnMe_4$. [b] Observed in an equimolar mixture of $RSnCl/RSnBr_3$.

TABLE II. Tin-119 NMR data for the Addition of Halide to the $RSnX_3$ Systems in Dichloromethane at 30 °C

Compound	$\delta(^{119}Sn)$	Compound	$\delta(^{119}Sn)$
$PhSnCl_3$	−65	$MeSnCl_3$	+6
$[PhSnCl_4]^-$ [a]	−260	$[MeSnCl_4]^-$ [a]	−254
$[PhSnCl_5]^{2-}$ [a]	−550		
$PhSnBr_3$	−225	$MeSnBr_3$	−167
$[PhSnBr_4]^-$ [b]	−637	$[MeSnBr_4]^-$ [b]	−384
$[PhSnBr_5]^{2-}$ [b]	−1007	$[MeSnBr_5]^{2-}$ [b]	−562
		$BuSnCl_3$	+6
		$[BuSnCl_4]^-$ [a]	−258
		$BuSnBr_3$	−144
		$[BuSnBr_4]^-$ [b]	−470
		$[BuSnBr_5]^{2-}$ [b]	−513

[a] Counter ion is $[(PhCH_2)Ph_3P]^+$. [b] Counter ion is Bu_4N^+.

The tin-119 NMR spectrum of a 1:1 mixture of $PhSnCl_3$ and $PhSnBr_3$ in dichloromethane at room temperature consists of a single broad resonance indicating that halogen exchange is occurring at an intermediate rate on the NMR timescale. Cooling to −30 °C resulted in the appearance of four sharp resonances of relative intensities 1:3:3:1. The two outermost resonances are due to the starting materials and two remaining resonances are assigned to the mixed halide compounds $PhSnCl_2Br$ and $PhSnClBr_2$ in a manner analogous to that used previously for the spectra of a solution containing equimolar quantities of $SnCl_4$ and $SnBr_4$ [9]. The statistical distribution of the species indicates that there are no steric factors affecting the halide distribution.

Similar results were obtained from mixtures of $MeSnCl_3$ and $MeSnBr_3$ except that a temperature of −100 °C is necessary to obtain sharp resonances for the four species. The chemical shift ranges between $RSnCl_3$ and $RSnBr_3$ are similar for both systems but the phenyl compounds show resonances to lower frequency of their methyl analogues.

Reactions of Organoyltin(IV)trihalides with Halide Ions

Phenyltin(IV) trichloride in dichloromethane solution reacts with chloride in a stepwise fashion to give $[PhSnCl_4]^-$ and $[PhSnCl_5]^{2-}$ as evidenced by changes in the position of the tin-119 NMR resonances (Table II). Addition of greater than a 2:1 mole ratio of chloride causes only a broadening of the tin-119 resonance without any significant change in the chemical shift. Unlike other workers [10] we have observed no evidence for the dissociation

$$2[PhSnCl_4]^- \rightleftharpoons Ph_2SnCl_2 + [SnCl_6]^{2-} \qquad (1)$$

although we note that $[SnCl_6]^{2-}$ is produced in the presence of moisture. In fact, we find the equilibrium for reaction (1) lies to the left in dichloromethane and $[PhSnCl_4]^-$ can be generated by reacting equimolar proportions of Ph_2SnCl_2 and $[SnCl_6]^{2-}$.

Addition of one mole equivalent of chloride to methyltin(IV)trichloride causes a change in $\delta(^{119}Sn)$ consistent with the formation of the anion $[MeSnCl_4]^-$. However, addition of a second mole equivalent of chloride causes only a small further shift in the position of the tin-119 resonance. Cooling the solution to −80 °C brings about little change in $\delta(^{119}Sn)$ (which is now at −290 ppm) and suggests that the formation constant for $[MeSnCl_5]^{2-}$ is substantially smaller than that for $[PhSnCl_5]^{2-}$. Both tribromides, $RSnBr_3$ (R = Me, Ph), react with additional bromide ion in a stepwise fashion to give $[RSnBr_4]^-$ and $[RSnBr_5]^{2-}$ anions (Table II). NMR data for some R = Bu analogues are also included in Table II for comparison.

The tin-119 NMR spectrum of a dichloromethane solution containing a 1:1 mixture of $[PhSnCl_4]^-$ and $[PhSnBr_4]^-$ gives five very broad signals at −90 °C ($\delta(^{119}Sn)$ −250, −410, −480, −558, −630 ppm) which can be ascribed to the mixed halo anions $[PhSnCl_xBr_{4-x}]^-$. The signal due to $[PhSnCl_4]^-$ is extremely broad with the remaining signals having full widths at half height of about 300 Hz. At −110 °C the signal previously at −480 ppm (probably due to $[PhSnCl_2Br_2]^-$) clearly resolves into two separate resonances, implying that Berry pseudorotation is being slowed within that stoichiometry. No tin-119 resonance could be detected for a 1:1 mixture of $[MeSnCl_4]^-$ and $[MeSnBr_4]^-$ in dichloromethane solution over the temperature range 30 to −100 °C.

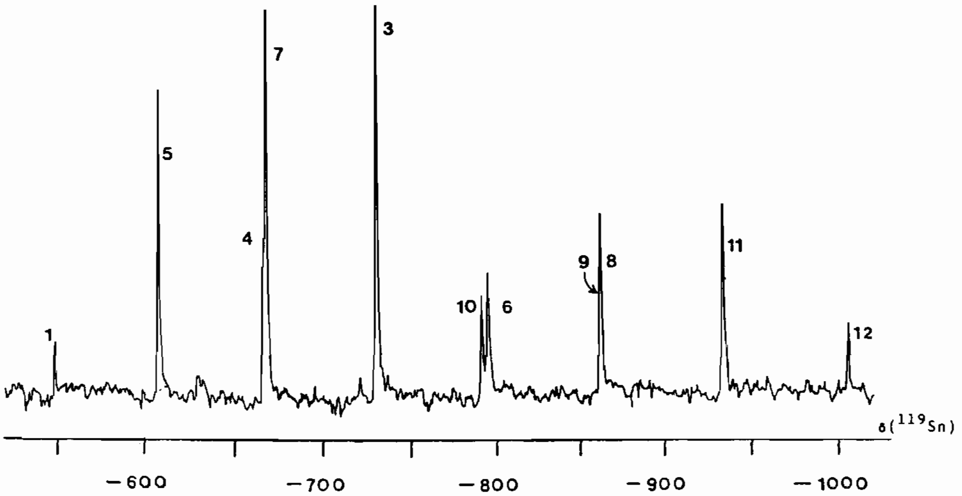


Fig. 1. Tin-119 NMR spectrum at −80 °C for a 1:1 mixture of $[PhSnCl_5]^{2-}$ and $[PhSnBr_5]^{2-}$ in dichloromethane solution. The species are identified in Table III.

TABLE III. Tin-119 NMR Data for the Mixed Halide System $[PhSnCl_xBr_{5-x}]^{2-}$ in Dichloromethane at −80 °C. Comparison between Observed and Calculated Chemical Shifts

Compound[a]	Isomer[b]	No.[c]	δ(^{119}Sn) Observed *vs.* $SnMe_4$	δ(^{119}Sn) Observed *vs.* $SnCl_4$	δ(^{119}Sn) Calculated *vs.* $SnCl_4$
$[PhSnCl_5]^{2-}$		1	−550	−400	−400(std)
$[PhSnCl_4Br]^{2-}$	(Cl)	2			−436
	(Br)	3	−727	−577	−598
$[PhSnCl_3Br_2]^{2-}$	(Cl)(Br, *c*)	4	−665	−515	−488
	(Cl)(Br, *t*)	5	−608	−458	−461
	(Br)	6	−789	−639	−640
$[PhSnCl_2Br_3]^{2-}$	(Cl)	7	−667	−517	−539
	(Br)(Cl, *c*)	8	−855	−705	−707
	(Br)(Cl, *t*)	9	−858	−708	−691
$[PhSnClBr_4]^{2-}$	(Cl)	10	−786	−636	−606
	(Br)	11	−924	−774	−774
$[PhSnBr_5]^{2-}$		12	−1007	−857	−857(std)

[a] Counter ion is Bu_4N^+. [b] The ligand in parentheses is *trans* to the phenyl group. [c] Resonances are identified by number in Fig. 1. Interaction parameters are: Cl–Cl = 0, Cl–Br = −46.8, Br–Br = −109.5, Ph–Cl = +42, Ph–Br = +147, δ charge = −569 ppm.

The tin-119 NMR spectrum of equimolar mixture of $[PhSnCl_5]^{2-}$ and $[PhSnBr_5]^{2-}$ in dichloromethane was a single broad resonance at room temperature, but on cooling to −80 °C eleven resonances were observed as shown in Fig. 1. The assignments of these signals to individual species in the $[PhSnCl_xBr_{5-x}]^{2-}$ series will be made in the 'Discussion'. Data are given in Table III.

Reactions of Organoyltin(IV)trihalides with $OPBu_3$ and PBu_3

Phosphorus-31 and tin-119 NMR spectra at −70 °C of dichloromethane solutions containing 1:1 molar proportions of $RSnX_3$ and $OPBu_3$ are consistent with the formation of five coordinate 1:1 adducts, $RSnX_3 \cdot OPBu_3$. The tin-119 doublets broaden above −70 °C and tin–phosphorus coupling is lost at approximately −40 °C. Data are given in Table IV. Figure 2 shows the doublet tin-119 spectra of $PhSnX_3(OPBu_3)$ adducts together with the tin-119 NMR spectra at various temperatures of a mixture containing $PhSnCl_3$, $PhSnBr_3$ and $OPBu_3$ in 1:1:2 proportions. At −70 °C four broad resonances are observed corresponding to the stoichiometries $PhSnCl_3L$, $PhSnCl_2BrL$, $PhSnClBr_2L$ and $PhSnBr_3L$ ($L = OPBu_3$). At −90 °C the resonances are sharper

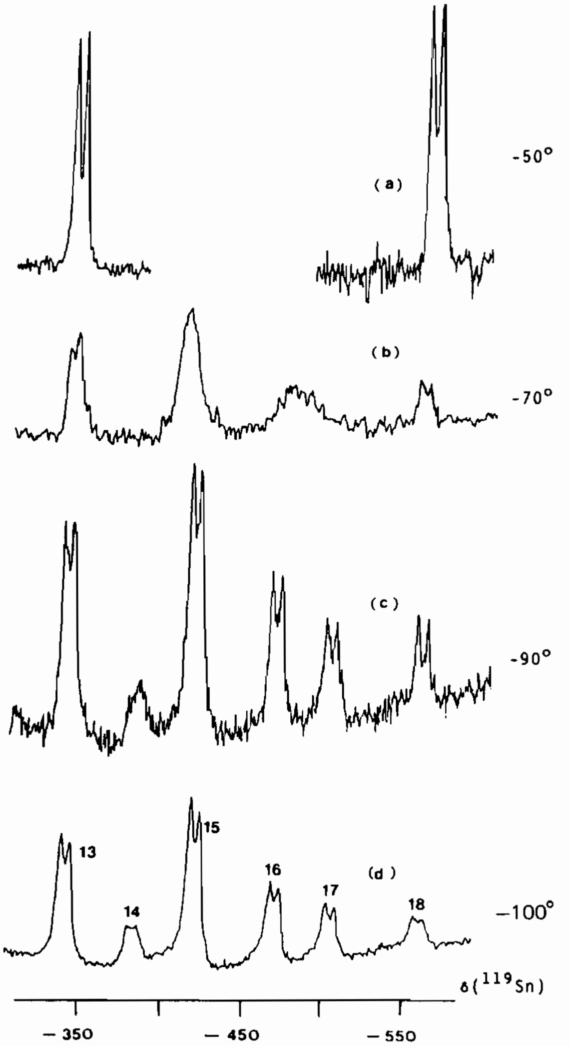


Fig. 2. Tin-119 NMR spectra of dichloromethane solutions of (a) $PhSnCl_3(OPBu_3)$ and $PhSnBr_3(OPBu_3)$ and for a mixture of these adducts at (b) −70 °C, (c) −90 °C and (d) −100 °C.

and tin–phosphorus coupling is obvious. Importantly, the signals due to the mixed halide stoichiometries are each split into two resonances of unequal intensities, while those due to the trichloro and tribromo compounds remain as simple doublets. At −100 °C the six resonances are all resolved into doublets. NMR data are given in Table IV.

The tin-119 NMR spectrum of a 1:2 mixture of $PhSnCl_3$ and $OPBu_3$ in dichloromethane solution at −70 °C consists of two triplets and a doublet of doublets (Fig. 3). The signals are in the region associated with six coordinate tin [11, 12] and this spectrum suggests that all three possible isomers of $PhSnCl_3(OPBu_3)_2$ are present in the solution and that exchange between them is slow on the NMR timescale at this temperature. Previously in this system, only one isomer has been identified in the solid state on the basis of ^{119m}Sn Mössbauer spectroscopy [13]. Addition of further quantities of $OPBu_3$ to the solution caused no further change in the spectra apart from the appearance of a phosphorus signal due to uncoordinated $OPBu_3$. The tin-119 NMR spectrum at −70 °C of a dichloromethane solution containing $PhSnBr_3$ and $OPBu_3$ in the molar ratio 1:2 shows a doublet of doublets but only one triplet, with total relative intensities of approximately 1:3. NMR data are given in Table IV. A mixture of $PhSnCl_3$, $PhSnBr_3$ and $OPBu_3$ in the molar ratio 1:1:4 gives a large number of resonances at −70 °C (Fig. 4) which are attributed to the mixed halide species $PhSnCl_xBr_{3-x}(OPBu_3)_2$.

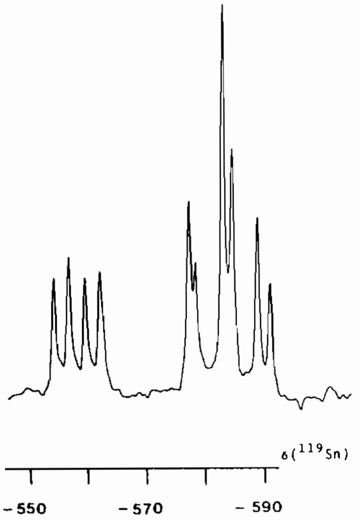


Fig. 3. Tin-119 NMR spectrum of $PhSnCl_3(OPBu_3)_2$ in dichloromethane at −70 °C.

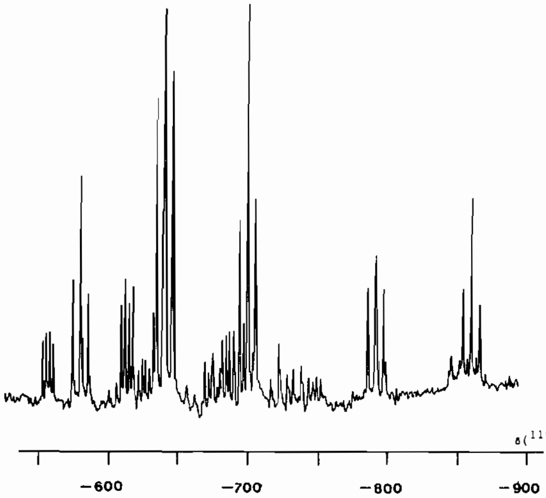


Fig. 4. Tin-119 NMR spectrum of a mixture of $PhSnCl_3(OPBu_3)_2$ and $PhSnBr_3(OPBu_3)_2$ in dichloromethane at −70 °C.

TABLE IV. Phosphorus-31 and Tin-119 NMR Data for Adducts between $OPBu_3$ and $RSnX_3$ Systems in Dichloromethane

Adduct[a]		$\delta(^{31}P)$	No.[b]	$\delta(^{119}Sn)$[c]	$^2J(Sn-P)$ (Hz)	Temperature (°C)
$PhSnCl_3L$		67.2		−340d	220	−50
$PhSnBr_3L$		65.8		−565d	234	−70
$MeSnCl_3L$		65.7		−265d	230	−90
$MeSnBr_3L$		64.3		−484d	240	−80
$PhSnCl_3L$			13	−340d	210	−100
$PhSnCl_2BrL$			14, 15	−382d −420d	230 180	−100 −100
$PhSnClBr_2L$			16, 17	−471d −505d	215 215	−100 −100
$PhSnBr_3L$			18	−561d	230	−100
$PhSnCl_3L_2$[d]	iv	65.0		−558 d of d	190, 90	−90
	v	67.7		−584t	220	−90
	vi	66.8		−582t	205	−90
$PhSnBr_3L_2$[d]	iv	66.5		−749 d of d	215, 122	−70
		64.6		−863t	220	−70
$MeSnCl_3L_2$[d]	iv	64.7		−512 d of d	200, 83	−100
	v	66.6		−525t	228	−100
	vi	65.3		−521t	218	−100
$MeSnBr_3L_2$		64.9		−744t	230	−100
		67.7		−751t	230	−100

[a] L = $OPBu_3$. [b] Resonances identified by number in Fig. 2. [c] d = doublet, t = triplet. [d] Structures iv to vi as given in the text.

Tributylphosphine reacts quite differently with $RSnX_3$. Addition of PBu_3 to a dichloromethane solution of $PhSnCl_3$ led to a rearrangement according to the equation

$$2PhSnCl_3 + 3PBu_3 \longrightarrow Ph_2SnCl_2(PBu_3) + SnCl_4(PBu_3)_2 \qquad (2)$$

The products were identified by their phosphorus-31 and tin-119 chemical shifts and their phosphorus–tin coupling constants. The reactions of PBu_3 with $PhSnBr_3$, $MeSnCl_3$ and $PhSnBr_3$ are more complicated and are still being investigated. Products have not yet been identified, but in no case was there evidence for the simple 1:1 adducts $RSnX_3(PBu_3)$.

Reactions of $[RSnX_4]^-$ with PBu_3 and $OPBu_3$

$[MeSnCl_4]^-$ and $[MeSnBr_4]^-$ each react with one mole of PBu_3 to give $[MeSnX_4(PBu_3)]^-$. Both complexes show only one sharp doublet in their tin-119 NMR spectra at room temperature which indicates that either only one isomer of the six coordinate species exists, or alternatively, that rapid isomer interchange between the various possible geometries is occurring. The spectra are invariant with temperature to −80 °C which implies that only one isomer of each $[MeSnX_4(PBu_3)]^-$ compound is present. Figure 5 shows the tin-119

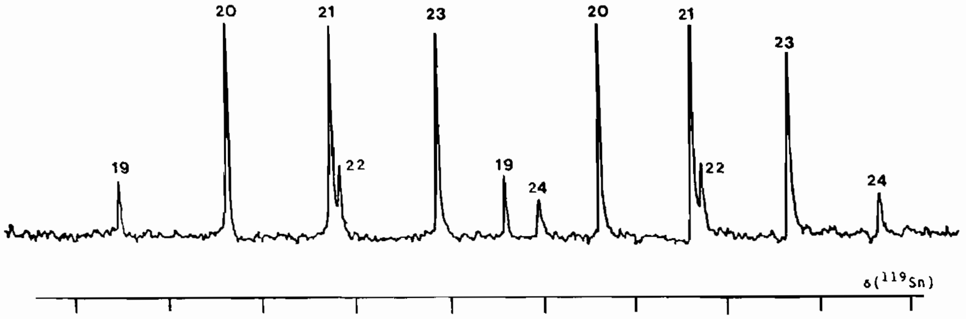


Fig. 5. Tin-119 NMR spectrum of a mixture of $[MeSnCl_4(PBu_3)]^-$ and $[MeSnBr_4(PBu_3)]^-$ in dichloromethane at −70 °C. Species are identified in Table V.

TABLE V. Phosphorus-31 and Tin-119 NMR Data for the Mixed Halide Systems *trans*-$[RSnCl_xBr_{4-x}(PBu_3)]^-$ in Dichloromethane

Compound[a]	No.[b]	$\delta(^{31}P)$	$\delta(^{119}Sn)$	$^2J(Sn-P)$	Temperature (°C)
trans-$[MeSnCl_4P]^-$ [c]	19	17.4	−450	3100	−70
trans-$[MeSnCl_3BrP]^-$	20	13.4	−472	3025	−70
trans-$[MeSnCl_2Br_2P]^-$ (Cl, *c*)	21	9.7	−493	2955	−70
(Cl, *t*)	22	9.7	−495	2965	−70
trans-$[MeSnClBr_3P]^-$	23	5.6	−515	2890	−70
trans-$[MeSnBr_4P]^-$ [d]	24	0.6	−536	2820	−70
trans-$[PhSnCl_4P]^-$ [c]		17.1	−502	3125	−35
trans-$[PhSnCl_3BrP]^-$		14.4	−529	3045	−35
trans-$[PhSnCl_2Br_2P]^-$		10.9	−555	2970	−35
trans-$[PhSnClBr_3P]^-$		7.0	−580	2895	−35
trans-$[PhSnBr_4P]^-$ [d]		2.3	−604	2840	−35

[a] P = PBu_3. [b] Resonances identified by number in Fig. 5. [c] Cation is $[(PhCH_2)_3PhP]^+$. [d] Cation is Bu_4N^+.

NMR spectrum of a 1:1 mixture of $[MeSnCl_4(PBu_3)]^-$ and $[MeSnBr_4(PBu_3)]^-$ at −70 °C. Six doublets are observed corresponding to the five compounds of stoichiometries $[MeSnCl_xBr_{4-x}(PBu_3)]^-$.

The anions $[PhSnCl_4]^-$ and $[PhSnBr_4]^-$ react similarly with PBu_3 and a mixture of $[PhSnCl_4(PBu_3)]^-$ and $[PhSnBr_4(PBu_3)]^-$ at −35 °C gives a spectrum similar to that described above for the $[MeSnCl_xBr_{4-x}(PBu_3)]^-$ system except that only five doublets were observed. Extensive crystallization occurs below −35 °C. Data are given in Table V.

Reaction between $[PhSnX_4]^-$ and $OPBu_3$ in dichloromethane solution did not result in simple 1:1 adduct formation. At room temperature the ^{31}P NMR spectra are broad but become sharp at −80 °C. At this temperature, the tin-119 NMR spectra show a number of resonances together with well defined doublets for the expected six coordinate 1:1 adduct $[PhSnX_4(OPBu_3)]^-$ (chloro: $\delta(^{119}Sn)$ −560 ppm, $^2J(Sn-P)$ 210 Hz; bromo: $\delta(^{119}Sn)$ −924 ppm, $^2J(Sn-P)$ 234 Hz) and show that the following equilibria occur in solution:

$$[PhSnX_4]^- + OPBu_3 \rightleftharpoons [PhSnX_4(OPBu_3)]^- \rightleftharpoons PhSnX_3(OPBu_3)_2 + [PhSnX_5]^{2-} \qquad (3)$$

It is interesting that $OPBu_3$ causes such a disproportionation whereas PBu_3 does not. It is also interesting to recall that reaction between PBu_3 and $RSnX_3$ did not result in simple adduct formation whereas PBu_3 does give simple 1:1 adducts with $RSnX_4^-$.

Discussion

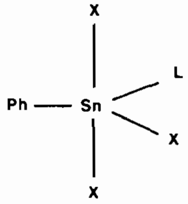
The tin-119 NMR spectra resulting from the mixing of different $RSnX_3$ species clearly indicate that halogen exchange occurs freely at a rate which is intermediate on the NMR timescale at room temperature. Cooling the solutions led to the observation of all the possible mixed halide species in the statistical distribution. Whereas mixtures of $SnCl_4$ and $SnBr_4$ showed resonances due to the mixed halide species at room temperature [3, 9] (although the signals were rather broad), the $RSnX_3$ systems give only exchange average signals at room temperature and require temperatures of −30 °C (R = Ph) and −100 °C (R = Me) in order to observe sharp signals for individual compounds. The effect of substituting one halide by an organoyl group is clearly to labilize the remaining halides with the methyl group being the more effective in this respect. This point is emphasized in experiments involving addition of halide to $RSnX_3$ systems. Addition of one mole equivalent of halide to $MeSnX_3$ clearly leads to formation of $[MeSnX_4]^-$ (Table II), but a 1:1 mixture of $[MeSnCl_4]^-$ and $[MeSnBr_4]^-$, in dichloromethane, was labile over the accessible temperature range. In contrast, the mixture of $[PhSnCl_4]^-$ and $[PhSnBr_4]^-$ at low temperature does show separate resonances for all the stoichiometries $[PhSnCl_xBr_{4-x}]^-$ and at −110 °C one of these is resolved into two separate resonances due to different isomers of the same stoichiometry within the five coordinate geometry. The latter spectrum represents a slowing down on the NMR timescale of the Berry pseudorotation mechanism which causes five coordinate complexes to be generally fluxional. However in this system the signals are broad and separation of the peaks is only just accessible within the available temperature range.

Addition of a further mole of halide to $[PhSnX_4]^-$ gives octahedral $[PhSnX_5]^{2-}$. However, addition of a further mole equivalent of chloride to

$[MeSnCl_4]^-$ causes only a small change in position of the tin-119 resonance and suggests that the equilibrium constant for addition of a second chloride to $MeSnCl_3$ is relatively small. It has previously been shown that, in acetonitrile solution, $MeSnCl_3$ is a weaker chloride acceptor than $PhSnCl_3$ [14, 15]. However, solid examples of both $[MeSnCl_5]^{2-}$ and $[PhSnCl_5]^{2-}$ have been reported [16] as has the crystal structure of the $[MeSnCl_4]^-$ anion [17]. The tin-119 NMR spectrum of a mixture of $[PhSnCl_5]^{2-}$ and $[PhSnBr_5]^{2-}$ (Fig. 1) shows a number of resonances which are due to $[PhSnCl_xBr_{5-x}]^{2-}$ species. Assignments of individual resonances are made on the basis of the pairwise additivity model first proposed by Vladimiroff and Malinowski [18]. Tin(IV)tetrachloride is the primary reference for all our calculations so all measured tin-119 chemical shifts were expressed relative to $SnCl_4$ for the purposes of calculation and the same values of the Cl–Cl, Cl–Br and Br–Br interaction parameters used previously [2, 3] were assumed; these are 0, −46.8 and −109.5 ppm respectively (Table III). We have also shown that charge effects the tin chemical shift in a simple manner and the shift correction for two negative charges is −569 ppm [2]. Using these values and the values of the chemical shifts of $[PhSnCl_5]^{2-}$ and $[PhSnBr_5]^{2-}$ (relative to $SnCl_4$), yields calculated values for the Ph–Cl and Ph–Br interaction parameters of +42 and +147 ppm respectively. Subsequent calculation of the tin chemical shifts for all the mixed halide complexes gives the values shown in Table III. It is the very large positive value of the Ph–Br interaction parameter which causes the unusual ordering of the resonances for the various tin species, depending upon the number of bromo *cis* to the phenyl group. The comparison between observed and calculated tin chemical shifts is listed in Table III, and although useful, the correlation is not as impressive as for earlier systems, which implies that the interactions in the present systems are becoming too complex for such a simple model.

The tin-119 NMR spectra of the approximately 1:1:2 mixture of $PhSnCl_3$, $PhSnBr_3$ and $OPBu_3$ (Fig. 2) are particularly informative. In this system cooling to −70 °C allowed observation of four signals corresponding to the four stoichiometries $PhSnCl_xBr_{3-x}L$. The splitting into two components of the signals due to mixed halide stoichiometries at still lower temperatures is due to the slowing down on the NMR timescale of the Berry pseudorotation of the five coordinate complexes which allows observation of two isomers for each mixed halide complex $PhSnCl_xBr_{3-x}L$ ($L = OPBu_3$, $x = 1, 2$). This observation suggests that the $PhSnX_3(OPBu_3)$ system has a higher barrier to pseudorotation than the $[PhSnX_4]^-$ systems where only one stoichiometry showed splitting at low temperature.

There are three possible distributions of the ligands in the trigonal bipyramidal adducts $PhSnX_3L$ as shown in structures **i** to **iii** with one, two or three halides in the equatorial plane respectively. The spectra eliminate structure **iii** since it would not give rise to isomers within the mixed halide stoichiometries. Structure **ii** is the stereochemistry expected for these adducts by analogy with known five coordinate compounds containing both phenyl groups and phosphine oxides. In all cases the electronegative oxygen donor occupies an axial position and the phenyl groups are equatorial [13, 19, 20]. The $PhSnX_3L$ adducts have not been previously reported, but a ligand distribution similar to that of the Ph_2SnCl_2 [20] adducts would not be surprising.



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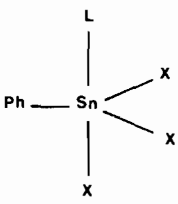

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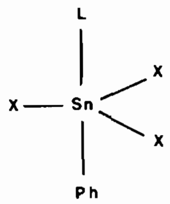
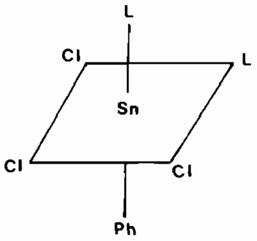


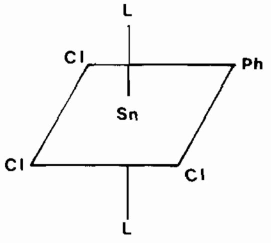
iii

The tin-119 NMR spectrum of the six coordinate $PhSnCl_3L_2$ (Fig. 3) shows the presence of all three possible isomers, which are shown in structures **iv**–**vi**. The doublet of doublets is assigned to structure **iv** since this is the only one with non-equivalent phosphorus atoms. The two triplets can be assigned to individual isomers on the basis of their relative intensities. The expected relative abundances for the structures **iv**–**vi** are 12:12:24, *i.e.* 1:1:2 which is the observed pattern. Hence the more intense triplet is assigned to structure **vi**. Only one isomer of the analogous $PhSnCl_3(OPPh_3)_2$ has been identified in the solid state [13] and it has structure **vi**. The tin-119 spectrum for $PhSnBr_3L_2$ contains a doublet of doublets and only one triplet. The doublet of doublets is assigned to isomer **iv** whilst the triplet appears to be an average signal for isomers **v** and **vi** since the relative intensities of the resonances are approximately 1:3. Isomers **v** and **vi** may become equivalent through a rapid facial twist mechanism. As the temperature of the solution is increased the triplet broadens more rapidly than does the doublet of doublets. At −25 °C the triplet has collapsed into a single broad resonance whilst the doublet of doublets still shows resolution. No tin-119 NMR spectrum could be obtained at +30 °C.

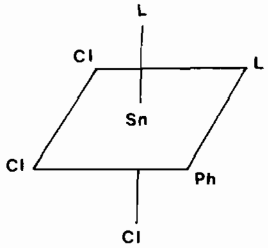
Although the pairwise additivity method has worked extremely well for mixed halide adducts with halide, phosphine, phosphine oxide and phenyl groups, it fails to work in the case of a 1:1 mixture of $PhSnCl_3(OPBu_3)_2$ and $PhSnBr_3(OPBu_3)_2$. Calculation of the interaction parameter between Ph



iv



v



vi

and $OPBu_3$ gives values which show too large a variation to be useful for subsequent calculations. This is the first time we have attempted to apply the technique to complexes with two types of ligand besides halide and evidently the interaction effects are no longer simply additive. Thus only qualitative remarks can be made about assignment of the many signals in the tin-119 spectrum. The compounds $PhSnCl_2BrL_2$ and $PhSnClBr_2L_2$ each have six possible isomers, and for each of these stoichiometries three isomers should give triplets and the other three should give doublet of doublets. In fact in the spectrum shown in Fig. 4 there appear to be a total of nine triplets and eight doublet of doublets in the tin-119 NMR spectrum of this mixture, consistent with the formation of all possible isomers of each stoichiometry in solution.

The compounds $[MeSnX_4]^-$ readily add one mole of PBu_3 to give the octahedral adducts $[MeSnX_4P]^-$ ($P = PBu_3$) in solution. As noted earlier, only one isomer is apparent but the tin-119 NMR spectrum of an individual compound does not distinguish between *cis* and *trans* (*i.e.* Me *trans* to P) geometry. The tin-119 NMR spectrum of a 1:1 mixture of $[MeSnCl_4P]^-$ and $[MeSnBr_4P]^-$ at −70 °C is shown in Fig. 5 and shows six doublets. The statistical distribution between the stoichiometries should be 1:4:6:4:1 and if the complexes were *trans* (*i.e.* Me *trans* to P) there would be six species in solution, as two alternate arrangements of the four halide ligands are possible for *trans*-$[MeSnCl_2Br_2P]^-$. Furthermore, the relative abundances of *trans-cis* $[MeSnCl_2Br_2P]^-$ and *trans-trans*-$[MeSnCl_2Br_2P]^-$ should be 2:1, so that the overall relative abundances would be 1:4:(4,2):4:1. This is exactly the pattern seen in Fig. 5. If, on the other hand, $[MeSnX_4P]^-$ adopted a *cis* stereochemistry, there would be 12 possible species in the $[MeSnCl_xBr_{4-x}P]^-$ mixture. Thus this spectrum makes the assignment of a *trans* configuration very secure. Tin-119 Mössbauer studies also indicate only the *trans* isomer in the solid state [10].

The tin-119 NMR spectrum of a 1:1 mixture of $[PhSnCl_4P]^-$ and $[PhSnBr_4P]^-$ is similar to that described above except that separate signals for the two possible isomers of $[PhSnCl_2Br_2P]^-$ are not observed at temperatures above those accompanied by extensive crystallization. Unfortunately these systems provide the second example of the breakdown of the pairwise additivity model. In this case all the interaction parameters have been determined previously, but a direct calculation of the chemical shifts gives very poor agreement with the observed values.

Conclusions

The results presented in this paper show that mixing experiments are capable of yielding far more information than mere observation of mixed halide species. In octahedral series the distinction between, *cis* and *trans* stereochemistries is straightforward. The most significant results have been obtained in the five coordinate series where isomerization due to slowing down of the Berry pseudorotation has been observed.

It is a disappointment that the pairwise additivity model appears to be inapplicable to complexes containing two different ligands besides the halides. However, its success in the $[PhSnX_5]^{2-}$ series widens the types of system to which it is applicable.

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