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THE PREPARATION AND ^{119}Sn AND ^{19}F NMR SPECTRA OF SOME TRIFLUOROMETHYLPHENYLTIN(IV) COMPOUNDS

MARY BARNARD, PETER J. SMITH* and R.F.M. WHITE

Chemistry Department, City of London Polytechnic, Sir John Cass School of Science and Technology, Jewry Street, London EC3N 2EY (Great Britain)

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Summary

The preparation of a series of new trifluoromethylphenyltin(IV) compounds, $Bu_nSn(C_6H_4CF_3\text{-}3)_{4-n}$, $(C_6H_4CF_3\text{-}3)SnCl_3$, $(C_6H_4CF_3\text{-}2)SnCl_3$, and some related adducts with 2,2′-bipyridyl and 1,10-phenanthroline, is described. ^{119}Sn and ^{19}F chemical shifts have been determined, together with values of $J(^{119}Sn—F)$ and $^3J(^{119}Sn—H_{ortho})$, and the possibility of a "through space" tin—fluorine coupling mechanism is also discussed.

Introduction

The versatile technique of heteronuclear magnetic double resonance [1] has greatly facilitated the measurement of ^{119}Sn chemical shifts of organotin compounds, and, at the present time, results have already been obtained for approximately 500 different derivatives [2].

Earlier tabulations of ^{119}Sn chemical shift data [3—6] have, in general, consisted of groups of largely unrelated organotin compounds, Recently, however, studies of a more systematic nature have appeared, e.g. organotin dialkylamides [7], alkoxides [8,9], selenides [10] and thiolates [11]. These have included the determination of equilibrium constants from the temperature and concentration dependence of the ^{119}Sn chemical shifts [4,8,9] and the elucidation of tin atom geometries in solution from the magnitude of the shifts [8,9]. We describe below the preparation of a number of new trifluoromethylphenyltin compounds and the determination of their ^{119}Sn chemical shifts by heteronuclear magnetic double resonance. The trends observed in the tin-119 chemical shifts of these molecules are discussed and the possibility of a "through space" tin—fluorine interaction is also considered.

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* Present address: The Tin Research Institute, Fraser Road, Greenford, Middlesex (Great Britain).

TABLE 1

NMR DATA FOR TRIFLUOROMETHYLPHENYLTIN COMPOUNDS

Compound	$\delta(^{119}\mathrm{Sn})$[a] (ppm)	$\delta(^{19}\mathrm{F})$[b] (ppm)	$J(^{119}\mathrm{Sn}$—F) (Hz)	$^{3}J(^{119}\mathrm{Sn}$—H_o) (Hz)
Bu_3SnPh	45			60 ± 3
$Bu_3SnC_6H_4CF_3$-2	25	—15.4	< 10[c]	60 ± 5
$Bu_3SnC_6H_4CF_3$-3	38	—15.5		63 ± 2
$Bu_2Sn(C_6H_4CF_3\text{-}3)_2$	68	—15.6		73 ± 2
$BuSn(C_6H_4CF_3\text{-}3)_3$	95	—15.1		58 ± 3
$Sn(C_6H_4CF_3\text{-}3)_4$	128[d]	—15.9		48 ± 5
$Sn(C_6H_4CF_3\text{-}3)_4$	139[e]	—17.9		50 ± 3
$SnPh_4$	140 ± 10			
$SnPh_4$	120 ± 20[f]			
$PhSnCl_3$	64[d]			120 ± 3
$PhSnCl_3$	63 ± 0.5[g]			122[h]
$(C_6H_4CF_3\text{-}2)SnCl_3$	85[i]	—20.7	28 ± 1	125 ± 3
$(C_6H_4CF_3\text{-}3)SnCl_3$	69	—16.1	11 ± 1	115 ± 3
$Ph_3Sn(CH_2)_6Me$	96[j]			55 ± 3
$PhSnMe_2(CH_2)_2CHMeOH$				54[k]
$Ph_3Sn(CH_2)_2CMe_2OH$				54[k]

[a] Related to Me_4Sn; values ± 2 ppm. [b] Related to ext. CF_3COOH; values ±0.5 ppm. [c] Upper limit estimated from the unresolved ^{19}F spectrum. In decoupling experiments line widths could be decreased by irradiating at the ^{119}Sn frequency. [d] Solution in $CDCl_3$. [e] Solution in DMSO. [f] Ref. 5. [g] Solution in CH_2Cl_2 [5]. [h] Ref. 12 (neat liq.). [i] Ca. 35 mole % Bu_2SnCl_2 impurity also present. [j] Solution in CH_2Cl_2. [k] Ref. 13.

Results and Discussion

The NMR results for the compounds studied are shown in Table 1. Unless otherwise stated the measurements refer to the neat liquids.

A. ^{119}Sn chemical shifts

The ^{119}Sn chemical shifts of the aryl- and substituted aryl-tin compounds are all found to be upfield of tetramethyltin. This is usual for organotin compounds containing one or more aromatic groups, and the reasons have been discussed in detail elsewhere [2].

Comparison of ^{119}Sn chemical shift values of the three tributyltin derivatives Bu_3SnPh, $Bu_3SnC_6H_4CF_3$-3 and $Bu_3SnC_6H_4CF_3$-2 shows that the electron-withdrawing effect of the trifluoromethyl group causes a deshielding of the tin nucleus. Progressive substitution at the tin atom in the series $Bu_{4-n}Sn(C_6H_4CF_3\text{-}3)_n$ by *meta*-trifluoromethylphenyl groups produces a regular displacement of the ^{119}Sn resonance to high field, as illustrated in Fig. 1. The experimentally measured ^{119}Sn shifts for two members of the related butylphenyltin series $Bu_{4-n}SnPh_n$ suggest similar behaviour, and linear extrapolation gives a ^{119}Sn shift of 140 ± 10 ppm for tetraphenyltin; the low solubility of this compound has prevented direct determination of this chemical shift.

The ^{119}Sn chemical shift found for tetrakis(*m*-trifluoromethylphenyl)tin in deuterochloroform solution is the first observed for a tetraaryltin compound. A solution of tetrakis(*m*-trifluoromethylphenyl)tin in DMSO which is known to coordinate strongly to tin(IV), shows a ^{119}Sn chemical shift which is ca. 10 ppm upfield from that of the same compound in deuterochloroform. This contrasts with an upfield shift of ca. 1.6 ppm found [6] for tetramethyltin in

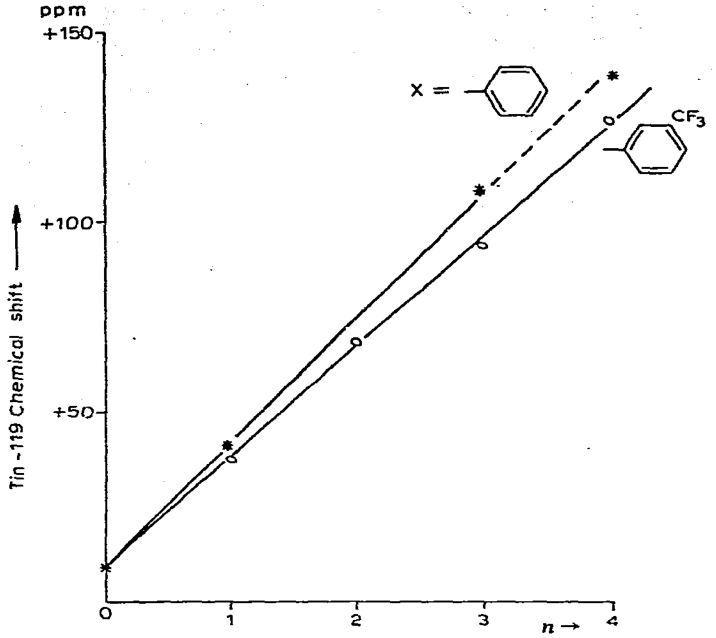

Fig. 1. ^{119}Sn chemical shifts for $Bu_{4-n}SnX_n$ compounds.

similar solvents and is consistent with the weaker acceptor properties of the tetraalkyltin compounds.

Comparison of the ^{119}Sn chemical shifts of the three tributyl derivatives shows that shielding of the tin nucleus increases in the order $Bu_3SnC_6H_4CF_3$-2 < $Bu_3SnC_6H_4CF_3$-3 < $Bu_3SnC_6H_5$ showing that, in accord with its greater inductive electron-withdrawing power, an *o*-trifluoromethylphenyl group is most effective at deshielding the tin nucleus. The three trichlorotin analogues, however, show the reverse pattern, shielding of the tin nucleus increasing in the order $C_6H_5SnCl_3$ < $(C_6H_4CF_3$-3$)SnCl_3$ < $(C_6H_4CF_3$-2$)SnCl_3$. Further, $C_6H_5SnCl_3$ itself, in which the tin atom is bound to three highly electronegative groups, shows a ^{119}Sn chemical shift which is ca. 20 ppm *upfield* from that of tributylphenyltin.

For the purposes of interpretation of observed shielding data, it is convenient to regard nuclear shielding as arising from three physical contributions: σ^{d}_{loc} due to magnetic fields from local diamagnetic currents, σ^{p}_{loc} from local paramagnetic currents and, finally, magnetic fields due to currents induced in electrons distant from the nucleus of interest [14]. In the present context we may neglect this last contribution. Many workers have assumed that, for nuclei other than the proton, changes in σ^{p}_{loc} are the dominant cause of the observed chemical shift. However recent work suggests that for some series of compounds changes in σ^{d}_{loc} may be substantial [15]. Grinter and Mason have discussed diamagnetic contribution in terms of a σ^{d}_{loc} obtained by summation over only the atom in question and those bonded directly to it; qualitatively an increase in the number of electrons in the vicinity of a nucleus leads to an increased shielding contribution for σ^{d}_{loc}, the diamagnetic correction becoming very large for heavy heteroatoms as σ^{d}_{loc} increases with increasing atomic number of the ligand.

The paramagnetic term σ^{p}_{loc} depends, amongst other things, on the inbalance in the population of the orbitals about the nucleus in question, and an increase in the number of electrons involved may give either an increased or decreased shielding contribution from σ^{p}_{loc}. Order of magnitude calculations indicate that as a result of replacement of the three butyl groups in Bu_3SnPh by chlorine atoms to give $PhSnCl_3$, σ^{d}_{loc} is increased by ca. 130 ppm; this, in conjunction with the observed shift would indicate a concomitant paramagnetic (i.e., to low field) contribution of 110 ppm.

The fact that the electron-withdrawing trifluoromethyl group in the 3-position increases the shielding of the tin nucleus in $(C_6H_4CF_3\text{-}3)SnCl_3$ is interpreted as arising from changes in the paramagnetic contribution, withdrawal of electrons from the tin atom possibly altering the balance of the electron population around the tin nucleus. Undoubtedly the trifluoromethyl group in the 2-position has a similar effect, giving rise to a larger high field shift. In this case however, there may be an additional "non-bonded" contribution to σ^{d}_{loc} from the fluorine atoms of the trifluoromethyl group which can approach close (i.e. to within ca. 2.5 Å) to the tin atom.

B. ^{19}F chemical shifts

The observed ^{19}F chemical shift values (Table 1) are of a very similar magnitude, with the fluorine atoms in *o*-trifluoromethylphenyltin trichloride being the least shielded in the compounds studied. The electron density at fluorine in tetrakis(*m*-trifluoromethylphenyl)tin dissolved in DMSO is lower than that found for the same compound in deuterochloroform, and may be due to deshielding of the fluorine nuclei by the magnetic anisotropic effect of the sulphoxide groups.

C. ^{119}Sn—F coupling constants

Resolved tin—fluorine coupling was observed only in the two trifluoromethylphenyltin trichlorides (Table 1). In order to discuss the $J(^{119}Sn{-}F)$ values in more detail the literature results for organotin(IV) fluoro compounds have been compiled in Table 2.

Inspection of Table 2 reveals a steady decrease in the magnitude of $J(^{119}Sn{-}F)$ as the number of bonds between tin and fluorine increases. The coupling observed in *m*-trifluoromethylphenyltin trichloride is formally through five bonds; tin—hydrogen coupling through the same number of bonds has been observed [24] in $Me_3SnC_6H_4Me\text{-}3$, where $^5J(^{119}Sn{-}CH_3)$ is 5.6 Hz, and also in $Cl_3SnC_6H_4Me\text{-}3$, where $^5J(^{119}Sn{-}CH_3)$ is 5.9 Hz in cyclohexane [25].

The Fermi contact interaction usually provides the principal mechanism for electron coupled spin—spin interaction between atomic nuclei. Many structures occur in which a pair of nuclei, although separated by several bonds, are physically only a small distance apart. It has been suggested that, when the physical separation of the nuclei is small, there may be a direct "through space" contribution to the coupling. McFarlane has indicated [26] that on geometrical considerations "through space" coupling to fluorine is likely for the magnetic nuclei of elements larger than helium in their *o*-trifluoromethylphenyl derivatives. In the absence of well defined criteria, many workers have relied on the observation of a coupling constant which is larger than might normally be expected as an indication of "through space" coupling.

TABLE 2

TIN—FLUORINE COUPLING CONSTANTS IN ORGANOTIN(IV) COMPOUNDS

Compound	$^{n}J(^{119}\text{Sn—F})$(Hz)		Conditions	Ref.
$(PhMe_2CCH_2)_3SnF$	1	2298	Conc. soln. in $CDCl_3$	16
Me_3SnCF_2H	2	265.5	Neat liq.	17
$Me_3SnCF_2CFH_2$	2	267		18
$Me_3SnCF_2CF_2H$	2	249.5		19
$Me_3SnCF_2CF_3$	2	217.8	Neat liq.	17
$Me_3SnCF(CF_3)_2$	2	167.5	Neat liq.	17
$Me_3SnCF_2CFHCF_3$	2	222		19
$Me_3SnCFCF_3CF_2H$	2	224		18
$(CF_3)_3SnI$	2	582		20
$(CF_3)_2SnI_2$	2	615		20
$(CF_3)_4Sn$	2	531	Neat liq.	20
$Et_2Sn(CF_2CF_3)_2$	2	228.2	10% soln. in CH_2Cl_2	21
$Et_2Sn(CF_2CF_3)I$	2	241.5	10% soln. in CH_2Cl_2	21
$(CH_2{=}CH)_2Sn(CF_2CF_3)_2$	2	272.8	10% soln. in CH_2Cl_2	21
$Me_3SnCF_2CF_2H$	3	10		19
$1,4\text{-}(Me_3Sn)_2C_6F_4$	3	22.2	20—30% soln. in CCl_4	22
$(CF_3CH_2CH_2)_3SnPh$	4	1.9	50 vol% soln. in PhH	23
$(CF_3CH_2CH_2)_2SnPh_2$	4	1.5	50 vol% soln. in PhH	23
$(CF_3CH_2CH_2)_3SnOMe$	4	2.8	50 vol% soln. in PhH	23
$(CF_3CH_2CH_2)_3SnCl$	4	4.0	50 vol% soln. in PhH	23
$(CF_3CH_2CH_2)_2SnCl_2$	4	5.0	50 vol% soln. in PhH	23
$CF_3CH_2CH_2SnCl_3$	4	2.3	50 vol% soln. in PhH	23
$(C_6H_4CF_3\text{-}2)SnCl_3$	4	28	Neat liq.	[a]
$(C_6H_4CF_3\text{-}3)SnCl_3$	5	11	Neat liq.	[a]

[a] This work.

Although $^4J(^{119}\text{Sn—F})$ in *o*-trifluoromethylphenyltin trichloride is considerably larger than $^4J(^{119}\text{Sn—F})$ reported for other tin compounds (Table 2) the ratio $^4J(^{119}\text{Sn—F})/\,^5J(^{119}\text{Sn—F})$ for the *o*- and *m*-trifluoromethyl derivatives is comparable with J(metal—*o*-substituent)/J(metal—*m*-substituent) observed for metal to fluorine or metal to hydrogen "through bond" couplings for a number of metal aryl compounds. The absolute values of the coupling constants in the available trifluoromethylphenyltin compounds provide no definite evidence of "through space" coupling.

From a study of the arylmercury compounds, *o*-, *m*-, and *p*-$(CF_3C_6H_4)_2Hg$ and *o*-, *m*-, *p*-$CF_3C_6H_4HgBr$, McFarlane has shown that the coupling constants involving ^{199}Hg all become approximately doubled in magnitude when an aryl group is replaced by bromine, with the exception of $^4J(^{199}\text{Hg—F})$ in the two *o*-derivatives [26]. In these cases the $^4J(^{199}\text{Hg—F})$ values are almost equal and it was concluded that a "through space" coupling mechanism is dominant in these compounds. An analogous comparison made on data for tin compounds shows that for *o*-trifluoromethylphenyltin derivatives $^4J(^{119}\text{Sn—F})$ is greater for the trichloride than for the tributyl compound so that this criterion affords no evidence for "through space" coupling in the tin—*o*-trifluoromethylphenyl system.

It is possible that other members of the series $(C_6H_4CF_3\text{-}2)_nSnCl_{4\text{-}n}$ or $(C_6H_4CF_3\text{-}3)_nSnCl_{4\text{-}n}$ may show the effects of through space coupling, but attempts to prepare these compounds have so far been unsuccessful.

D. *Tin—o-proton coupling constants*

There have been very few reports of $^3J(^{119}Sn—H_{ortho})$ coupling constants in aryltin compounds [12,13,24]. Values of $^3J(^{119}Sn—H_o)$ for the compounds studied, together with some literature results for comparison, are shown in Table 1.

The $^3J(^{119}Sn—H_o)$ values for the three pairs of compounds, $Bu_3SnPh/PhSnCl_3$, $Bu_3SnC_6H_4CF_3$-2/($C_6H_4CF_3$-2)$SnCl_3$ and $Bu_3SnC_6H_4CF_3$-3/($C_6H_4CF_3$-3)$SnCl_3$ are all seen to be approximately doubled in magnitude on passing from the first compound to the second in each pair. This is probably due to an increase in the effective nuclear charge of the tin together with an increase in the *s*-character of the Sn—$C_{aromatic}$ bond of the compounds containing the three electronegative chlorine substituents over that in the Sn—$C_{aromatic}$ bonds of the corresponding tributyltin derivatives. The $^3J(^{119}Sn—H_o)$ values in the phenyltin trihalides, $PhSnX_3$ (X is Cl, Br or I), are found to increase in a similar manner as the electronegativity of the halogen atom increases [27].

Recent work has shown [13] that the addition of tris(dipivaloylmethanato)-europium(III) to phenyltin compounds produces a marked downfield shift of the *o*-protons and hence enables their $^3J(^{119}Sn—H_o)$ values to be conveniently determined. Two such compounds have been included in Table 1.

E. *Organotin complexes*

m-Trifluoromethylphenyltin trichloride readily formed six-coordinate 1/1 adducts with 2,2'-bipyridyl and 1,10-phenanthroline, as with other organotin trichlorides. However, the low solubility of these complexes, in common with that of tetraphenyltin, prevented the measurement of their ^{119}Sn chemical shifts.

Experimental

Instrumentation

NMR spectra were obtained using a Jeol-C-60-H instrument, operating at a proton frequency of 60 MHz, and a ^{19}F frequency of 56 MHz. Spectra were recorded in the field sweep mode throughout. The ^{119}Sn frequency (ca. 22.37 MHz) was provided by a Schlumberger frequency synthesiser model FS 30, and ^{119}Sn chemical shifts were obtained by heteronuclear magnetic double resonance [1]. ^{119}Sn and ^{19}F chemical shifts are denoted as positive if they fall upfield of the reference standards.

GLC analysis was performed using a Varian Series 1200 gas liquid chromatograph. The apparatus consisted of a 1' stainless steel column of 3 mm bore, containing 60—80 Celite impregnated with 3% QFl silicone as the stationary phase. The column and flame ionisation detector temperatures were 85 and 250° respectively, and a pre-column injector at 170° was used to ensure complete vaporisation of the sample. A flow rate of 10 cm^3/min of dry nitrogen gas was employed.

Preparations

$Bu_{4-n}Sn(C_6H_4CF_3\text{-}3)_n$ and $Bu_3SnC_6H_4CF_3$-2 were prepared from the apropriate n-butyltin chloride and the Grignard reagent. The preparation of tris-(*m*-trifluoromethylphenyl)butyltin, which is typical, is described: A solution of butyltin trichloride (10 g; 0.036 mole) in dry benzene was slowly added dropwise to a stirred ethereal solution of *m*-trifluoromethylphenylmagnesium bromide [from *m*-bromobenzotrifluoride (25 g; 0.11 mole) and magnesium (2.7 g; 0.11 mole)] under an atmosphere of dry nitrogen. A pale yellow precipitate of magnesium salts separated out towards the end of the addition, and the mixture was refluxed with stirring for 8 h. On cooling, the mixture was hydrolysed by stirring with a saturated solution of ammonium chloride, and the organic layer was then separated, washed twice with water and dried over anhydrous sodium sulphate. The solvent was removed at the water pump leaving a pale brown liquid, which was distilled in vacuo to give tris(*m*-trifluoromethylphenyl)butyltin as a colourless liquid, b.p. 158-160°/0.2 mm (10.8 g; 50%).

Analytical data for the new compounds are shown in Table 3.

The reaction of dibutyltin dichloride and monobutyltin trichloride with *o*-trifluoromethylphenylmagnesium bromide led only to the recovery of partially substituted products, even under forcing conditions.

$(C_6H_4CF_3\text{-}3)SnCl_3$ was prepared by adding stannic chloride (6.4 g; 0.02 mole) dropwise to tris-(*m*-trifluoromethylphenyl)butyltin (5g; 0.008 mole), whereupon the mixture immediately turned a pale brown colour. After heating for 3 h at 90—100°, the resulting brown liquid was distilled in vacuo through a Vigreux column to give n-butyltin trichloride, b.p. 48°/0.2 mm, and *m*-trifluoromethylphenyltin trichloride as a colourless liquid, b.p. 58—60°/0.2 mm (2.9 g; 33%). (Found: C, 22.9; H, 1.1; Sn, 32.1. $C_7H_4Cl_3F_3Sn$ calcd.: C, 22.7; H, 1.1; Sn, 32.1%). The aryltin trichloride was hydrolysed very rapidly on exposure to air.

Reaction of o-trifluoromethylphenyltributyltin with stannic chloride

Stannic chloride (11 g; 0.04 mole) was added to *o*-trifluoromethylphenyltributyltin (3 g; 0.007 mole) and the mixture immediately turned a pale-brown colour. After heating at 90—100° for 4 h, the resulting brown liquid was distilled in vacuo through a Vigreux column to give butyltin trichloride, b.p. 48—50°/0.2 mm, a colourless liquid, b.p. 74°/0.2 mm and a small amount of dibutyltin dichloride, b.p. 80°/0.2 mm, which solidified in the condenser.

The NMR spectrum of the second fraction showed that it contained *o*-trifluoro-

TABLE 3

ANALYTICAL DATA FOR TRIFLUOROMETHYLPHENYLBUTYLTIN COMPOUNDS

Compound	B.p. (°C/0.2 mm)	Analyses: Found (calcd.) (%)			Yield (%)
		C	H	Sn	
$Bu_3SnC_6H_4CF_3\text{-}3$	114—116	52.3 (52.4)	6.9 (7.1)	27.6 (27.4)	48
$Bu_3SnC_6H_4CF_3\text{-}2$	112—114 116—117[a]	52.3 (52.4)	7.2 (7.1)	27.2 (27.4)	27
$Bu_2Sn(C_6H_4CF_3\text{-}3)_2$	134—135	49.6 (50.5)	5.3 (5.0)	22.4 (22.7)	23
$BuSn(C_6H_4CF_3\text{-}3)_3$	158—160	49.3 (49.1)	3.4 (3.4)	19.5 (19.5)	50

[a] At 0.005 mm [28].

TABLE 4

GLC RESULTS FOR ORGANOTIN COMPOUNDS

Compound	B.p. (°C/0.2 mm)	Retention time (Rel. to $BuSnCl_3$)
$BuSnCl_3$	48—50	1.0
$PhSnCl_3$	60—62	2.0
$(C_6H_4CF_3\text{-}3)SnCl_3$	58—60	2.4
$(C_6H_4CF_3\text{-}2)SnCl_3$	74	3.9
Bu_2SnCl_2	80	5.3
$Bu_3SnC_6H_4CF_3\text{-}2$	112—114	6.6
Bu_3SnCl	94	7.7

methylphenyltin trichloride [$^3J(^{119}Sn—H_o)$ 125 Hz], together with an appreciable amount of n-butyltin compounds.

GLC analysis showed that the mixture contained dibutyltin dichloride (ca. 35 mole%), monobutyltin trichloride (ca. 10 mole%) and *o*-trifluoromethylphenyltin trichloride. The retention times of these and some related organotin compounds are listed in Table 4.

The reaction of *o*-trifluoromethylphenyltrimethyltin with boron trichloride has also been reported [29].

Adducts of $(C_6H_4CF_3\text{-}3)SnCl_3$

Solutions of 2,2′-bipyridyl (0.42 g; 0.003 mole) and *m*-trifluoromethylphenyltin trichloride (1 g; 0.003 mole) in absolute ethanol were mixed to give immediately a white precipitate of the complex. This was filtered off and re-dissolved in the minimum quantity of boiling ethanol. The resulting cloudy solution was filtered hot and the filtrate, on standing at room temperature, deposited colourless needle crystals of *m*-trifluoromethylphenyltin trichloride bipyridyl. These were filtered off and dried under high vacuum, m.p. 200—202° (dec.) (0.8 g; 56%). (Found: C: 38.5; H, 2.7; Sn, 22.6. $C_{17}H_{12}Cl_3F_3N_2Sn$ calcd.: C, 38.7; H, 2.3; Sn, 22.6%). The 1,10-phenanthroline complex was prepared in a similar manner, as a white powder, m.p. 265° (dec.) (67% yield). (Found: C, 41.5; H, 2.4; Sn, 21.5 $C_{19}H_{12}Cl_3F_3Sn$ calcd.: C, 41.4; H, 2.2; Sn, 21. 6%).

Miscellaneous organotin compounds

The following compounds were prepared using literature methods: tetraphenyltin [30], tetrakis(*m*-trifluoromethylphenyl)tin [31], and phenyltin trichloride (by the Kocheshkov redistribution reaction of tetraphenyltin with stannic chloride, in a 1/3 molar ratio, at 200°).

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