Journal of Organometallic Chemistry, 371 (1989) 145–154
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 09911

Quaternary ammonium tributyldifluorostannates: their structure in solution, including a novel *trans*-F bridged species, $\{(Bu_3SnF)_2F\}^-$

Stephen J. Blunden and Robin Hill

International Tin Research Institute, Kingston Lane, Uxbridge, Middlesex UB8 3PJ (Great Britain)

(Received February 16th, 1989)

Abstract

^{19}F and ^{119}Sn variable temperature NMR studies have been carried out on toluene solutions of two quaternary ammonium tributyldifluorostannates, $\{Bu_4N\}\{Bu_3SnF_2\}$ and $\{(C_6H_5CH_2)Me_2NC_{14}H_{29}\}\{Bu_3SnF_2\}$. They show in both cases the presence of two distinct tributyltin species in equilibrium, the *trans*-$\{Bu_3SnF_2\}^-$ and *trans*-$\{(Bu_3SnF)_2F\}^-$ anions. The latter is believed to be a novel type of species. The effect of substituting F by Cl was investigated by a ^{119}Sn NMR study of two analogous compounds, $\{(C_6H_5CH_2)Me_2NC_{14}H_{29}\}\{Bu_3SnClF\}$ and $\{(C_6H_5CH_2)Me_2NC_{14}H_{29}\}\{Bu_3SnCl_2\}$. The ^{119m}Sn Mössbauer data for the above compounds are also presented and discussed.

Introduction

In recent years, tributyltin compounds, in particular bis(tributyltin) oxide, have found [1] extensive use as fungicides in organic solvent based wood preservatives. It has been reported [2] that the total tin content of timber treated with bis(tributyltin) oxide decreases with time. Although a pathway for this phenomenon, involving the formation of tetrabutyltin, has been elucidated [3], a line of thought, aimed at overcoming this problem, was to use less volatile tributyltin compounds, e.g. tributyltin fluoride, Bu_3SnF. However, owing to the low solubility of this organotin species, in order to achieve dissolution in organic solvents it is necessary [4] to add a suitable quaternary ammonium fluoride, R_4NF, and thereby produce a species of empirical formula $(R_4N)^+(Bu_3SnF_2)^-$.

We report, herein, results of an NMR investigation of two such species that has led to the elucidation of their structure in solution, together with similar studies of analogous compounds. In addition, Mössbauer parameters of these derivatives are reported.

0022-328X/89/$03.50

Experimental

Synthesis

The following compounds were obtained from Ciba–Geigy Marienberg GMBH, W. Germany, and were used without further purification: $\{(C_6H_5CH_2)Me_2NC_{14}H_{29}\}\{Bu_3SnF_2\}$ (I), $\{(C_6H_5CH_2)Me_2NC_{14}H_{29}\}\{Bu_3SnClF\}$ (III), and $\{(C_6H_5CH_2)Me_2NC_{14}H_{29}\}\{Bu_3SnCl_2\}$ (IV).

Tetrabutylammonium tributyldifluorostannate, $\{Bu_4N\}\{Bu_3SnF_2\}$ (II) was prepared by the azeotropic dehydration of equimolar quantities of $Bu_4NF \cdot 3H_2O$ and Bu_3SnF in boiling toluene using a Dean and Stark separator, and was used without further purification.

Spectroscopic studies

NMR spectra were recorded on a JEOL FX60Q spectrometer, with field frequency lock to external D_2O. ^{119}Sn spectra were recorded at 22.24 MHz under nuclear Overhauser suppressed conditions. ^{119}Sn chemical shifts ($\delta(^{119}Sn)$) are relative to Me_4Sn at 30 °C and are accurate to ± 0.1 ppm. ^{19}F spectra were recorded at 56.22 MHz; ^{19}F chemical shifts ($\delta(^{19}F)$) are relative to CF_3CO_2H at 30 °C and are accurate to ± 0.1 ppm.

The ^{119m}Sn Mössbauer spectra were obtained by using a constant acceleration microprocessor spectrometer (E.S. Technology Limited, Oxford) with a 512-channel data store. A 5 mCi $Ba^{119m}SnO_3$ source was used at room temperature and the samples were cooled to 80 K by means of a liquid nitrogen cryostat. The spectra were computer-fitted to a sum of Lorentzian curves by a least squares procedure. The experimental error in the measured values of isomer shift (δ), quadrupole splitting (ΔE_q) and linewidths (Γ) is ± 0.1 mm s^{-1}.

Results and discussion

^{19}F and ^{119}Sn NMR spectra of I (20% *m*/v in toluene), at 80 °C, were recorded and are shown in Fig. 1. When the temperature was lowered progressively, the NMR spectra showed increasingly broadened resonances until at 0 °C evidence of further structure appeared. Additional cooling to -20 °C resulted in the spectrum shown in Fig. 2. Below this temperature, the spectra remained essentially unchanged except that the peaks became broader due to increased solution viscosity.

Examination of the ^{19}F spectrum at -20 °C (Fig. 2), indicated the presence of satellites, due to ^{19}F–$^{117/119}Sn$ coupling, associated with most of the major peaks. In addition, the asymmetry of the peak at -58.6 ppm, suggests an unresolved resonance.

The ^{19}F and ^{119}Sn NMR spectra of a sample of an analogous quaternary ammonium tributyldifluorostannate, II, were recorded for a 20% *m*/v toluene solution over the same temperature range as for I. With the exception of small differences in relative peak intensities and chemical shift positions, spectral changes observed were essentially the same in both cases, except that owing to the lower solution viscosity, optimum resolution for II was achieved at -40 °C (Fig. 3). One feature worth specific mention, was that in the ^{19}F spectrum of II, at -40 °C, a triplet was observed at -55.4 ppm. Thus, the unresolved feature in the ^{19}F spectrum of I, at -20 °C, was ascribed to such a multiplet.

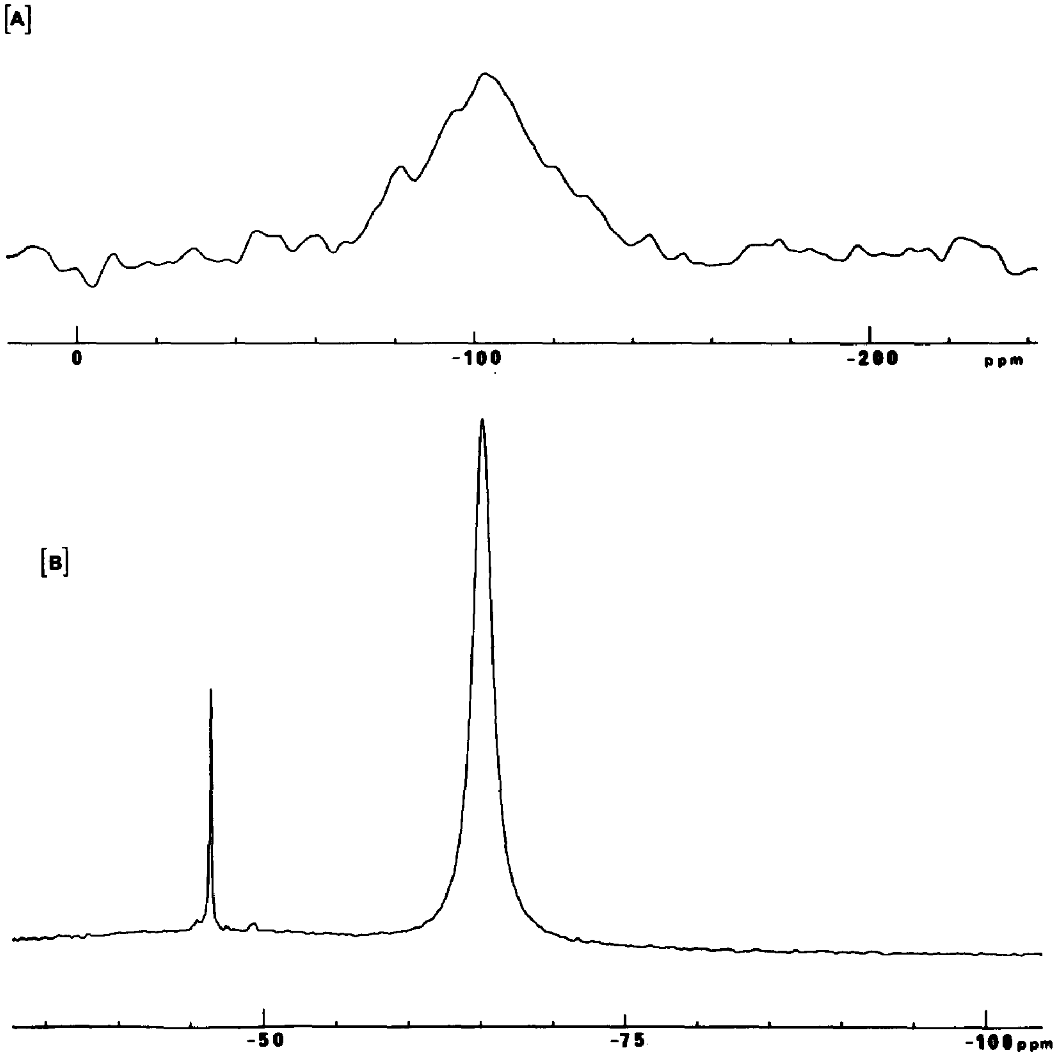


Fig. 1. (A) ^{119}Sn and (B) ^{19}F NMR spectra of I at +80 °C.

The ^{119}Sn NMR spectra shown in Fig. 2 and 3 may be interpreted in terms of ^{119}Sn–^{19}F coupling interactions as shown in Fig. 4 and 5. Thus it is apparent that two different tin environments are present in solution at these temperatures. The ^{19}F NMR spectra indicate the presence of four different fluorine environments with chemical shifts and coupling interactions as given in Table 1. It should be noted that integration of the spectrum of II revealed that the doublet and triplet features were in the ratio 2/1.

The reported NMR data can only be interpreted in terms of the presence of two organotin species in solution. The first is judged to be the *trans*-$\{Bu_3SnF_2\}^-$ anion, structure A. Thus, resonances at $\delta(^{19}F)$ −58.6 ppm (Table 1) and $\delta(^{119}Sn)$ −135.1 ppm (Fig. 4) and $\delta(^{19}F)$ −61.5 ppm (Table 1) and $\delta(^{119}Sn)$ −147.1 ppm (Fig. 5) in the NMR spectra of I and II, respectively, are ascribed to this species. With respect to the identity of the second, the observed NMR spectra are consistent with the anion $\{(Bu_3SnF)_2F\}^-$, which may have three alternative structures, **B**, **C**, or **D**. It

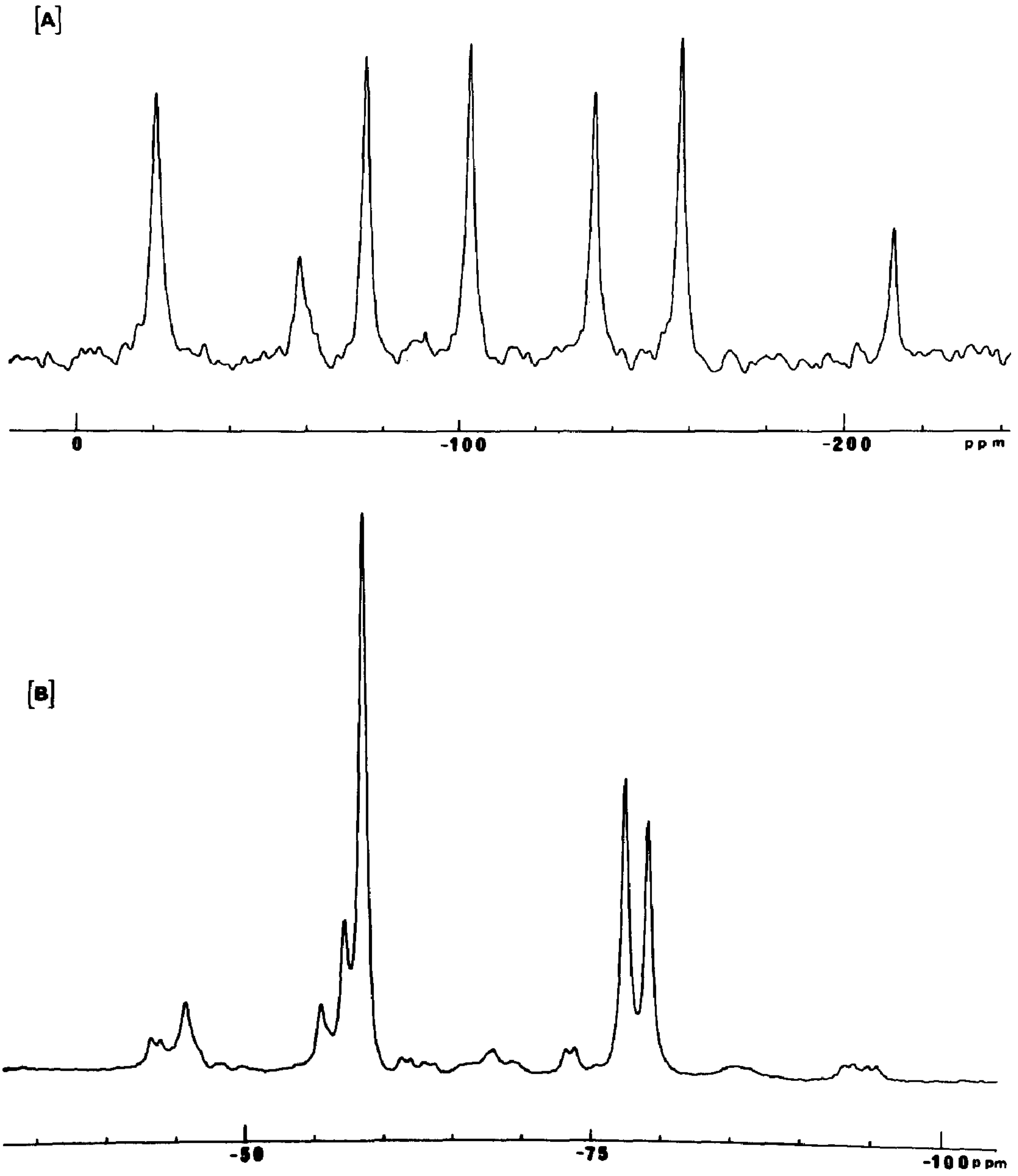


Fig. 2. (A) ^{119}Sn and (B) ^{19}F NMR spectra of I at −20 °C.

has been reported [5] that the $^{1}J(^{119}Sn-^{19}F)$ coupling interaction in polymeric tributyltin fluoride is 1291 Hz. This compound is expected to contain chains of F–Sn–F–Sn–F atoms, in which, *trans*-Bu_3SnF_2 units share common fluorine atoms, on the basis of an X-ray diffraction study of trimethyltin fluoride [6]. The similarity of the magnitude of the $^{1}J(^{119}Sn-^{19}F)$ coupling interaction observed for tributyltin fluoride and that of the bridging fluorine in $\{(Bu_3SnF)_2F\}^-$ (1220 and 1212 Hz for I and II respectively) may imply that the anionic species, in each case, is **B**. In addition, the bridging fluorine atom must be symmetrically disposed, at least on the

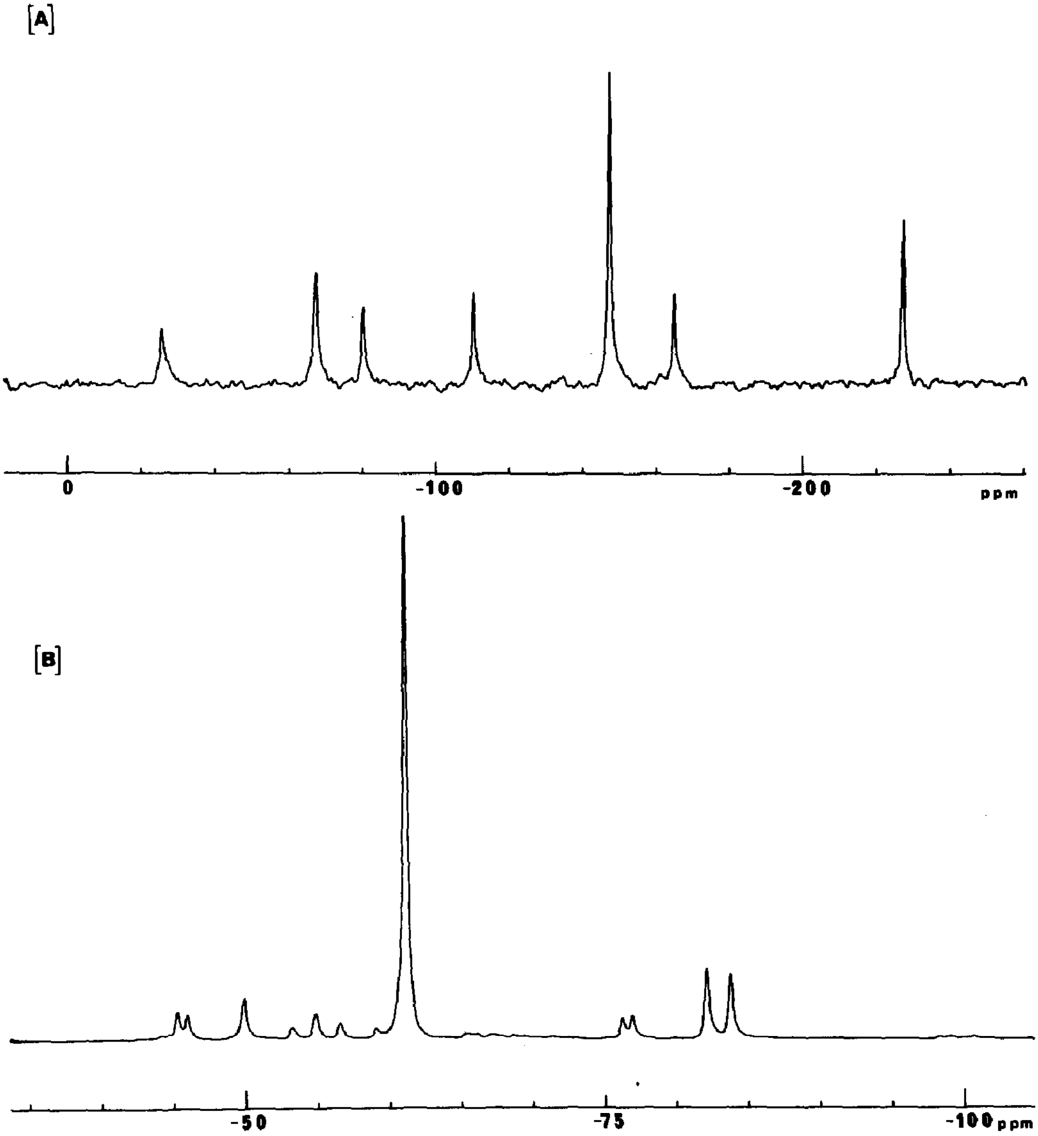
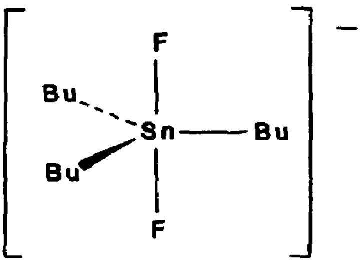


Fig. 3. (A) ^{119}Sn and (B) ^{19}F NMR spectra of II at −40 °C.



(A)

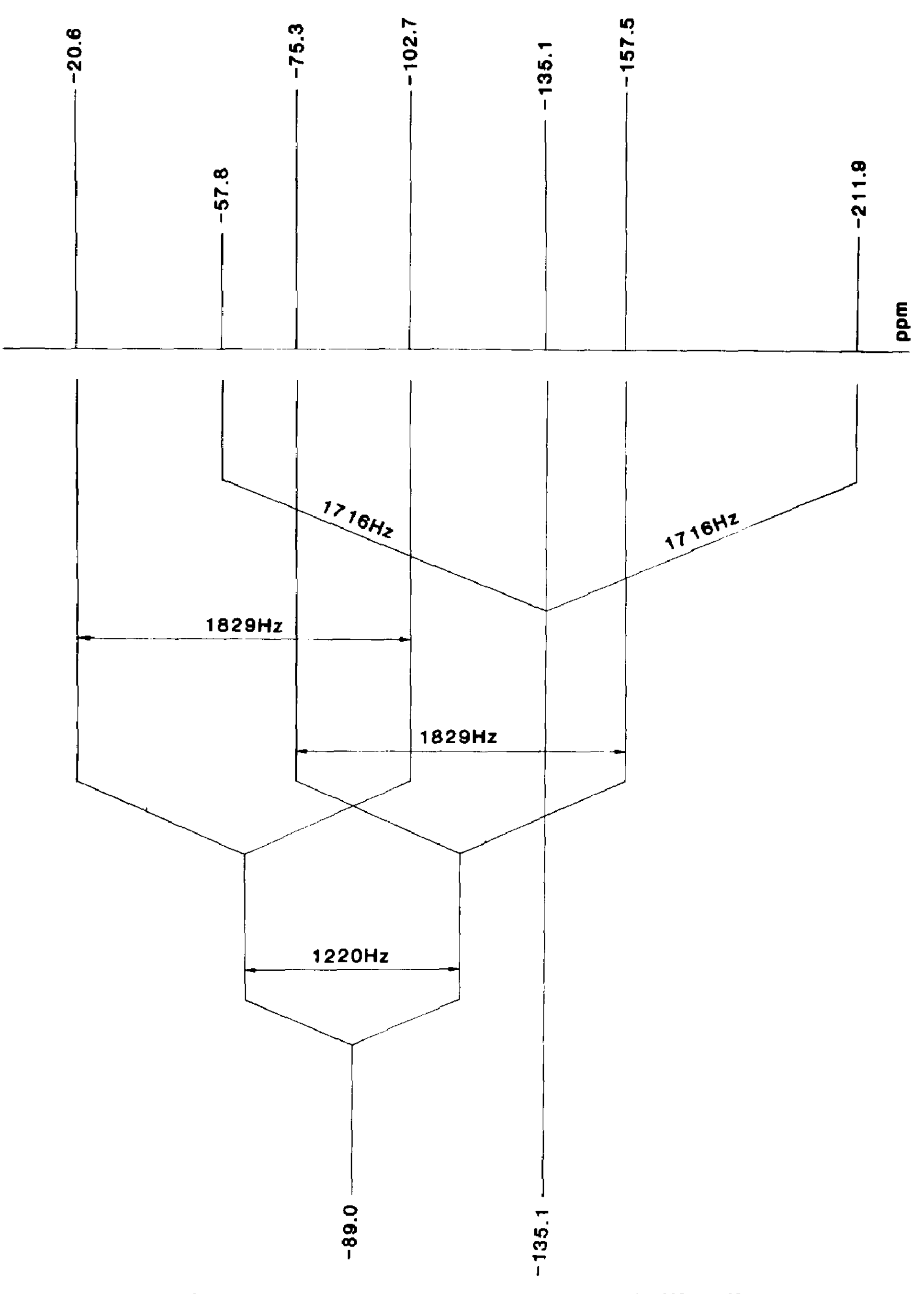
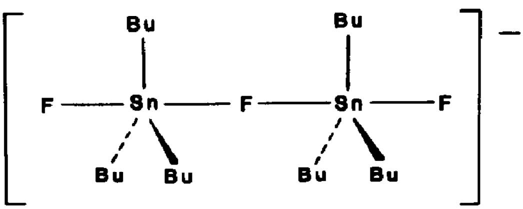


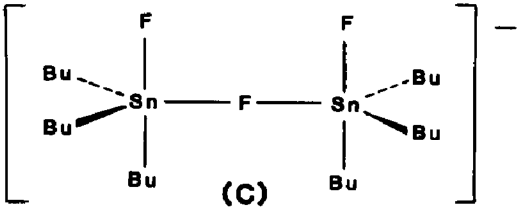
Fig. 4. Schematic ^{119}Sn NMR spectrum of I at −20 °C showing $^{1}J(^{119}Sn-^{19}F)$ coupling interactions.

NMR time scale, between the two tin atoms, as evidenced by the triplet feature in the ^{19}F NMR spectra. To our knowledge, this is the first observation of a structure of type **B** in organotin chemistry.

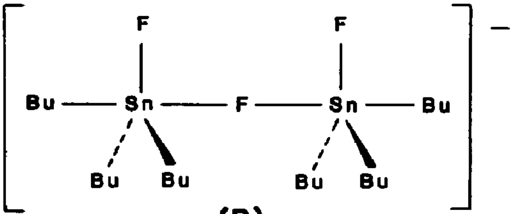
A singlet is observed at all temperatures in the ^{19}F NMR spectra of I (at approx. −46 ppm) and in the −40 °C spectrum of II (at 50.3 ppm). These do not have associated tin satellites, and so the fluorine atoms which give rise to these are not directly bonded to tin. It can be seen that in a mixture of F$^-$ and tributyltin fluoride



(B)



(C)



(D)

the formation of both $\{Bu_3SnF\}^-$ and $\{(Bu_3SnF)_2F\}^-$ does not fully account for the fluoride ion concentration, and so the singlet is ascribed to the free fluoride ion in solution.

The changes in the ^{19}F and ^{119}Sn NMR spectra over the temperature range studied indicate the occurrence of an exchange between $(Bu_3SnF_2)^-$ and $\{(Bu_3SnF)_2F\}^-$ in solutions of both I and II. Additionally, it can be seen from Fig. 2 and 3 that ions of $\{(Bu_3SnF)_2F\}^-$ were formed to a greater extent from I than from II. Hence, the counter cation influences the stability of the two tributyltin anions, the larger cation favouring $\{(Bu_3SnF)_2F\}^-$.

Table 1

^{19}F NMR parameters for I and II at −20 and −40 °C, respectively [a]

Compound	$\delta(^{19}F)$ (ppm)	Multiplicity	$^2J(^{19}F\text{–}Sn\text{–}^{19}F)$ (Hz)	$^1J(^{19}F\text{–}^{119}Sn)$ (Hz)
I	−45.8	Singlet	–	–
	−57.2	Triplet	93	1220
	−58.6	Singlet	–	1720
	−78.3	Doublet	92	1830
II	−50.3	Singlet	–	–
	−55.4	Triplet	93	[b]
	−61.5	Singlet	–	1783
	−83.4	Doublet	94	1890

[a] Toluene solution (20% *m*/v). [b] Not observed.

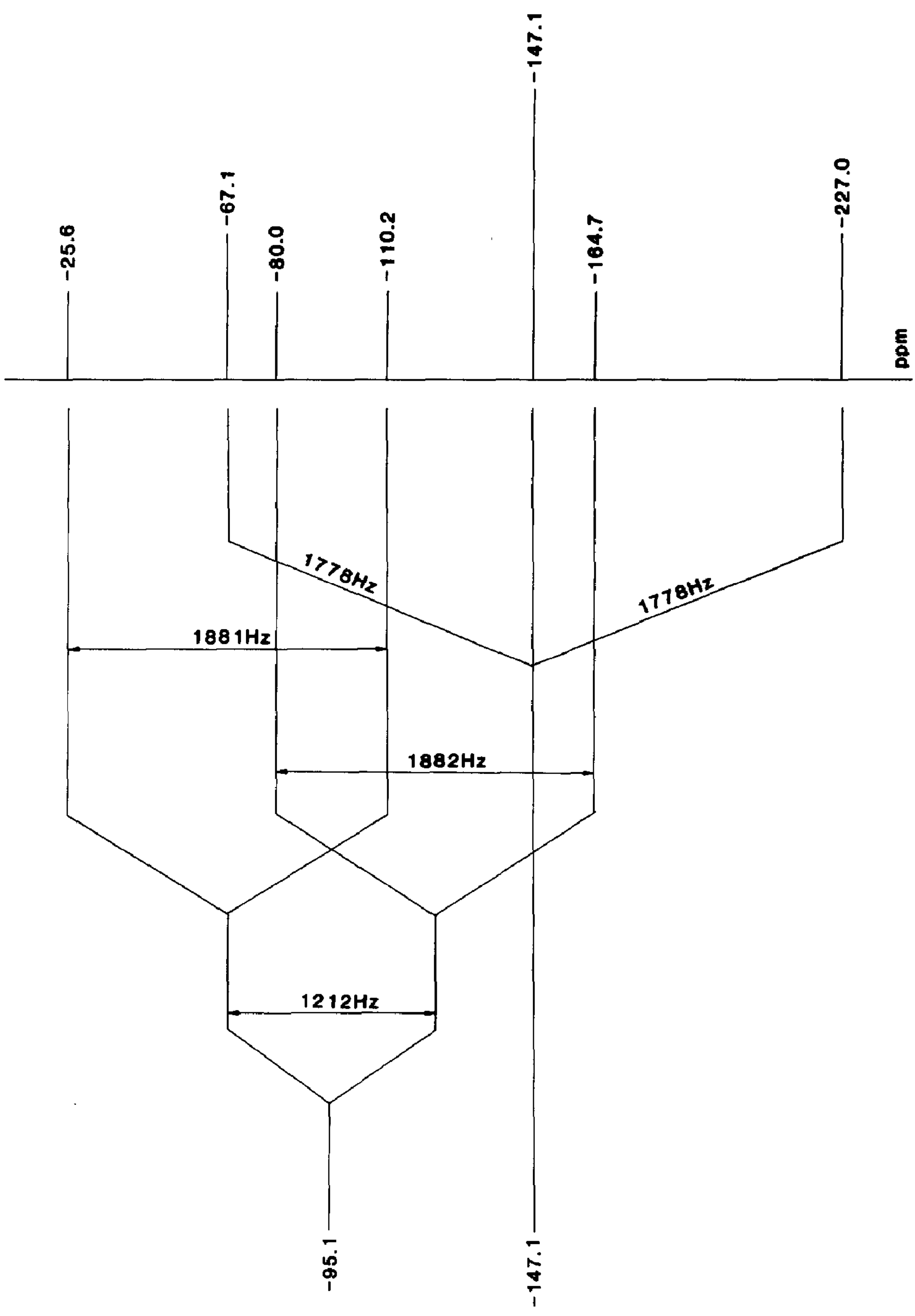


Fig. 5. Schematic ^{119}Sn NMR spectrum of II at $-40\,^{\circ}$C showing $^{1}J(^{119}\mathrm{Sn}-^{19}\mathrm{F})$ coupling interactions.

In order to investigate the effect of substituting F by Cl, ^{119}Sn NMR spectra were recorded for two analogous derivatives, III and IV, over the temperature range $+80$ to $-40\,^{\circ}$C in toluene solution (20% *m*/v). In the case of III at $80\,^{\circ}$C, a single peak (line width approx 48 Hz), centred at -46.9 ppm, was observed which on cooling to $40\,^{\circ}$C became progressively broader (line width approx. 500 Hz). Further cooling to

Table 2

^{119}Sn chemical shift data for IV [a]

Temperature (°C)	$\delta(^{119}Sn)$ (ppm)
80	14.0
40	−11.8
30	−17.0
0	−31.5
−20	−38.5
−40	−44.2

[a] Toluene solution (20% *m*/v).

0°C resulted in the appearance of possibly three very broad and overlapping resonances (each line width approx. 950 Hz), centred at approximately 0, −20 and −50 ppm. Additional cooling led to precipitation of the sample from solution. On the basis of this observation, it seems possible that this compound may also exist in more than one form, but, additional investigations would be required to verify this. The NMR study of IV (Table 2) showed a single resonance at all temperatures (line widths approx. 20 Hz at +80°C and 10 Hz at −40°C), which moved to lower frequency on reducing the temperature. Tributyltin chloride has a ^{119}Sn NMR chemical shift in non-coordinating solvents of approximately 144 ppm. Additionally, it is known [7] that ^{119}Sn NMR chemical shifts are indicative of coordination number, an increase in which is accompanied by a shift to low frequency. Thus, the observed chemical shift changes (Table 2) may be interpreted in terms of the following exchange process in solution:

$$Bu_3SnCl + Cl^- \rightleftharpoons (Bu_3SnCl_2)^-$$

with the anionic organotin species being favoured by lowering of the temperature.

^{119m}Sn Mössbauer parameters were obtained for compounds I–IV and are reported in Table 3 together with published values for tributyltin fluoride (V) and tetrabutylammonium tributyldichlorostannate (VI). As expected, the isomer shifts are in the order IV > III > I and VI > II, in line with the greater electronegativity of fluorine than of chlorine [10]. Five-coordinate triorganotin complexes, R_3SnX_2, may exist in different trigonal bipyramidal isomeric forms, two of which are the *cis* and *trans* structures. Mössbauer ΔEq values have been reported for these and are expected to be in the ranges 1.70–2.40 mm s^{-1} and 3.00–4.00mm s^{-1} for *cis* and

Table 3

^{119}Sn Mössbauer parameters

Sample	δ (mm s^{-1})	ΔEq (mm s^{-1})	Γ_1 (mm s^{-1})	Γ_2 (mm s^{-1})
I	1.25	3.14	1.16	1.28
II	1.19	2.90	1.19	1.33
III	1.39	3.80	1.07	1.01
IV	1.50	3.48	1.17	1.23
V	1.40 [a]	3.71 [a]	[b]	[b]
VI	1.52 [c]	3.55 [c]	[b]	[b]

[a] Ref. 8. [b] Not reported. [c] Ref. 9.

trans, respectively [7]. Thus, on the basis of this, all the compounds shown in Table 3 would be predicted to adopt the *trans* configuration. The NMR studies of I and II have shown the presence of two structure in toluene solution, i.e. **A** together with **B** or **C** or **D**. In distinguishing between the latter three structures, **C** and **D** may be eliminated since no evidence was obtained for a ΔEq value in the range 1.70–2.40 mm s^{-1} in the spectra of either I or II. Thus, the parameters reported in Table 3 must be a weighted mean of **A** and **B**. It is unlikely that Mössbauer spectroscopy will distinguish between these closely related structures.

Conclusion

This work has demonstrated that the quaternary ammonium tributyldifluorostannates $\{(C_6H_5CH_2)Me_2NC_{14}H_{29}\}\{Bu_3SnF_2\}$ and $\{Bu_4N\}\{Bu_3SnF_2\}$ each give two distinct tributyltin species in toluene solution, namely the *trans*-$\{Bu_3SnF_2\}^-$ and *trans*-$\{(Bu_3SnF)_2F\}^-$ anions, which have been shown to be in equilibrium. To our knowledge, the latter represents a novel type of structure in organotin chemistry.

Acknowledgements

The International Tin Research Institute is thanked for permission to publish this paper. The authors are grateful to Ciba–Geigy Marienberg GMBH for generous gifts of three of the quaternary ammonium tributyldifluorostannates used in this study. Miss B. Patel, ITRI, is thanked for experimental assistance.

References

1 S.J. Blunden, P.A. Cusack and R. Hill. The Industrial Uses of Tin Chemicals, Royal Society of Chemistry, London, 1985.
2 F. Imsgard, B. Jensen, H. Plum and H. Landsiedel, Rec. Ann. Conv. Brit. Wood Preserv. Assoc., (1985) 47.
3 S.J. Blunden and R. Hill, Appl. Organomet. Chem., 2 (1988) 251.
4 S.J. Blunden and R. Hill, unpublished work, 1988.
5 R.K. Harris, K.J. Packer and P. Reams, Chem. Phys. Lett., 115 (1985) 16.
6 H.C. Clark, R.J. O'Brien and J. Trotter, J. Chem. Soc., (1964) 2232.
7 A.G. Davies and P.J. Smith, in G. Wilkinson (Ed.), in Comprehensive Organometallic Chemistry, Vol. 2, Pergamon Press, New York, 1982, p. 519.
8 R.H. Herber, J. Chem. Phys., 54 (1971) 3755.
9 J.W. Nicholson, J.A. Douek and A.J. Crowe, J. Organomet. Chem., 219 (1981) 309.
10 L.A. Hobbs and P.J. Smith, J. Organomet. Chem., 206 (1981) 59.