

Syntheses and multinuclear NMR studies of some trialkyltin(IV) bis(fluorosulfonyl)imides[†]

Ashwani Vij, Sukhjinder Singh and R. D. Verma

Department of Chemistry, Panjab University, 160014 Chandigarh (India)

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Abstract

Trialkyltin(IV) bis(fluorosulfonyl)imides, $R_3\text{SnN}(\text{SO}_2\text{F})_2$ [$R = \text{Me, Et, Pr}^n \text{ and Bu}^n$], have been prepared by metathesis of the corresponding chlorides with the silver bis(fluorosulfonyl)imide–benzene complex in dichloromethane. The compounds are viscous oily liquids that have been characterized by their elemental analyses, IR, ^1H , ^{13}C , ^{19}F and ^{119}Sn NMR spectra, and mass spectrometry. Low ^{119}Sn chemical shifts suggest an appreciable cationic character of the organotin(IV) moiety in these compounds. Trimethyltin(IV) bis(fluorosulfonyl)imide forms coordination complexes with pyridine and dimethylsulfoxide which are ionic in nature. ^{119}Sn Mössbauer data of the pyridine complex reveals *trans*-TBP geometry around tin in $[\text{Me}_3\text{SnPy}_2]^+[\text{N}(\text{SO}_2\text{F})_2]^-$.

Introduction

Organotin(IV) salts of strong protonic acids [1, 2] and superacids [3] have been reported. Structural investigations of these compounds have concentrated on their ^{119}Sn Mössbauer and vibrational spectra. A crystal structure has also been reported [4] for $\text{Me}_2\text{Sn}(\text{SO}_3\text{F})_2$. The chemistry of the corresponding organotin(IV) derivatives of strong nitrogen acids like bis(fluorosulfonyl)imide [5], $\text{HN}(\text{SO}_2\text{F})_2$, has found less attention. Reaction of *N*-chlorobis(fluorosulfonyl)imide with trimethyltin(IV) chloride resulted in the formation of trimethyltin(IV) bis(fluorosulfonyl)imide and chlorine [6]. The lack of structural information on these compounds stimulated our interest in carrying out structural investigations with the help of infrared, multinuclear (^1H , ^{13}C , ^{19}F and ^{119}Sn) NMR and mass spectral studies.

Experimental

Chemicals

$\text{HN}(\text{SO}_2\text{Cl})_2$ [7], AsF_3 [8], $\text{HN}(\text{SO}_2\text{F})_2$ [9], $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ [5], Et_3SnCl [10] and Pr^n_3SnCl [11] were prepared as reported previously. Me_3SnCl

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(Aldrich), Bu^n_3SnCl and Bu^n_3SnH (Fluka) were used as such. Solvents used were of AR grade and were dried prior to use.

Analytical

Tin was determined gravimetrically as SnO_2 after decomposing the compounds with a few drops of a 1:1 mixture of HNO_3 and H_2SO_4 (AR grade) and igniting it to a constant weight. Sulfur and fluorine were determined as described earlier [12] after fusing the compounds with a 1:2 mixture of $\text{Na}_2\text{O}_2\text{:Na}_2\text{CO}_3$ in a nickel crucible for ~ 36 h at *c.* 550°C . Carbon, hydrogen and nitrogen were determined microanalytically.

Instrumentation

The IR spectra of the compounds were recorded on a Perkin-Elmer PE-1430 ratio recording spectrophotometer as neat liquids/Nujol/Kel-F oil mulls between AgCl plates. The ^1H and ^{19}F NMR spectra were recorded on a Varian EM-390 spectrometer at 90 MHz. These were also recorded along with ^{13}C and ^{119}Sn NMR spectra on Jeol FX-90Q spectrometer operating at 90 MHz with frequencies tuned at 89.60 (^1H), 22.47 (^{13}C), 84.31 (^{19}F) and 33.37 (^{119}Sn) MHz. Me_4Si (^1H , 0 ppm), CDCl_3 (^{13}C , 77.1 ppm) and CFCl_3 (^{19}F , 0 ppm) were used as internal standards while Me_4Sn (^{119}Sn , 0 ppm) was taken in a sealed capillary and served as an external standard. In the case of neat liquids, a specially designed capillary containing the appropriate reference in C_6D_6 was placed concentrically in the 5-mm NMR tube and the spectra recorded. The $^nJ[^{119}\text{Sn}-^{13}\text{C}]$ ($n = 1-3$) and $^nJ[^{119}\text{Sn}-^1\text{H}]$ ($n = 2, 3$) values were obtained from the ^{13}C and ^1H NMR spectra, respectively. The positive chemical shifts are downfield from the reference.

The ^{119}Sn Mössbauer spectrum of $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2 \cdot 2\text{py}$ was recorded at the University of Bath (UK) at 78 K. The isomer shift is relative to SnO_2 . Molar conductance values of $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2 \cdot 2\text{D}$ ($\text{D} = \text{py/DMSO}$) were measured in DMSO at 25°C using a Toshniwal conductivity bridge (type CLO1/02A). Mass spectra were recorded on a Varian VG Analytical 11-2505-70S mass spectrometer at 70 eV. All manipulations, i.e. synthetic reactions and sample preparation for spectroscopic investigations, were carried out under a dry nitrogen atmosphere.

Synthetic reactions

A similar procedure was adopted for the preparation of all trialkyltin(IV) bis(fluorosulfonyl)imides. In a typical preparation, a solution of Me_3SnCl (1.7176 g, 8.62 mmol) in about 10 ml dichloromethane was added to a solution of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ (3.1593 g, 8.63 mmol) in the same solvent resulting in the immediate precipitation of AgCl . To ensure completion of the reaction, the contents were stirred vigorously for 30 min. Filtration followed by removal of all volatiles from the filtrate *in vacuo* gave a colorless oily liquid in 98% yield.

$\text{Bu}^n_3\text{SnN}(\text{SO}_2\text{F})_2$ was also prepared by taking Bu^n_3SnH (3.47 g, 11.92 mmol) in ~ 15 ml CFCl_3 , in a glass reactor fitted with a Kontes Teflon needle

valve. The contents were degassed and $\text{HN}(\text{SO}_2\text{F})_2$ (2.16 g, 11.92 mmol) was transferred into the reactor. The contents were allowed to warm slowly to room temperature. A vigorous reaction accompanied by the evolution of non-condensable gas was observed at *c.* 10 °C. Removal of all volatiles, under vacuum, gave $\text{Bu}^n_3\text{SnN}(\text{SO}_2\text{F})_2$ in quantitative yield.

Coordination complexes of $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ with py/DMSO

Excess pyridine (0.55 g, 6.95 mmol) was added to a solution of $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ (1.12 g, 3.26 mmol) in ~25 ml CCl_4 . The white solid obtained after stirring the contents for about 38 h was filtered, washed twice with the same solvent and finally dried *in vacuo*.

The DMSO complex was prepared similarly by stirring $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ (1.32 g, 3.84 mmol) and DMSO (0.62 g, 7.93 mmol) in CCl_4 .

Analytical data

Trimethyltin(IV) bis(fluorosulfonyl) imide: $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$

Analysis: Calc. for $\text{C}_3\text{H}_9\text{SnNS}_2\text{O}_4\text{F}_2$ (%): Sn, 34.5; S, 18.6; F, 11.0. Found: Sn, 35.2; S, 17.8; F, 10.8. IR (neat liquid) (cm^{-1}): 3018 vw; 2978 w; 1490 w; 1384 vs, br; 1220 s, sh; 1185 vs, br; 1130 ms; 1020 w; 932 w, sh; 862 s; 795 vs, br; 762 w, sh; 635 sh; 570 ms; 495 m; 462 m; 435 m. MS (EI) major ^{120}Sn fragments (*m/z*): 330 $\{[\text{Me}_2\text{SnN}(\text{SO}_2\text{F})_2]^+, 3.5\%\}$; 185 $\{[\text{Me}_2\text{SnOF}]^+, 29.5\%\}$; 169 $\{[\text{Me}_2\text{SnF}]^+, 41.4\%\}$; 165 $\{[\text{Me}_2\text{Sn}]^+, 25.2\%\}$; 155 $\{[\text{SnOF}]^+, 11.5\%\}$; 139 $\{[\text{SnF}]^+, 12.7\%\}$; 135 $\{[\text{MeSn}]^+, 11.3\%\}$; 120 $\{[\text{Sn}]^+, 13.7\%\}$. ^{119}Sn NMR (ppm from TMT): neat liquid, +242.5; solution A[†], +248.6; DMSO, +32.9; py, +8.5.

Triethyltin(IV) bis(fluorosulfonyl)imide: $\text{Et}_3\text{SnN}(\text{SO}_2\text{F})_2$

Analysis: Calc. for $\text{C}_6\text{H}_{15}\text{SnNS}_2\text{O}_4\text{F}_2$ (%): Sn, 30.7; S, 16.6; F, 9.8. Found: Sn, 31.4; S, 16.2; F, 9.4. IR (neat liquid) (cm^{-1}): 2962 m; 2915 m; 2862 m; 1479 ms; 1380 vs, br; 1220 sh; 1170 vs, br; 1119 s; 1020 m; 963 mw; 921 w; 850 s; 780 vs; 752 sh; 678 m; 580 vs; 490 mw; 462 w; 432 vw. MS (EI) major ^{120}Sn fragments (*m/z*): 358 $\{[\text{Et}_2\text{SnN}(\text{SO}_2\text{F})_2]^+, 12.1\%\}$; 213 $\{[\text{Et}_2\text{SnOF}]^+, 25.5\%\}$; 207 $\{[\text{Et}_3\text{Sn}]^+, 16.6\%\}$; 197 $\{[\text{Et}_2\text{SnF}]^+, 74.9\%\}$; 177 $\{[\text{Et}_3\text{Sn}-\text{C}_2\text{H}_6]^+, 6.5\%\}$; 155 $\{[\text{SnOF}]^+, 11.3\%\}$; 149 $\{[\text{EtSn}]^+, 39.3\%\}$; 139 $\{[\text{SnF}]^+, 36.4\%\}$; 121 $\{[\text{SnH}]^+, 10.1\%\}$. ^{119}Sn NMR (ppm from TMT): neat liquid, +242.7; solution A, +249.1.

*Tri-*n*-propyltin(IV) bis(fluorosulfonyl)imide: $\text{Pr}^n_3\text{SnN}(\text{SO}_2\text{F})_2$*

Analysis: Calc. for $\text{C}_9\text{H}_{21}\text{SnNS}_2\text{O}_4\text{F}_2$ (%): Sn, 27.7; S, 15.0; F, 8.9. Found: Sn, 27.5; S, 14.3; F, 8.9. IR (neat liquid) (cm^{-1}): 2960 m; 2932 m; 2872 m; 1480 sh; 1378 vs, br; 1280 w; 1220 sh; 1180 vs, br; 1120 m; 1060 m; 1020m; 1000 ms; 920 w; 850 vs; 788 w; 750 sh; 670 mw; 570 vs; 490 w; 462 w, sh; 425 w. MS (EI) major ^{120}Sn fragments (*m/z*): 386

*v=very, s=strong, m=medium, w=weak, br=broad and sh=shoulder.

[†]Solution A=1:1 mixture of CH_2Cl_2 and CDCl_3 .

$\{[\text{Pr}_2\text{SnN}(\text{SO}_2\text{F})_2]^+, 17.0\%\}$; 249 $\{[\text{Pr}_3\text{Sn}]^+, 26.3\%\}$; 241 $\{[\text{Pr}_2\text{SnOF}]^+, 30.5\%\}$; 225 $\{[\text{Pr}_2\text{SnF}]^+, 72.9\%\}$; 205 $\{[\text{Pr}_3\text{Sn}-\text{C}_3\text{H}_8]^+, 6.3\%\}$; 163 $\{[\text{PrSn}]^+, 32.4\%\}$; 155 $\{[\text{SnOF}]^+, 8.3\%\}$; 139 $\{[\text{SnF}]^+, 30.3\%\}$; 121 $\{[\text{SnH}]^+, 12.2\%\}$. ^{119}Sn NMR (ppm from TMT): neat liquid, +232.4; solution A, +238.8.

Tri-n-butyltin(IV) bis(fluorosulfonyl)imide: $\text{Bu}^n_3\text{SnN}(\text{SO}_2\text{F})_2$

Analysis: Calc. for $\text{C}_{12}\text{H}_{27}\text{SnNS}_2\text{O}_4\text{F}_2$ (%): Sn, 25.2; S, 13.6; F, 8.1. Found: Sn, 25.8; S, 13.0; F, 7.9. IR (neat liquid) (cm^{-1}): 2956 vs, br; 2868 vs; 1480 sh; 1464 vs; 1380 vs, br; 1310 w; 1220 sh; 1182 vs, br; 1120 s; 1070 ms; 1020 mw; 965 m; 930 w; 850 vs; 775 vs, br; 750 sh; 670 w; 575 vs, br; 495 mw; 460 w; 425 m. MS (EI) major ^{120}Sn fragments (m/z): 414 $\{[\text{Bu}_2\text{SnN}(\text{SO}_2\text{F})_2]^+, 4.2\%\}$; 291 $\{[\text{Bu}_3\text{Sn}]^+, 20.4\%\}$; 269 $\{[\text{Bu}_2\text{SnOF}]^+, 34.6\%\}$; 253 $\{[\text{Bu}_2\text{SnF}]^+, 100\%\}$; 233 $\{[\text{Bu}_3\text{Sn}-\text{C}_4\text{H}_{10}]^+, 7.3\%\}$; 177 $\{[\text{BuSn}]^+, 58.0\%\}$; 155 $\{[\text{SnOF}]^+, 7.7\%\}$; 139 $\{[\text{SnF}]^+, 21.8\%\}$; 121 $\{[\text{SnH}]^+, 19.8\%\}$. ^{119}Sn NMR (ppm from TMT): neat liquid, +229.0; solution A, +234.5.

Trimethyltin(IV) bis(fluorosulfonyl)imide-bis(pyridine):

$\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2 \cdot 2\text{py}$

Analysis: Calc. for $\text{C}_{13}\text{H}_{19}\text{SnN}_3\text{S}_2\text{O}_4\text{F}_2$ (%): Sn, 23.6; S, 12.8; F, 7.6; C, 31.1; H, 3.8; N, 8.4. Found: Sn, 23.9; S, 12.5; F, 7.4; C, 30.9; H, 3.5; N, 8.1. IR (Nujol bands deleted) (cm^{-1}): 1640 m; 1610 m; 1535 mw; 1490 ms; 1415 m; 1375 vs; 1325 s; 1210 w; 1178 vs, br; 1100 vs; 1020 sh; 980 w; 950 ms; 930 sh; 860 sh; 800 s, br; 735 sh; 680 m; 630 ms; 557 m; 480 w; 435 w. Molar conductance ($\Lambda_{0.0033}$)(in DMSO at 25 °C): $33.2 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. ^{119}Sn Mössbauer (78 K)(MM s^{-1}): isomer shift, 1.32; quadrupole splitting, 3.91; Γ , 0.83 and 0.87.

Trimethyltin(IV) bis(fluorosulfonyl)imide-bis(dimethyl sulfoxide):

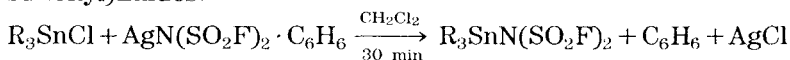
$\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2 \cdot 2\text{DMSO}$

Analysis: Calc. for $\text{C}_7\text{H}_{21}\text{SnNS}_4\text{O}_6\text{F}_2$ (%): Sn, 23.7; S, 25.6; F, 7.6; C, 16.8; H, 4.2; N, 2.8. Found: Sn, 24.0; S, 25.0; F, 7.4; C, 16.9; H, 4.1; N, 2.7. IR (Nujol bands deleted) (cm^{-1}): 1440 w; 1375 vs; 1365 sh; 1320 w; 1220 sh; 1180 vs; 1108 m; 1040 ms; 980 w; 950 ms; 930 sh; 860 sh; 800 s, br; 750 m, br; 720 sh; 655 m; 605 m; 570 vs; 465 w, sh. Molar conductance ($\Lambda_{0.0027}$)(in DMSO at 25 °C): $34.9 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$.

Results and discussion

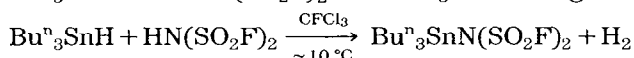
Synthesis

$\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ was reportedly obtained by Ruff [6] by the reaction of Me_3SnCl with $\text{ClN}(\text{SO}_2\text{F})_2$. In the present work, metathesis between R_3SnCl ($\text{R}=\text{Me}$, Et, Pr^n or Bu^n) and $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ in dichloromethane provides an alternative route for the preparation of trialkyltin(IV) bis(fluoro-sulfonyl)imides.



The use of $\text{AgN}(\text{SO}_2\text{F})_2 \cdot \text{C}_6\text{H}_6$ instead of the uncomplexed silver salt is preferred due to its solubility in CH_2Cl_2 , which facilitates the reaction in a homogeneous solution phase.

The tributyltin(IV) derivative has also been obtained by the reaction of Bu^n_3SnH with $\text{HN}(\text{SO}_2\text{F})_2$ in CFCl_3 according to:



Absence of solvent or higher temperature in this reaction results in darkening of the contents and an inconsistent mixture of products being obtained.

Trialkyltin(IV) bis(fluorosulfonyl)imides are colorless, moisture-sensitive oily liquids which cannot be distilled up to $170^\circ\text{C}/0.5$ Torr and are soluble in the usual organic solvents. The 1:2 coordination complexes of $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ with py and DMSO are fine white powdery solids which are insoluble in non-polar solvents. These do not melt up to 170°C and are hygroscopic.

Infrared spectra

The infrared spectra of $\text{R}_3\text{SnN}(\text{SO}_2\text{F})_2$ in the $1500\text{--}700\text{ cm}^{-1}$ region contain bands due to both the alkylstannyl and the bis(fluorosulfonyl)imide groups. Band assignments in this region are, therefore, tentative.

The $\nu_{\text{as}}\text{SO}_2$ band has been found to be diagnostic in differentiating ionic and covalently bonded $\text{N}(\text{SO}_2\text{F})_2$ groups [13, 14]. This frequency appears at $\sim 1480\text{ cm}^{-1}$ in derivatives where $\text{N}(\text{SO}_2\text{F})_2$ is covalent [6, 15, 16], about 100 cm^{-1} higher than found in ionic $\text{N}(\text{SO}_2\text{F})_2$ derivatives [5], viz. $\sim 1375\text{ cm}^{-1}$. This may be ascribed to the dispersal of negative charge from nitrogen in covalent derivatives, thus favoring $\text{S--O } p\pi\text{--}d\pi$ bonding. The appearance of a very strong broad band at $\sim 1380\text{ cm}^{-1}$ in the present trialkyltin(IV) derivatives indicates the polar nature of the Sn--N bond. The bands at ~ 1220 , ~ 1180 and $\sim 1120\text{ cm}^{-1}$ may be assigned as $\nu_{\text{s}}\text{SO}_2$ modes. The appearance of $\nu_{\text{s}}\text{Sn--C}$ at $\sim 495\text{ cm}^{-1}$ in the infrared spectra of the present compounds suggest non-planarity of the R_3Sn moiety. This is in contrast to the absence of $\nu_{\text{s}}\text{Sn--C}$ in the infrared spectra of $\text{R}_3\text{Sn}(\text{SO}_3\text{X})$ ($\text{X}=\text{F}$ or CF_3), where the alkylstannyl group is planar [17]. A weak band at $\sim 460\text{ cm}^{-1}$ may be tentatively assigned as an Sn--N bond.

The infrared spectra of the 2:1 adducts py/DMSO of $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ show further lowering of $\nu_{\text{as}}\text{SO}_2$ to $\sim 1375\text{ cm}^{-1}$, indicative of an ionic character. The most important feature of the spectra is the presence of $\nu_{\text{as}}\text{Sn--C}$ at $\sim 570\text{ cm}^{-1}$ and the absence of $\nu_{\text{s}}\text{Sn--C}$ in the $550\text{--}480\text{ cm}^{-1}$ region which suggests planarity of the R_3Sn group, probably with a *trans*-trigonal bipyramidal (TBP) environment around tin. The appearance of a band at $\sim 1235\text{ cm}^{-1}$ and the upward shift of bands at 601 and 403 cm^{-1} in free pyridine [18] to 628 and 422 cm^{-1} , respectively, in the py complex indicates coordination of pyridine to tin. The lowering of $\nu_{\text{s}=\text{O}}$ in the DMSO complex to 945 cm^{-1} from the free base value of 1050 cm^{-1} also indicates coordination of DMSO to tin.

Nuclear magnetic resonance spectra

The ^1H and ^{13}C NMR data for $\text{R}_3\text{SnN}(\text{SO}_2\text{F})_2$ are given in Tables 1 and 2, respectively. The $^2J[^{119}\text{Sn}-^1\text{H}]$ values for $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ were found to be 63.8 and 62.3 Hz in the neat liquid and in solution A, respectively. However, in donor solvents the $^2J[^{119}\text{Sn}-^1\text{H}]$ values increase to 68.8 (py) and 72.4 (DMSO) Hz, which correspond to a higher s-electron contribution to the bonding orbitals of the central tin atom.

Recently, Lockhart *et al.* [19] have suggested that the average Me—Sn—Me angle (θ) in methyltin(IV) compounds can be estimated from the relation:

$$\theta = 0.0161|^2J[^{119}\text{Sn}-^1\text{H}]^2| - 1.32|^2J[^{119}\text{Sn}-^1\text{H}]| + 133.4 \quad (1)$$

The Me—Sn—Me angles estimated from the $^2J[^{119}\text{Sn}-^1\text{H}]$ values of $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ (Table 1) in the neat liquid and in solution are 114.7° and 113.6° , respectively. These angles suggest flattening of the normal tetrahedron about tin(IV) due to the long Sn—N bond. However, in donor solvents, $\sim 120^\circ$ angles (calculated from NMR) suggest a planar Me_3Sn moiety.

The $^1J[^{119}\text{Sn}-^{13}\text{C}]$ values derived from the ^{13}C NMR spectra are probably more accurate for structure determination. If the Fermi contact term is envisaged as a preponderant contributor to the s-electron character in the Sn—C bond, then the $^1J[^{119}\text{Sn}-^{13}\text{C}]$ value is very sensitive to it. Trialkyltin(IV) bis(fluorosulfonyl)imides show $^1J[^{119}\text{Sn}-^{13}\text{C}]$ values in the range 340–418 Hz which is typical of the $\text{sp}^3\text{--sp}^3$ character of the Sn—C bond with a non-planar R_3Sn moiety [20, 21]. The $^1J[^{119}\text{Sn}-^{13}\text{C}]$ value of 404.1 Hz for solution $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ (Table 2) is greater than for the corresponding halide derivatives [19], i.e. $^1J[^{119}\text{Sn}-^{13}\text{C}]$ for Me_3SnX in CCl_4 are 379.7 ($\text{X}=\text{Cl}$) and 368.9 Hz ($\text{X}=\text{Br}$). The higher value of $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ may be explained on the basis of the greater electronegativity of $\text{N}(\text{SO}_2\text{F})_2$ and thus the greater cation character of the Me_3Sn group. An increase in the $^1J[^{119}\text{Sn}-^{13}\text{C}]$ value in donor solvents by ~ 90 Hz supports the proposed orbital rehybridization or coordination of tin by solvent molecules.

Lockhart *et al.* [19] have further suggested that $^1J[^{119}\text{Sn}-^{13}\text{C}]$ can be linearly correlated to the average Me—Sn—Me angle (determined by X-ray crystallography) using the relation:

$$^1J[^{119}\text{Sn}-^{13}\text{C}] = 11.4\theta - 875 \quad (2)$$

Application of eqn. (2) to 1J values for $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2$ in the neat and solution states suggests Me—Sn—Me angles of 113.3° and 112.2° , respectively, which are in excellent agreement with the angles calculated from the $^2J[^{119}\text{Sn}-^1\text{H}]$ values using eqn. (1). In donor solvents, the $\sim 120^\circ$ angles [calculated using eqn. (2)] further support the TBP structure.

The $^2J[^{119}\text{Sn}-^{13}\text{C}]$ values are lower than the $^3J[^{119}\text{Sn}-^{13}\text{C}]$ values in $\text{R}_3\text{SnN}(\text{SO}_2\text{F})_2$ ($\text{R}=\text{Pr}^n$ and Bu^n) and are in accordance with the earlier observations for other organotin(IV) derivatives [20, 22].

The ^{19}F resonance value at $\sim +55$ ppm (Table 1) in the present compounds (in the neat liquid/solution state) are intermediate between those for covalent [6, 15, 16] and ionic [5] derivatives, which may be ascribed to the polar

TABLE 1

¹H and ¹⁹F NMR spectral data for trialkyltin(IV) bis(fluorosulfonyl)imides

Compound	Solvent ^b	Chemical shift (δ) [ppm from TMS (¹ H)/CFCl ₃ (¹⁹ F)]		Coupling constants (Hz) ^c				∠Me-Sn-Me (°) ^a	¹⁹ F
		CH ₃	CH ₂	² J (α)	² J (β)	³ J (α)	³ J (β)		
Me ₃ SnX	neat liq.	0.91 (s)	—	61.6	63.8	—	—	114.7	55.5
Me ₃ SnX	A	0.96 (s)	—	59.9	62.3	—	—	113.6	55.6
Me ₃ SnX	py	0.81 (s)	—	65.2	68.8	—	—	118.8	52.5
Me ₃ SnX	DMSO	0.83 (s)	—	70.0	72.4	—	—	122.2	52.5
Et ₃ SnX	A	—1.40–1.45 (m)–	—	48.3	55.7	82.5	86.9	—	55.3
Pr ⁿ ₃ SnX	A	1.03 (t)	1.3–2.0 (m)	—	—	—	—	—	55.4
Bu ⁿ ₃ SnX	A	0.97 (t)	1.2–2.0 (m)	—	—	—	—	—	55.2

^aCalculated from eqn. (1) [21].^bSolution A = 1:1 mixture of CH₂Cl₂ and CDCl₃ [14].^cα = [¹¹⁷Sn–¹H] and β = [¹¹⁹Sn–¹H]; s = singlet, t = triplet and m = multiplet.

TABLE 2

 ^{13}C NMR spectral data for trialkyltin(IV) bis(fluorosulfonyl)imides

Compound	Solvent ^b	^{13}C (ppm) CDCl_3 (77.1)				$^nJ[^{119}\text{Sn}-^{13}\text{C}]$			$\angle \text{Me}-\text{Sn}-\text{Me}$ ($^\circ$) ^a
		C_1	C_2	C_3	C_4	$n=1$	$n=2$	$n=3$	
Me_3SnX	neat liq.	1.6	—	—	—	416.8	—	—	113.3
Me_3SnX	A	1.4	—	—	—	404.1	—	—	112.2
Me_3SnX	py	-0.7	—	—	—	492.0	—	—	119.1
Me_3SnX	DMSO	-0.2	—	—	—	528.3	—	—	123.1
Et_3SnX	A	13.3	9.4	—	—	365.2	32.2	—	—
Pr^nSnX	A	24.7	18.9	18.0	—	344.3	26.8	73.2	—
Bu^nSnX	A	19.3	27.4	26.7	13.1	341.2	31.5	75.7	—

^aCalculated from eqn. (2) [21].^bSolution A = 1:1 mixture of CH_2Cl_2 and CDCl_3 [14].

nature of the Sn—N bond in $\text{R}_3\text{SnN}(\text{SO}_2\text{F})_2$. An upfield shift of this signal to +52.5 ppm in donor solvents (py/DMSO) supports the formation of ionic coordination complexes. The molar conductance values for $\text{Me}_3\text{SnN}(\text{SO}_2\text{F})_2 \cdot 2\text{D}$ in DMSO are 33.2 (D=py) and 34.9 (D=DMSO) and lie within the range 23–41 $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, characteristic of 1:1 electrolytes in DMSO [23]. The ^{119}Sn Mössbauer spectrum of the py complex ($\delta = 1.32$; $\Delta E_q = 3.91 \text{ mm s}^{-1}$) supports a *trans*-TBP geometry for $[\text{Me}_3\text{Sn}(\text{py})_2]^+ [\text{N}(\text{SO}_2\text{F})_2]^-$, as is expected for this cation [24].

The ^{119}Sn chemical shift, $\delta(^{119}\text{Sn})$, for the present trialkyltin(IV) compounds lie in the range +235 to +250 ppm (in solution). These values lie well below the range suggested for tetracoordinated organotin(IV) compounds [25], i.e. +200 to -90 ppm. The unusually low chemical shift of $\text{R}_3\text{SnN}(\text{SO}_2\text{F})_2$ may be explained on the following basis: (a) the increased electronegativity of the $\text{N}(\text{SO}_2\text{F})_2$ ligand [5, 26, see 27]; and (b) Sn—N $p\pi$ - $d\pi$ bonding not being favored because of extensive delocalization of the nitrogen lone pair over the O—S—N—S—O π -framework.

A downfield shift of the $\delta(^{119}\text{Sn})$ value upon dilution may be ascribed to the breakdown of intermolecular association in solution. In donor solvents, the $\delta(^{119}\text{Sn})$ value shows an upfield shift of ~200 ppm from that found in $\text{R}_3\text{SnN}(\text{SO}_2\text{F})_2$. This is indicative of the enhanced electron density on tin from the donor molecules.

Mass spectrometry

The absence of the molecular ion peak suggest the complete instability of $[\text{R}_3\text{SnN}(\text{SO}_2\text{F})_2]^+$, which loses an alkyl group to form $[\text{R}_2\text{SnN}(\text{SO}_2\text{F})_2]^+$ as a peak appearing at the highest m/z value. The formation of $[\text{R}_2\text{SnF}]^+$ fragments by the loss of $1/2(\text{SO}_2\text{NSO}_2\text{F})_2$ from the $[\text{M}-\text{R}]^+$ peak supports the affinity of fluorine for the electropositive tin. The $[\text{R}_2\text{Sn}]^+$ fragment was observed in all the cases but peak intensities were not determined in R-Et, Pr^n and Bu^n as these were overlapped by the $[\text{R}_2\text{SnH}]^+$ peak. However,

observation of $[^{116}\text{Sn}]^+$ in these cases supports the formation of this fragment. In addition to the ^{120}Sn -containing fragments, peaks at m/z 181 $\{[\text{HN}(\text{SO}_2\text{F})_2]^+\}$, 99 $\{[\text{SO}_3\text{F}]^+\}$, 83 $\{[\text{SO}_2\text{F}]^+\}$, 80 $\{[\text{SO}_3]^+\}$, 67 $\{[\text{SOF}]^+\}$ and 64 $\{[\text{SO}_2]^+\}$ were also observed.

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