# $^{119}$Sn and $^{19}$F spectroscopic studies of fluoro complexes derived from triphenyltin(IV) chloride and trimethyltin(IV) chloride

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## Abstract

$^{119}$Sn and $^{19}$F variable temperature NMR measurements have been used to study reactions of fluoride ion with $Ph_3SnCl$ and $Me_3SnCl$. Monomeric fluoro complexes $[R_3SnClF]^-$ and $[R_3SnF_2]^-$ are formed for both R=Ph and Me. Fluoride-bridged dimers $[(R_3SnX)F(R_3SnX')]^-$ (X=F, Cl; X'=F, Cl) are formed in solution for R=Me but not for R=Ph. Formation of tin–fluorine bonds is thermodynamically favoured over formation of tin–chloride bonds. The stereochemistry of the tin compounds formed in solution is dependent on the nature of the solvent and NMR data indicate the existence of several structural interconversion processes in solution. The presence of fluoride ion induces migration of phenyl groups which leads to formation of $[Ph_2SnF_4]^{2-}$, $[PhSnF_5]^{2-}$ and $[SnF_6]^{2-}$ from the original $Ph_3SnCl$. No analogous methyl group migration is observed when fluoride is added to solutions of $Me_3SnCl$.

## Introduction

We recently presented $^{119}$Sn NMR data for formation of simple tin(IV) halide species $[SnX_5]^-$, $[SnX_6]^{2-}$ as well as for mixed halides complexes $[SnX_nX'_{6-n}]^{2-}$ and adducts involving neutral Lewis bases $SnX_4L_2$ [1]. Also reported were results of NMR investigations of the Lewis acidity of a series of organoyltin compounds $R_nSnX_{4-n}$(R=Ph, Me, Bu; X=Cl, Br; $n$=1–3) and adducts thereof [2–6]. Whilst there have been reports of inorganic mixed halide complexes $[SnX_nX'_{6-n}]^{2-}$ involving fluoride, chloride and bromide [7], until now there appear to be only few reports of studies involving fluoro complexes of organoyltin(IV) in solution [8–10]. This paucity of data for fluoride systems probably arises because most organoyltin(IV) fluorides are polymeric in the solid state and of low solubility which generally precludes their investigation in solution. However, we found that in the presence of additional ligands, many fluoro complexes involving organoyltin(IV) compounds are soluble and we now report results of our NMR investigations of reaction of fluoride ion with triphenyltin(IV) chloride and trimethyltin(IV) chloride.

## Experimental

All $^{119}$Sn NMR spectra were recorded for sample solutions prepared from the appropriate molar ratios of $R_3SnCl$ (R=Ph, Me) and tetrabutylammonium fluoride trihydrate ($Bu_4NF \cdot 3H_2O$) and/or tetrabutylammonium chloride ($Bu_4NCl$). Typically, the concentration of $R_3SnCl$ used was in the range 0.1–0.3 M.

NMR spectra were recorded on a JEOL GX 270 spectrometer, $^{119}$Sn at 100.75 MHz using external deuterium lock, $^{19}$F at 254.19 MHz and $^{13}$C at 67.94 MHz using internal deuterium lock. $^{119}$Sn chemical shifts were referenced against external $Me_4Sn$, $^{19}$F chemical shifts were referenced against external $CFCl_3$ and $^{13}$C chemical shifts were referenced against internal TMS. Spectra generally were recorded with complete proton decoupling. Temperatures were maintained using a JEOL GVT3 temperature controller.

## Results and discussion

### *Reactions of tetrabutylammonium fluoride trihydrate ($Bu_4NF \cdot 3H_2O$) with triphenyltin chloride ($Ph_3SnCl$)*

The $^{119}$Sn NMR spectrum at −100 °C of a freshly prepared dichloromethane solution containing an equimolar ratio of $Bu_4NF \cdot 3H_2O$ and $Ph_3SnCl$ contains three resonances, a singlet, a doublet and a triplet, with relative intensities of approximately 1:10:1. The $^{119}$Sn singlet resonance at −251 ppm has been assigned previously to five-coordinate $[Ph_3SnCl_2]^-$ [2] whilst the doublet at −285 ppm is now assigned to $[Ph_3SnClF]^-$ and the triplet to $[Ph_3SnF_2]^-$, based on the $^{119}$Sn chemical shifts [11] and multiplicities of the resonances. The corresponding $^{19}$F NMR spectrum contains only

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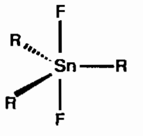
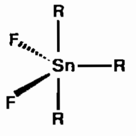
two singlets ($\delta(^{19}F)$ −162.0 and −164.4 ppm) both with $^{117/119}Sn$ satellites which, based on their relative intensities and coupling constant values, are assigned to $[Ph_3SnClF]^-$ and $[Ph_3SnF_2]^-$, respectively (Table 1). Increasing the fluoride to $Ph_3SnCl$ molar ratio causes the $^{119}Sn$ triplet resonance to grow in relative intensity and when the fluoride to $Ph_3SnCl$ ratio reaches 3:1, only the triplet resonance remains. Addition of further fluoride ion causes the triplet resonance to broaden but no additional $^{119}Sn$ resonances are observed and it appears that only the five-coordinated $[Ph_3SnF_2]^-$ species is formed. The $^{19}F$ spectrum contains resonances for both $[Ph_3SnF_2]^-$ and uncoordinated fluoride ion indicating that intermolecular fluoride exchange is slow at −100 °C.

The $^{19}F$ and $^{119}Sn$ NMR data for $[Ph_3SnF_2]^-$ could be interpreted in terms of the two possible isomeric five-coordinate structures **I** and **II**, each containing equivalent fluorine atoms. However the $^{13}C$ NMR spectrum of the solution containing fluoride and $Ph_3SnCl$ in a 3:1 molar ratio, contains only one set of resonances attributed to phenyl groups ($\delta(^{13}C)$, 126.7 (*m*), 127.5 (*o*), 136.2 (*p*) and 146.5 (*i*) ppm with *J*(C–F) 24 Hz) which indicates that the three phenyl groups are equivalent and must therefore occupy equatorial positions as shown in structure **I**. Similarly, observation of equivalent phenyl groups in solutions containing $[Ph_3SnClF]^-$ implies structure **III** for this species. These results agree with earlier conclusions about the structures of similar systems [1, 2, 12–14] and are also supported by Mössbauer spectroscopy of $Ph_3SnF$ [15] which indicates trigonal planar $Ph_3Sn$ units linked by bridging fluorides.



I



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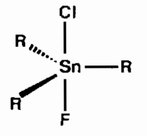


III

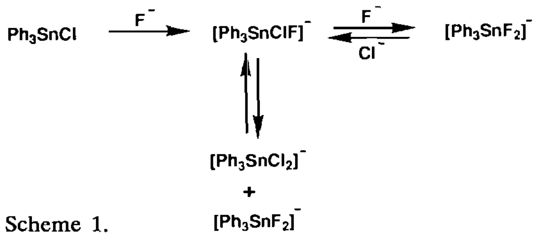
Interestingly, no $^{119}Sn$ resonance for $Ph_3SnCl$ was observed despite the fact that resonances attributed to $[Ph_3SnCl_2]^-$, $[Ph_3SnClF]^-$ and $[Ph_3SnF_2]^-$ were observed simultaneously in the same solution. This implies that all triphenyltin(IV) chloride was converted to five-coordinated tin species possibly via the equilibria shown in Scheme 1. Furthermore, a solution made by mixing fluoride and $Ph_3SnCl$ in a molar ratio of 2:1, contains $^{119}Sn$ resonances for $[Ph_3SnF_2]^-$ and $[Ph_3SnClF]^-$ with approximate relative intensity of 20:1. No resonance corresponding to $[Ph_3SnCl_2]^-$ was found for this solution. Only $^{119}Sn$ resonances due to $[Ph_3SnF_2]^-$ are observed once the fluoride to $Ph_3SnCl$ ratio is 2.2:1 or larger. These observations indicate that formation of tin–fluorine bonds are thermodynamically favoured over tin–chlorine bonds.

Examination of spectra over the temperature range −100 to 25 °C was informative. The $^{119}Sn$ spectrum at −100 °C of a solution made by mixing an equimolar ratio of $Bu_4NF \cdot 3H_2O$ and $Ph_3SnCl$ contains resonances for $[Ph_3SnCl_2]^-$, $[Ph_3SnClF]^-$ and $[Ph_3SnF_2]^-$. The resonance due to $[Ph_3SnCl_2]^-$ broadens as the temperature is raised from −100 to −60 °C and disappears at about −40 °C. Concurrently the doublet resonance due to $[Ph_3SnClF]^-$ broadens between −40 and −20 °C and disappears at about 0 °C. The triplet resonance assigned to $[Ph_3SnF_2]^-$ remains at 25 °C even though it is broad. The $^{119}Sn$ chemical shifts for the various species move less than 10 ppm towards higher frequency over the temperature range investigated. It appears $[Ph_3SnCl_2]^-$ is more labile than $[Ph_3SnClF]^-$ which is in turn more labile than $[Ph_3SnF_2]^-$. The lability probably involves halide exchange with intermolecular tin–chlorine exchange being more labile than tin–fluorine exchange.

TABLE 1. NMR data for species derived from reaction of fluoride ion with triphenyltin(IV) chloride

| Complex | Solvent | $\delta(^{119}Sn)$ (ppm) | $\delta(^{19}F)$ (ppm) | *J*(Sn–F) (Hz) | Temperature (°C) |
|---|---|---|---|---|---|
| $Ph_3SnCl$[a] | $CH_2Cl_2$ | −46 | | | 25 |
| | $CH_3OH$ | −177 | | | 25 |
| | $CH_3OH$ | −204 | | | −100 |
| $[Ph_3SnCl_2]^-$ | $CH_3COCH_3$ | −245 | | | −100 |
| | $CH_2Cl_2$ | −251 | | | −100 |
| $[Ph_3SnClF]^-$ | $CH_2Cl_2$ | −285(d) | −162.0 | 1905 | −100 |
| | $CH_3COCH_3$ | −286(d) | −163.5 | 1904 | −100 |
| $[Ph_3SnF_2]^-$ | $CH_2Cl_2$ | −343(t) | −164.4 | 1990 | −100 |
| | $CH_3COCH_3$ | −343(t) | −167.5 | 2003 | −100 |
| $[Ph_2SnF_4]^{2-}$ | $CH_2Cl_2$ | −592(quint) | −125.0 | 2695 | −100 |
| $[PhSnF_5]^{2-}$ | $CH_2Cl_2$ | −692(d-quint) | −140.0(d)[b] | 2430 | −100 |
| | | | −140.4(quint)[b] | 1180 | −100 |
| $[SnF_6]^{2-}$ | $CH_2Cl_2$ | −803(sept) | −152.6 | 1625 | −100 |

[a] No resonance found at 25 °C in acetone, two broad resonances (−218 and −147 ppm) were observed at −100 °C in acetone. [b] *J*(F–F), 20 Hz.



Scheme 1.

The $^{19}F$ and $^{119}Sn$ NMR spectra of the above solution change with time and additional weak resonances appear. After 7 days, the new resonances became more intense and were subsequently identified as due to six-coordinate species $[PhSnF_5]^{2-}$, $[Ph_2SnF_4]^{2-}$ and $[SnF_6]^{2-}$ [7]. These compounds are rearrangement products arising from phenyl group migration. A mass balance for the process requires formation of $Ph_4Sn$ as one of the species but no direct NMR evidence for this was observed. However, the solutions do become cloudy and it is known that $Ph_4Sn$ has only poor solubility in dichloromethane. No differences were observed when dichloromethane was replaced by acetone as solvent. Solubility difficulties precluded use of methanol as solvent. It is noteworthy that there is no evidence of such phenyl group migration when fluoride is replaced by chloride or bromide, however labile phenyl group migration has been previously reported for reaction of tributylphosphine ($PBu_3$) with $PhSnCl_3$ where the products were $SnCl_4(PBu_3)_2$ and $Ph_2SnCl_2(PBu_3)$ [4].

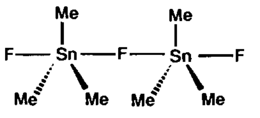
### *Reactions of tetrabutylammonium fluoride trihydrate ($Bu_4NF \cdot 3H_2O$) with trimethylchloride ($Me_3SnCl$)*

#### *Dichloromethane solutions*

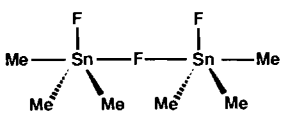
Mixtures of $Bu_4NF \cdot 3H_2O$ and $Me_3SnCl$ of molar ratios between 1:2 and 3:1 were prepared in dichloromethane solution. Initially there is considerable precipitation as $Bu_4NF \cdot 3H_2O$ is added to $Me_3SnCl$. This precipitate was separated and identified as $Me_3SnF$ by elemental analysis (Found: C, 19.44; H, 4.99. Calc. for $C_3H_{12}FSn$: C, 19.71; H, 4.96%) and by $^{119}Sn$ and $^{19}F$ chemical shifts in methanol (Table 1). However the precipitate begins to dissolve with further addition of $Bu_4NF \cdot 3H_2O$ and solutions are completely clear when the fluoride to $Me_3SnCl$ ratio approaches 7:4. The reaction of $Bu_4NF \cdot 3H_2O$ with $Me_3SnCl$ was monitored by $^{119}Sn$ and $^{19}F$ NMR spectroscopy and data are summarized in Table 2. NMR spectra of solutions made from fluoride and $Me_3SnCl$ in ratios smaller than 7:4 contain some precipitate.

Figure 1 shows $^{119}Sn$ spectra of solutions made from various fluoride to $Me_3SnCl$ ratios. Tin complexes which have $^{119}Sn$ chemical shift over the range −20 to −80 ppm (i.e. 180–240 ppm lower than $\delta(^{119}Sn)$ for $Me_3SnCl$) shown in Fig. 1 are assigned as five-coordinated. The triplet (denoted 7 in Fig. 1) is assigned to $[Me_3SnF_2]^-$, to which structure **I** is assigned on the basis that a singlet with $^{119/117}Sn$ satellites appears in the $^{19}F$ NMR spectrum of the same solution and the corresponding $^{13}C$ NMR spectrum shows only one methyl resonance ($\delta(^{13}C)$, −1.6 ppm; $J$(C–F) 26 Hz) indicating the three methyl groups are equivalent. This conformational assignment is in accord with other studies which indicate that the most electronegative groups in five-coordinate complexes occupy axial positions [1, 2, 12–14] and is further supported by the X-ray diffraction study of solid trimethyltin fluoride [16] which is polymeric with bridging fluorides in the axial positions and methyl groups in equatorial positions of a trigonal bipyramid.

A doublet of doublets (denoted 3 in Fig. 1) is observed in the $^{119}Sn$ spectra of solutions containing less than three equivalents of fluoride for each $Me_3SnCl$ and indicates a species which has two non-equivalent fluorides bonded to each tin atom. The corresponding $^{19}F$ NMR spectrum contains a doublet and a triplet (denoted 3′ in Fig. 2) with relative intensity ratio of 2:1. Both $^{19}F$ resonances are accompanied by $^{119/117}Sn$ satellites. The above NMR data can be interpreted in terms of the formation of a fluoride-bridged dimer, $[(Me_3SnF)_2F]^-$, which may have any of several alternative structures **IV**, **V**, **VI** and **VII**. However structure **IV** is favoured because of its similarity with $[Me_3SnF_2]^-$, i.e. because it contains apically coordinated fluorides. Blunden and Hill [8] have recently suggested a similar structure for the closely related compound $[(Bu_3SnF)_2F]^-$. The similarity of the magnitude of the coupling constant $J$(Sn–F) involving the non-bridging fluorides in $[Me_3SnF_2]^-$ (1500 Hz) and in $[(Me_3SnF)_2F]^-$ (1640 Hz) also supports structure **IV** for the latter species. The $J$(Sn–F) for bridging fluorides in polymeric tributyltin fluoride (1291 Hz) [17] and in $[(Me_3SnF)_2F]^-$ (1100 Hz) are also similar. Furthermore, that $[(Me_3SnF)_2F]^-$ has structure **IV** is supported by the solid state structure of polymeric trimethyltin fluoride [16] in which a F–Sn(Me$_3$)–F–Sn(Me$_3$)–F chain is formed.



IV



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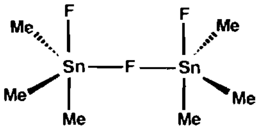
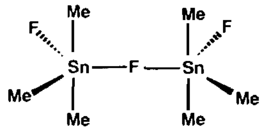
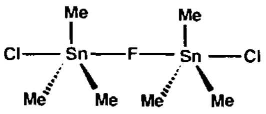


VI



VII



VIII

TABLE 2. NMR data at −100 °C for species derived from reaction of fluoride ion with trimethyltin(IV) chloride

| Complex | Solvent | $\delta(^{119}Sn)$ (ppm) | $\delta(^{19}F)$ (ppm) | $J$(Sn–F) (Hz) | $J$(F–F) (Hz) |
|---|---|---|---|---|---|
| $Me_3SnCl$ | $CH_2Cl_2$ | 172[a] | | | |
| | $CH_3OH$ | 12(42[a]) | | | |
| | $CH_3COCH_3$ | 107[a, b] | | | |
| $[Me_3SnCl_2]^-$ | $CH_3COCH_3$ | −81 | | | |
| | $CH_2Cl_2$ | −53 | | | |
| $Me_3SnF \cdot CH_3OH$ | $CH_3OH$ | 30(d) | −156.0 | 1630 | |
| $[Me_3SnClF]^-$ | $CH_3COCH_3$ | −63(d) | −134.1 | 1514 | |
| | $CH_2Cl_2$ | −38(d) | | | 1600 |
| *trans*-$[(Me_3SnCl)_2F]^-$ | $CH_2Cl_2$ | −21(d) | −123.1 | 1080 | |
| | $CH_3COCH_3$ | −44(d) | −117.5 | 1086 | |
| *trans*-$[(Me_3SnF)_2F]^-$ | $CH_2Cl_2$ | −36(d-d) | −139.6(d) | 1640 | 86 |
| | | | −107.0(t) | 1100 | 86 |
| | $CH_3COCH_3$ | −43(d-d) | −138.6(d) | 1690 | 90 |
| | | | −106.9(t) | 1164 | 90 |
| $[(Me_3SnF)F(Me_3SnCl)]^-$ | $CH_3COCH_3$ | −32(d) | −114.6(d) | 1172 | 84 |
| | | −34(d-d) | −114.6(d) | 1095 | 84 |
| | | | −141.6(d) | 1695 | 84 |
| $[(Me_3SnF)F(Me_3SnCl)]^-$ | $CH_2Cl_2$ | −11(d) | −116.1(d) | 950 | 85 |
| | | −12(t) | −143.7(d) | 1327 | 85 |
| $[Me_3SnF_2]^-$ | $CH_2Cl_2$ | −74(t) | −119.6 | 1500 | |
| | $CH_3COCH_3$ | −73(t) | −119.5 | 1520 | |
| | $CH_3OH$ | −20(t) | −133.5 | 1318 | |

[a]Observed at 25 °C. [b]Two resonances (one broad at 50 ppm and one sharp at 35 ppm) observed at −100 °C.

The doublet $^{119}Sn$ resonance (denoted 2 in Fig. 1) is assigned to a fluorine-bridged dimer *trans*-$[(Me_3SnCl)_2F]^-$ (structure **VIII**) from a comparison of the magnitude of its $J$(Sn–F) value (1080 Hz) with that for the bridging fluorine in *trans*-$[(Me_3SnF)_2F]^-$ (1100 Hz). This assignment is supported by the presence of a second set of $^{119/117}Sn$ satellites associated with the corresponding $^{19}F$ resonance. For a fluoride bridging two tin atoms, Sn–F–Sn, the $^{19}F$ resonance must have two sets of accompanying $^{119/117}Sn$ satellites. The first set of $^{119/117}Sn$ satellites corresponds to the situation where the bridging fluoride is bonded to one only one NMR active tin nucleus (i.e. $^{119}Sn$ or $^{117}Sn$). For this situation the tin satellite sub-spectrum is a doublet situated at 0.5 $J$(Sn–F) about the central $^{19}F$ resonance. The intensity of each satellite set will be 16.18% that of the central $^{19}F$ resonance. The second set of $^{117/119}Sn$ satellites corresponds to the situation where the bridging fluoride is bonded to two NMR active tin nuclei and gives rise to a triplet sub-spectrum where the satellites are at $J$(Sn–F) about the central $^{19}F$ resonance. The intensity of each satellite set will be 0.65% of the intensity of the central $^{19}F$ resonance. Comparison of a computer-simulated $^{19}F$ NMR spectrum of *trans*-$[(Me_3SnCl)_2F]^-$ with the observed spectrum (Fig. 2) clearly shows both sets of satellites, even though there are some unidentified resonances of weak intensity overlapping them on the low frequency side of the central resonance.

The $^{119}Sn$ doublet (denoted 6 in Fig. 1) is assigned to $[Me_3SnClF]^-$. The apparent triplet (denoted 5 in Fig. 1) and the doublet (denoted 4 in Fig. 1) are assigned to $[(Me_3SnF)F(Me_3SnCl)]^-$. This assignment requires that the apparent triplet, 5, should actually be a doublet of doublets but the spectral resolution was too low to enable confirmation of this multiplicity. Interpretation of the $^{19}F$ NMR spectra of dichloromethane solutions is ambiguous and these assignments could not be corroborated. Fortunately spectra in acetone solution were clearer and support these assignments (see below).

The $^{119}Sn$ singlet (denoted 1 in Fig. 1) was tentatively assigned to $[Me_3SnCl_2]^-$. However $^{119}Sn$ NMR spectra of dichloromethane solutions at −100 °C with $Bu_4NCl$ to $Me_3SnCl$ molar ratios of 1:4, 1:2, 1:1 and 2:1 show singlet resonances at 68, 30, −43 and −53 ppm, respectively. Examination of the spectra for each of these solutions over the temperature range from −100 to 25 °C showed little change in position for the latter three resonances whilst the resonance at 68 ppm broadens and shifts to 101 ppm at 25 °C. These observations are interpreted in terms of the following exchange process in solution

$$Me_3SnCl + Cl^- \rightleftharpoons [Me_3SnCl_2]^-$$

and the resonances observed for ratios 1:4, 1:1 and 2:1 are average for the two tin species in the equilibrium. Perhaps the resonance at −53 ppm is the closest to

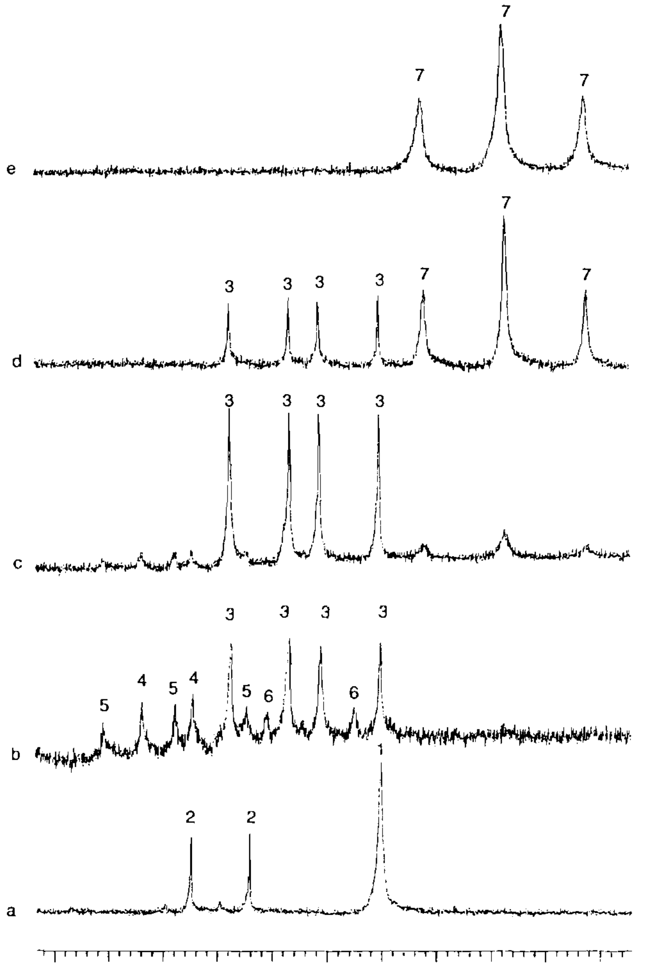


Fig. 1. $^{119}Sn$ NMR spectra at −100 °C on 0.25 M [Sn] dichloromethane solutions containing $Bu_4NF \cdot 3H_2O$ and $Me_3SnCl$ at molar ratios of 1:2 (a), 3:2 (b), 7:4 (c), 2:1 (d) and 3:1 (e).

the actual chemical shift of $[Me_3SnCl_2]^-$. A similar exchange process has been reported for the analogous tributyltin(IV) system [8].

In order to understand the process of reaction of fluoride with $Me_3SnCl$ in dichloromethane solvent, it is useful to find the relationship between the formation of tin species and the fluoride to tin ratio used to prepare the solutions. It appears that formation of tin–fluoride bonds is thermodynamically favoured and that one tin species can be converted to another by adjusting the fluoride to $Me_3SnCl$ ratio. However, the species formed do not completely parallel the solution stoichiometry. For example *trans*-$[(Me_3SnF)_2F]^-$ is not totally converted to $[Me_3SnF_2]^-$ until the fluoride to tin ratio approaches 5:2. This indicates the existence of a series of equilibria which become clearer when acetone is used as solvent (Scheme 2).

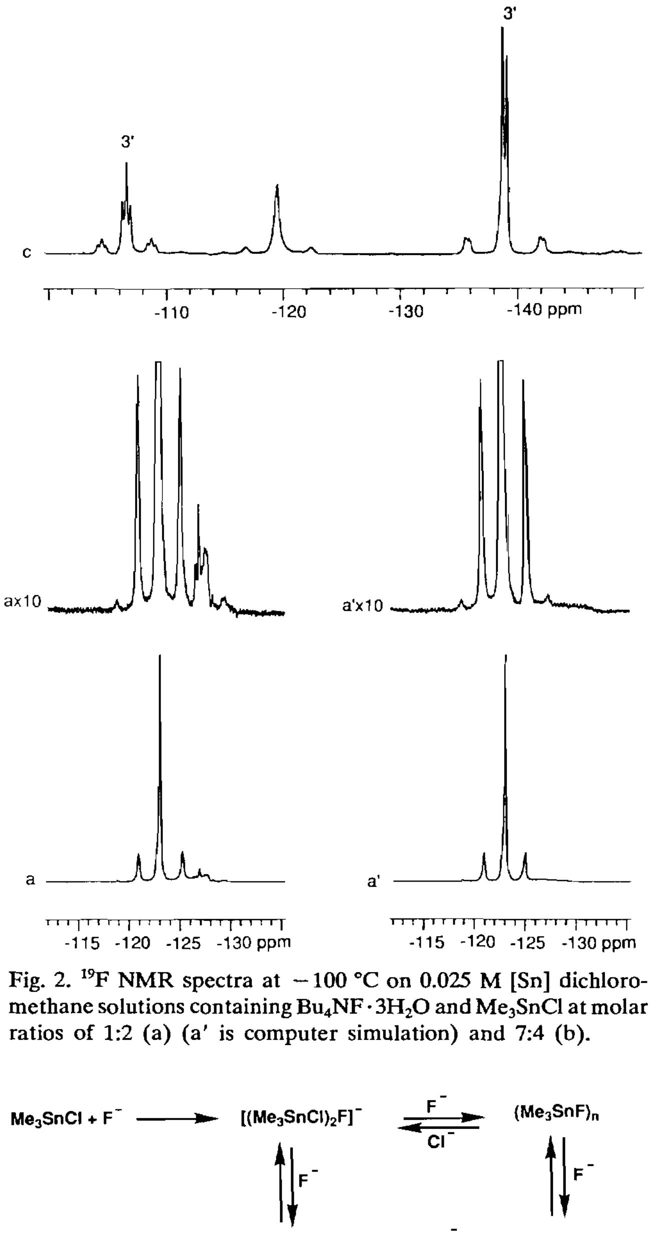
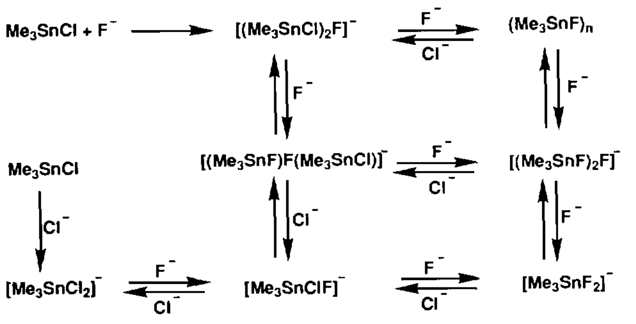


Fig. 2. $^{19}F$ NMR spectra at −100 °C on 0.025 M [Sn] dichloromethane solutions containing $Bu_4NF \cdot 3H_2O$ and $Me_3SnCl$ at molar ratios of 1:2 (a) (a' is computer simulation) and 7:4 (b).



Scheme 2.

## *Acetone solutions*

Preparation of samples from fluoride and $Me_3SnCl$ in acetone instead of dichloromethane solution is also accompanied by some $Me_3SnF$ precipitation, however these solutions became completely clear as the fluoride to $Me_3SnCl$ ratio approaches 3:4. The spectra of acetone solutions containing samples with fluoride to $Me_3SnCl$ ratios of 1:2 and greater than 2:1 were similar to those of dichloromethane solutions except for small changes in chemical shift positions (Fig. 3). All NMR data obtained on acetone solutions are listed in Table 2.

Resonances attributed to *trans*-$[(Me_3SnCl)_2F]^-$ were observed in acetone at $-100$ °C for solution of 1:2 ratio of fluoride to $Me_3SnCl$. The $^{119}Sn$ spectrum contains a doublet at $-44$ ppm with the coupling constant $J$(Sn–F) (1086 Hz) similar to that observed in dichloromethane solution (1080 Hz). The $^{19}F$ spectrum shows a main resonance associated with two sets of $^{119/117}Sn$ satellites as was described above for dichloromethane solvent, indicative of a fluoride-bridged species. Resonances for *trans*-$[(Me_3SnF)_2F]^-$, $[Me_3SnF_2]^-$ and $[Me_3SnCl_2]^-$ are also observed in acetone solutions (Fig. 3). The species $[Me_3SnClF]^-$ is clearly identified in acetone solution (the doublet denoted 6 in Fig. 3). This latter assignment is supported by the $^{119}Sn$ and $^{19}F$ NMR spectra of an acetone solution containing $Me_3SnCl$, chloride and fluoride in molar ratio 1:1:1 in which the most intense resonances are observed at the same shift positions. The $^{119}Sn$ resonances denoted 4 and 5 in Fig. 3, a doublet and a doublet of doublets, support the assignments for $[(Me_3SnF)F(Me_3SnCl)]^-$ (structure **IX**). The corresponding $^{19}F$ spectrum contains two equal intensity doublets, one of which is accompanied by two sets of tin satellites (Table 2), supporting the formation of $[(Me_3SnF)F(Me_3SnCl]^-$.

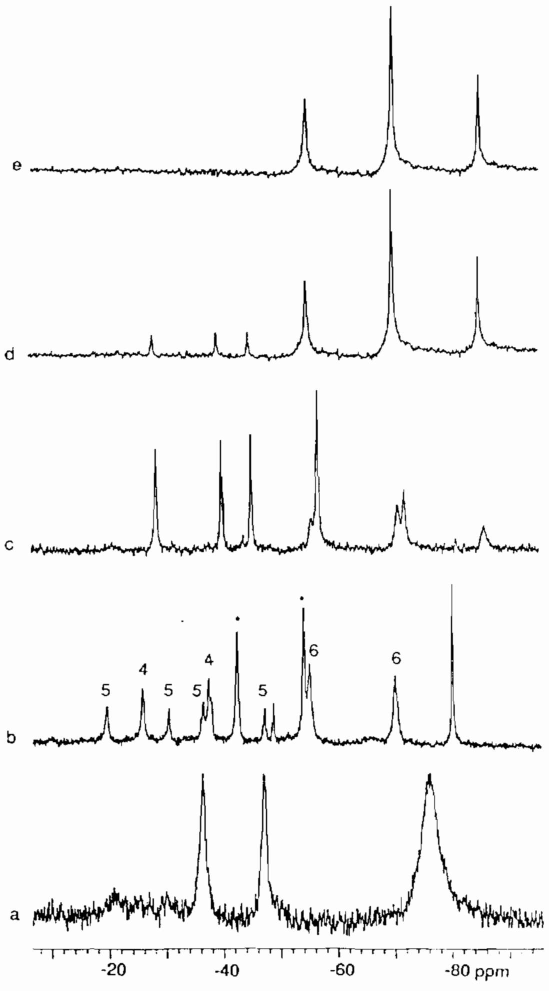
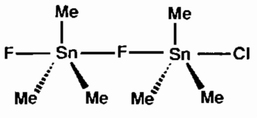


Fig. 3. $^{119}Sn$ NMR spectra at $-100$ °C on 0.25 M [Sn] acetone solutions containing $Bu_4NF \cdot 3H_2O$ and $Me_3SnCl$ at molar ratios of 1:2 (a), 1:1 (b), 3:2 (c), 2:1 (d) and 3:1 (e).

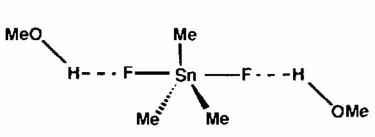


IX

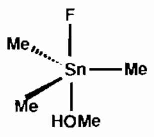
The $^{119}Sn$ doublet (denoted * in Fig. 3) at $-48$ ppm with $J$(Sn–F) of 1172 Hz remains unassigned although a comparison of the magnitude of the coupling constant with those of fluoride-bridged species (which have $J$(Sn–F) in the range 1080–1172 Hz), implies this doublet resonance also may arise from a fluoride-bridged species. Further assignment was unsuccessful because the $^{19}F$ resonance associated with this tin species was very broad. The unidentified species only appears in acetone solutions with fluoride to $Me_3SnCl$ ratios between 1:2 and 3:2.

*Methanol solutions*

In contrast to the results obtained for dichloromethane and acetone solvents, the $^{119}Sn$ NMR spectra at $-100$ °C of methanol solutions containing different fluoride to $Me_3SnCl$ ratios are very simple and contain only a singlet, a doublet and a triplet resonance. Except for the fluoride to $Me_3SnCl$ ratio of 2:1 all other spectra were recorded on methanol solutions which contained some precipitate. The $^{119}Sn$ triplet resonance is assigned to $[Me_3SnF_2]^-$ and its high frequency shift (at $-20$ ppm compared to $-74$ ppm in dichloromethane and $-73$ ppm in acetone) and smaller $J$(Sn–F) value (1318 Hz) may be due to formation of fluoride–hydrogen bonds as shown in structure **X**. The $^{119}Sn$ doublet resonance is attributed to a monomeric methanol adduct of $Me_3SnF$, possibly with the five-coordinate structure **XI**. The singlet $^{119}Sn$ resonance is assigned to an exchange average for $Me_3SnCl$ and $[Me_3SnCl_2]^-$ similar to that described above for dichloromethane solvent. A summary of the NMR data of reactions of fluoride with trimethyltin(IV)chloride in methanol solution is given in Table 2.



X



XI

## Conclusions

Both acetone and methanol may act as donor ligands in the systems investigated and the $^{119}$Sn NMR data for four-coordinated $R_3SnCl$ (R = Ph and Me) can be interpreted based on the presence of equilibrium

$$R_3SnCl + Solvent \rightleftharpoons R_3SnCl\ Solvent$$

(R = Ph and Me, Solvent = methanol and acetone)

which lies more strongly to the right for methanol than for acetone, in line with its stronger Lewis basicity. The fact that $[Me_3SnF_2]^-$ has similar $^{119}$Sn and $^{19}$F chemical shifts and the coupling constant $J$(Sn–F) in both acetone and dichloromethane but different from those in methanol reflect the fact that only the latter solvent can participate in hydrogen bonding. The fact that fluoride-bridged dimers are observed in dichloromethane and acetone solution but not in methanol is also attributed to the stronger Lewis base strength of methanol.

There is no evidence for methyl group migration involving reactions of trimethyltin(IV) complexes. It may be that the phenyl group, which is more strongly electron withdrawing than the methyl group, gives the Sn–C bond more ionic character in triphenyltin and subsequently renders it more easily broken in the presence of additional ligands. Furthermore, fluoride is more electronegative than chloride which would make the tin atom more electropositive in phenyltin(IV)–fluoride than in phenyltin(IV)–chloride systems. This would also increase the ionic character of the Sn–C bond in fluoro complexes thereby leading to phenyl group migration. The fact that fluoride-bridged triorganotin(IV) species are formed for alkyl derivatives (R = Me, $^n$Bu) but not for R = Ph may be steric in nature. The three phenyl groups bonded in an equatorial plane about tin are likely to adopt a propellor-like configuration to minimise mutual electronic repulsion. This configuration is likely to put steric stress on any monoatomic ligand capable of bridging the two tin centres.

There is no evidence for formation of any chloride-bridged dimers, $[(R_3SnX)Cl(R_3SnX')]$ (R = Ph, Me; X = F, Cl; X′ = F, Cl) despite the fact that all three possible fluoride-bridged dimers are observed. The fact that chloride is less electronegative or more weakly electron withdrawing than fluoride makes chloride in $[(R_3SnX)Cl]^-$ (X = F, Cl) a weaker Lewis acid than fluoride in $[(R_3SnX)_2F]^-$ (X = F, Cl). Consequently, chloride-bridged dimers $[(R_3SnX)Cl(R_3SnX')]^-$ are anticipated to be more labile than the fluoride analogues, $[(R_3SnX)F(R_3SnX')]^-$.

## Acknowledgement

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