

PREPARATION AND CRYSTAL STRUCTURES OF THE CROWDED ORGANOTIN FLUORIDES $(\text{PhMe}_2\text{Si})_3\text{CSnMe}_2\text{F}$, $(\text{Me}_3\text{Si})_3\text{CSnMe}_2\text{F}$, AND $(\text{Me}_3\text{Si})_3\text{CSnPh}_2\text{F}$ *

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Summary

X-Ray diffraction studies have established that crystals of the organotin fluorides $(\text{Me}_3\text{Si})_3\text{CSnMe}_2\text{F}$, $(\text{Me}_3\text{Si})_3\text{CSnPh}_2\text{F}$, and $(\text{PhMe}_2\text{Si})_3\text{CSnMe}_2\text{F}$ are made up of discrete molecules with no intermolecular $\text{F} \cdots \text{Sn}$ interactions. The data for $(\text{PhMe}_2\text{Si})_3\text{CSnMe}_2\text{F}$ are of good quality ($R = 0.029$, $R' = 0.040$), and provide the first measurement of an Sn-F bond length (1.965(2) Å) in a four-coordinate tin species.

Introduction

Except for $(\text{C}_6\text{H}_{11})_3\text{SnF}$ (C_6H_{11} = cyclohexyl) [1], which has three fairly large groups on tin, the only simple neutral organotin fluorides which have previously been structurally characterized in the solid state, viz. Me_2SnF_2 [2], Me_3SnF [3], $(\text{Me}_3\text{SiCH}_2)_3\text{SnF}$ [4], and $n\text{-Bu}_3\text{SnF}$ [5], all contain penta- or, in the case of Me_2SnF_2 , hexa-coordinate tin as a result of intermolecular bridging by F between two tin centres. (The tin atoms in $\{t\text{-Bu}_2\text{Sn}(\text{OH})(\text{F})\}_2$ are also penta-coordinate, but as a result of intermolecular $\text{O} \rightarrow \text{Sn}$ coordination [6]. The tin atom in the ionic species $[\text{Et}_4\text{N}][\text{Me}_2\overline{\text{Sn}}(\text{F})\text{OC}_6\text{H}_4\text{S}-2]$ is likewise pentacoordinate [7], but in this case because of intramolecular interaction between sulphur and tin.) The crystal of $(\text{C}_6\text{H}_{11})_3\text{SnF}$ was judged to contain essentially four-coordinate tin, but weak directionally specific intermolecular interactions between the fluorine and tin appear to determine the crystal packing [1]. It seemed of interest to establish whether the presence of a single very bulky ligand on tin could completely inhibit intermolecular $\text{F} \cdots \text{Sn}$ interaction, and with this in mind the compounds $\text{TsiSnMe}_2\text{F}$ ($\text{Tsi} = (\text{Me}_3\text{Si})_3\text{C}$) (III), $\text{TpsiSnMe}_2\text{F}$ (I) ($\text{Tpsi} = (\text{PhMe}_2\text{Si})_3\text{C}$), $\text{TsiSnPh}_2\text{F}$ (II)

* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

were prepared, and studied by X-ray diffraction. The Mössbauer spectra of I and III were also determined.

Experimental

Spectra

The ^1H NMR spectra (of CH_2Cl_2 solutions) (at 90 MHz) were recorded with a Perkin–Elmer R32 spectrometer; ^{11}B (at 25.7 MHz) and ^{19}F spectra (at 75.4 MHz) (of $\text{CH}_2\text{Cl}_2/\text{CDCl}_3$ solutions) were recorded with a Bruker WP80SY spectrometer (δ values are given relative to external $\text{BF}_3 \cdot \text{OEt}_2$ and external CFCl_3 , respectively), and ^{13}C (at 90.7 MHz), and ^{119}Sn spectra (at 134.1 MHz) (of $\text{CH}_2\text{Cl}_2/\text{CDCl}_3$) solutions) on a Bruker WM360 spectrometer (δ values are relative to external SiMe_4 and external SnMe_4 , respectively). The ^{11}B , ^{13}C , and ^{119}Sn spectra were recorded with proton decoupling.

Mass spectra were by electron impact (70 eV) unless otherwise indicated; for chemical ionization (CI) NH_3 was used; only selected peaks are given. Where relevant, peaks are those for ions containing ^{28}Si , ^{35}Cl , and ^{120}Sn ; since the natural abundance of ^{120}Sn is ca. 33%, abundances of tin-containing ions should be multiplied by 3 for comparison with ions without tin.

Reaction of $\text{TsiSnMe}_2\text{Cl}$ with AgBF_4 , and preparation of $\text{TsiSnMe}_2\text{F}$ (III)

(a) A solution of $\text{TsiSnMe}_2\text{Cl}$ (0.50 g, 1.20 mmol) in CH_2Cl_2 (10 cm^3) was added to AgBF_4 (0.25 g, 1.25 mmol) in CH_2Cl_2 (15 cm^3) and the mixture was stirred for 30 min with protection from light then filtered through charcoal (previously washed with CH_2Cl_2). The filtrate was evaporated under vacuum to leave a solid which was judged to be $\text{TsiSnMe}_2\text{BF}_4$ (0.54 g, 95%); $\delta(\text{H})$ 0.24 (27H, s, SiMe_3) and 0.76 (6H, s, $^2J(^1\text{H}-^{119}\text{Sn})$ 53.1 Hz, SnMe_2); $\delta(\text{C})$ 4.3 (SiMe_3) and 5.80 ppm (SnMe_2); $\delta(^{11}\text{B})$ –1.15 ppm (br); $\delta(\text{F})$ –204.1 ppm (no resonance from ^{119}Sn could be detected between 330 and –260 ppm); m/z (CI) 455 (45%, $[\text{M} + \text{NH}_3 - \text{Me}]^+$), 381 (100, $[\text{M} - \text{BF}_4]^+$), 366 (35, $[\text{M} - \text{BF}_4 - \text{Me}]^+$), 275 (10), 201 (30, $[\text{M} - \text{BF}_4 - \text{SnMe}_4]^+$), 165 (45, $[\text{Me}_3\text{Sn}]^+$), 73 (40, $[\text{Me}_3\text{Si}]^+$).

(b) The procedure described in (a) was repeated, but with stirring of the reaction mixture for 3 h. Work-up as before then gave $\text{TsiSnMe}_2\text{F}$ (0.36 g, 75%), m.p. (sealed tube) 313°C (Found: C, 35.9; H, 8.1. $\text{C}_{12}\text{H}_{33}\text{FSi}_3\text{Sn}$ calc: C, 36.1; H, 8.3%); $\delta(\text{H})$ 0.24 (27H, s, SiMe_3) and 0.46 (6H, d, $^3J(^1\text{H}-^{19}\text{F})$ 3.9 Hz, SnMe_2); $\delta(\text{F})$ –203.6 ppm (septet, $^3J(^1\text{H}-^{19}\text{F})$ 3.9 Hz); $\delta(\text{C})$ 4.75 (s, SiMe_3) and 3.85 ppm (d, $^2J(^{13}\text{C}-^{19}\text{F})$ 10.0 Hz, SnMe_2); $\delta(\text{Sn})$ 146.9 ppm (d, $^1J(^{19}\text{F}-^{119}\text{Sn})$ 2376 Hz); m/z (CI) 401 (20%, $[\text{M} + \text{H}]^+$), 385 (60, $[\text{M} - \text{Me}]^+$), 381 (65, $[\text{M} - \text{F}]^+$), 205 (100, $[\text{M} - \text{SnMe}_4 - \text{Me}]^+$), 201 (70, $[\text{M} - \text{Me}_3\text{SnF} - \text{Me}]^+$), 165 (10, 73 (30)).

Preparation of $\text{TsiSnPh}_2\text{F}$ (II)

A solution of $\text{TsiSnPh}_2\text{Cl}$ [8] (0.50 g, 9.3 mmol) in CH_2Cl_2 (20 cm^3) was added to AgBF_4 (0.20 g, 1.03 mmol) and the mixture was stirred for 1 h with protection from light then filtered through charcoal (previously washed with CH_2Cl_2) and evaporated. The residue (which was assumed to be $\text{TsiSnPh}_2\text{BF}_4$) was recrystallized from MeOH (20 cm^3) to give $\text{TsiSnPh}_2\text{F}$ (0.39 g, 80%), m.p. 128°C (Found: C, 50.4; H, 8.0. $\text{C}_{20}\text{H}_{37}\text{FSi}_3\text{Sn}$ calc: C, 50.6; H, 7.1%); $\delta(\text{H})$ 0.29 (27H, s, SiMe_3) and 7.33–7.84 (10H, m, Ph); $\delta(\text{C})$ 5.7 ($^3J(^{13}\text{C}-^{119}\text{Sn})$ 16.3 Hz, SiMe_3) 127.8

($^3J(^{13}\text{C}-^{119}\text{Sn})$ 46.8 Hz, C(3)), 128.0 (C(4)), 136.6 ($(^2J(^{13}\text{C}-^{119}\text{Sn})$ 37.2 Hz, C(2)) and 143.7 (C(1) (*ipso*)); $\delta(\text{F})$ -212.9 ($^1J(^{19}\text{F}-^{119}\text{Sn})$ 2463 Hz); $\delta(\text{Sn})$ -40.8 (d); *m/z* 509 (60%), [*M* - Me] $^+$, 431 (15, [*M* - Ph - Me] $^+$), 329 (40, [*M* - SnMe₄ - Me] $^+$), 289 (30), 267 (100, [*M* - Me₃SnPh - Me] $^+$), 251 (20), 227 (30), 205 (45), 201 (30), 175 (25), 135 (30, [PhMe₂Si] $^+$), 73 (40, [Me₃Si] $^+$).

Preparation of TpsiSnMe₂Cl

A solution of TpsiLi [9] (9.5 mmol) in THF (20 cm³) (THF = tetrahydrofuran) was added dropwise under N₂ with stirring to a solution of Me₂SnCl₂ (2.7 g, 12.2 mmol) in 1/1 v/v THF/Et₂O (40 cm³). The mixture was refluxed for 1 h then the solvent was removed under reduced pressure. The residue was extracted with CH₂Cl₂ (75 cm³), and the extract was filtered then evaporated to leave a solid, which was recrystallized from MeOH to give TpsiSnMe₂Cl (4.5 g, 80%), m.p. 186 °C (Found: C, 53.7; H, 6.6. C₂₇H₃₉ClSi₃Sn calc: C, 53.9, H, 6.5%); $\delta(\text{H})$ 0.61 (18H, s, SiMe₂), 0.74 (6H, s, $^2J(^{119}\text{Sn}-^1\text{H})$ 54 Hz, SnMe₂), and 6.7-7.43 (15H, m, Ph); $\delta(\text{C})$ 4.55 ($^3J(^{13}\text{C}-^{117/119}\text{Sn})$ 51.7 Hz, SiMe₂), 7.8 ($^1J(^{13}\text{C}-^{119}\text{Sn})$ -377 Hz, SnMe₂), 11.8 (quaternary C), 127.4 (C(3)), 128.8 (C(4)), 135.6 (C(2)), and 139.5 ppm (C(1) (*ipso*)); $\delta(\text{Sn})$ 115.9 ppm; *m/z* 587 (10%, [*M* - Me] $^+$), 551 (35, [*M* - HCl - Me] $^+$), 325 (15, [*M* - Me₂PhSnCl - Me] $^+$), 309 (55), 207 (45), 135 (100), and 73 (45).

Preparation of TpsiSnMe₂F (I)

A solution of TpsiSnMe₂Cl (0.50 g, 0.85 mmol) in CH₂Cl₂ (20 cm³) was added to AgBF₄ (0.20 g, 1.03 mmol) and the mixture was stirred for 1 h with protection from the light then filtered through charcoal (previously washed with CH₂Cl₂). The ¹H NMR spectrum of the solution ($\delta(\text{H})$ 0.60 (6H, s), 0.65 (18H, s) and 7.18-7.6 (15H, m)) suggested that the product was not the fluoride, and so probably the tetrafluoroborate, thus a few drops of MeOH were added and the solution was then evaporated under reduced pressure to leave TpsiSnMe₂F (0.46 g, 95%), m.p. 172 °C (Found: C, 55.3; H, 6.6. C₂₇H₃₉FSi₃Sn calc: C, 55.4; H, 6.6%), $\delta(\text{H})$ 0.55 (6H, d $^2J(^1\text{H}-^{119}\text{Sn})$ 54 Hz, SnMe₂), 0.65 (18H, s, SiMe₂), and 7.18-7.57 (15H, m, Ph); $\delta(\text{C})$ 4.3 (SiMe₂), 5.7 (d, $^2J(^{13}\text{C}-^{19}\text{F})$ 9.6 Hz, SnMe₂), 127.3 (C(3)), 128.9 (C(4)), 135.5 (C(2)), and 139.7 ppm (C(1) (*ipso*)); $\delta(\text{F})$ -191.2 ppm (s, $^1J(^{19}\text{F}-^{119}\text{Sn})$ 2367 Hz); $\delta(\text{Sn})$ 124.5 ppm (s, $^1J(^{19}\text{F}-^{119}\text{Sn})$ 2374 Hz); *m/z* 571 (10%, [*M* - Me] $^+$), 493 (7, [*M* - SiMe₃] $^+$), 344 (20, [*M* - Me₃SnPh] $^+$), 329 (50, [*M* - Me₃SnPh - Me] $^+$), 289 (20, [Ph₂MeSn] $^+$), 227 (35, [PhMe₂Sn] $^+$), 135 (55), 77 (100, [Me₂SiF] $^+$) and 73 (40).

Structure determinations

(I) TpsiSnMe₂F (I)

Crystal data: C₂₇H₃₉FSi₃Sn, *M* 585.6, triclinic, *a* 9.216(1), *b* 9.655(1), *c* 16.033(2) Å, α 93.05(1), β 92.81(1), γ 94.21(1)°, *U* 1418.8(1) Å³, *Z* 2, *D_c* 1.37 g cm⁻³, *F*(000) 604. Monochromated Mo-K α radiation, λ 0.71069 Å, μ 10.5 cm⁻¹. Space group *P*1̄ from successful structure refinement.

A crystal of ca. 0.4 × 0.4 × 0.4 mm was used for data collection on an Enraf-Nonius CAD4 diffractometer. Intensities for *h* ± *k* ± *l* reflections with 2 < θ < 25° were measured by a $\theta/2\theta$ scan with a scan-width $\Delta\theta = (0.8 + 0.35 \tan \theta)$ °. The scan rate was determined by a rapid pre-scan at 10° min⁻¹ in θ , and any reflections with *I* < $\sigma(I)$ were coded as unobserved. The remaining reflections were

re-scanned subject to a maximum $I/\sigma(I)$ of 50 and a maximum scan time of 60 s. Two standard reflections were monitored every 30 min, and showed no significant variation. After correction for Lorentz and polarization effects (Lp), but not for absorption, equivalent data were averaged to leave 4552 reflections with $|F^2| > \sigma(F^2)$ which were used in the structure refinement. The values of $\sigma(F^2)$ were taken as $[\sigma^2(I) + (0.04I)^2]^{1/2}/Lp$.

The positions of the Si, Sn, C, and F atoms were found by heavy atom methods and refined by full matrix least squares with anisotropic temperature factors. A difference map revealed the positions of the hydrogen atoms, which were refined with isotropic temperature factors. Refinement converged at $R = 0.029$, $R' = 0.040$ (weighting scheme $w = 1/\sigma^2(F)$). A final difference map had peaks of up to $0.6 \text{ e}\text{\AA}^{-3}$ near the Sn atom but was elsewhere featureless.

The structure solution and refinement were carried out on a PDP11/34 computer using the Enraf-Nonius structure determination package. Scattering factors for

TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR TpsiSnMe₂F (I) (with estimated standard deviations in parentheses)

Atom	x	y	z
Sn	1878.8(2)	1591.6(2)	1671.5(1)
Si(1)	4101.8(6)	-406.4(6)	2523.2(4)
Si(2)	1611.5(7)	756.7(7)	3655.8(4)
Si(3)	4268.4(7)	2750.5(7)	3240.5(4)
F	1123(2)	3404(2)	1940(1)
C(1)	3029(2)	1132(2)	2837(1)
C(2)	5854(3)	116(3)	2041(2)
C(3)	4598(3)	-1498(3)	3407(2)
C(4)	3038(2)	-1556(2)	1683(2)
C(5)	1992(3)	-2614(3)	1866(2)
C(6)	1237(3)	-3440(3)	1237(2)
C(7)	1472(4)	-3230(3)	410(2)
C(8)	2509(4)	-2226(3)	205(2)
C(9)	3273(3)	-1410(3)	837(2)
C(10)	3243(3)	4153(3)	3739(2)
C(11)	5696(3)	2278(3)	4026(2)
C(12)	5275(3)	3678(2)	2406(2)
C(13)	6763(3)	3563(3)	2305(2)
C(14)	7510(3)	4318(3)	1734(2)
C(15)	6816(4)	5223(3)	1266(2)
C(16)	5374(4)	5382(3)	1351(2)
C(17)	4613(3)	4630(3)	1923(2)
C(18)	86(3)	1932(3)	3569(2)
C(19)	2442(3)	981(3)	4754(2)
C(20)	680(2)	-1060(3)	3611(1)
C(21)	-602(3)	-1434(3)	3116(2)
C(22)	-1340(3)	-2726(4)	3133(2)
C(23)	-827(4)	-3697(2)	3647(2)
C(24)	388(4)	-3372(3)	4147(2)
C(25)	1135(3)	-2070(3)	4137(2)
C(26)	3054(4)	2090(4)	601(2)
C(27)	-99(3)	421(4)	1263(2)

TABLE 2

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) IN TpsiSnMe₂F (I) (with estimated standard deviations in parentheses)

Sn–F	1.965(2)	Sn–C(1)	2.185(2)
Sn–C(26)	2.132(3)	Sn–C(27)	2.128(3)
Si(1)–C(1)	1.903(2)	Si(1)–C(2)	1.871(3)
Si(1)–C(3)	1.870(3)	Si(1)–C(4)	1.887(2)
Si(2)–C(1)	1.926(2)	Si(2)–C(18)	1.875(3)
Si(2)–C(19)	1.881(3)	Si(2)–C(20)	1.891(3)
Si(3)–C(1)	1.930(2)	Si(3)–C(10)	1.875(3)
Si(3)–C(11)	1.874(3)	Si(3)–C(12)	1.891(3)
C(4)–C(5)	1.404(3)	C(4)–C(9)	1.397(4)
C(5)–C(6)	1.379(4)	C(6)–C(7)	1.376(5)
C(7)–C(8)	1.375(5)	C(8)–C(9)	1.386(4)
C(12)–C(13)	1.401(4)	C(12)–C(17)	1.389(4)
C(13)–C(14)	1.379(4)	C(14)–C(15)	1.357(4)
C(15)–C(16)	1.361(5)	C(16)–C(17)	1.386(5)
C(20)–C(21)	1.404(3)	C(20)–C(25)	1.397(4)
C(21)–C(22)	1.379(4)	C(22)–C(23)	1.375(5)
C(23)–C(24)	1.353(5)	C(24)–C(25)	1.389(4)
F–Sn–C(1)	103.37(8)	F–Sn–C(26)	99.6(1)
F–Sn–C(27)	99.8(1)	C(1)–Sn–C(26)	120.6(1)
C(1)–Sn–C(27)	120.0(1)	C(26)–Sn–C(27)	108.6(1)
C(1)–Si(1)–C(2)	113.3(1)	C(1)–Si(1)–C(3)	114.2(1)
C(1)–Si(1)–C(4)	110.1(1)	C(2)–Si(1)–C(3)	105.8(1)
C(2)–Si(1)–C(4)	104.3(1)	C(3)–Si(1)–C(4)	108.5(1)
C(1)–Si(2)–C(18)	111.3(1)	C(1)–Si(2)–C(19)	112.0(1)
C(1)–Si(2)–C(20)	116.8(1)	C(18)–Si(2)–C(19)	108.1(1)
C(18)–Si(2)–C(20)	104.8(1)	C(19)–Si(2)–C(20)	103.2(1)
C(1)–Si(3)–C(10)	113.1(1)	C(1)–Si(3)–C(11)	110.9(1)
C(1)–Si(3)–C(12)	114.9(1)	C(10)–Si(3)–C(11)	107.9(1)
C(10)–Si(3)–C(12)	103.1(1)	C(11)–Si(3)–C(12)	106.2(1)
Sn–C(1)–Si(1)	103.75(9)	Sn–C(1)–Si(2)	108.5(1)
Sn–C(1)–Si(3)	108.9(1)	Si(1)–C(1)–Si(2)	114.7(1)
Si(1)–C(1)–Si(3)	112.7(1)	Si(2)–C(1)–Si(3)	108.1(1)
Si(1)–C(4)–C(5)	122.5(2)	Si(1)–C(4)–C(9)	121.0(2)
C(5)–C(4)–C(9)	116.5(2)	C(4)–C(5)–C(6)	121.1(3)
C(5)–C(6)–C(7)	120.7(3)	C(6)–C(7)–C(8)	120.0(3)
C(7)–C(8)–C(9)	119.3(3)	C(4)–C(9)–C(8)	122.4(2)
Si(3)–C(12)–C(13)	122.0(2)	Si(3)–C(12)–C(17)	121.4(2)
C(13)–C(12)–C(17)	116.2(2)	C(12)–C(13)–C(14)	121.6(2)
C(13)–C(14)–C(15)	120.2(3)	C(14)–C(15)–C(16)	120.2(3)
C(15)–C(16)–C(17)	120.0(3)	C(12)–C(17)–C(16)	121.6(3)
Si(2)–C(20)–C(21)	122.2(2)	Si(2)–C(20)–C(25)	121.8(2)
C(21)–C(20)–C(25)	115.6(2)	C(20)–C(21)–C(22)	122.1(3)
C(21)–C(22)–C(23)	120.1(3)	C(22)–C(23)–C(24)	119.9(3)
C(23)–C(24)–C(25)	120.5(3)	C(20)–C(25)–C(24)	121.9(2)

neutral atoms were taken from ref. 10. Final atomic coordinates are listed in Table 1, and bond lengths and angles in Table 2; the structure with atom numbering is shown in Fig. 1. Lists of hydrogen atom coordinates, temperature factors and final structure factors are available from the authors.

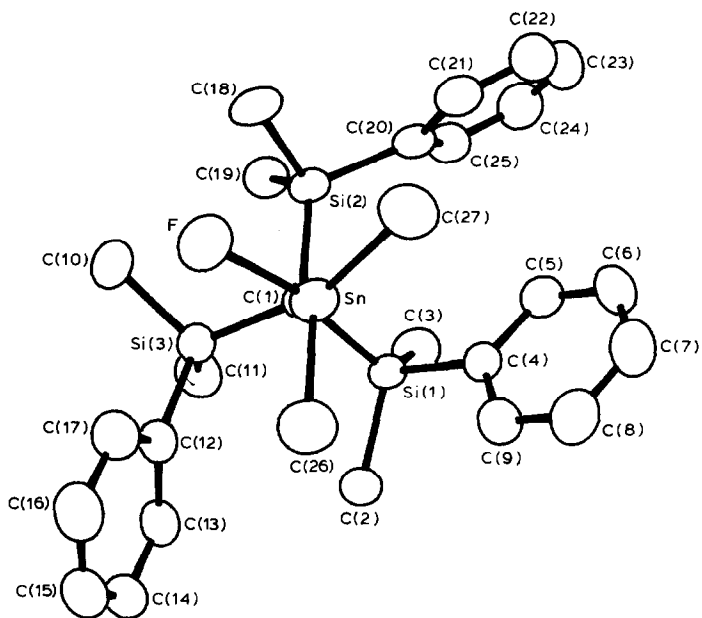


Fig. 1. Molecular structure of $(\text{Me}_2\text{PhSi})_3\text{CSnMe}_2\text{F}$ (I) with atom numbering scheme.

TABLE 3

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) FOR $\text{TsiSnPh}_2\text{F}$ (II) (with estimated standard deviations in parentheses)

Atom	x	y	z
Sn	2282.2(8)	2220.7(5)	1252.8(4)
Si(1)	5696(3)	1633(2)	970(2)
Si(2)	4998(4)	3605(2)	1113(2)
Si(3)	4941(4)	2412(3)	2499(2)
F	1267(9)	2823(5)	2041(4)
C(1)	4625(11)	2460(6)	1460(5)
C(2)	4868(15)	1396(9)	44(7)
C(3)	7672(15)	1893(10)	821(8)
C(4)	5654(16)	558(8)	1440(8)
C(5)	6766(17)	4005(10)	1507(9)
C(6)	3609(16)	4381(8)	1360(8)
C(7)	5140(17)	3619(9)	83(8)
C(8)	3950(18)	1489(11)	2927(8)
C(9)	4315(20)	3370(12)	2990(8)
C(10)	6939(18)	2256(11)	2738(9)
C(11)	1205(12)	2822(8)	330(7)
C(12)	1273(15)	2489(9)	-369(8)
C(13)	464(20)	2897(12)	-921(8)
C(14)	-367(16)	3586(9)	-832(9)
C(15)	-431(15)	3902(9)	-134(9)
C(16)	357(13)	3537(9)	451(7)
C(17)	1422(13)	978(7)	1412(7)
C(18)	1404(21)	343(11)	935(10)
C(19)	1016(25)	-503(12)	1133(12)
C(20)	187(21)	-577(11)	1761(12)
C(21)	0(18)	47(11)	2187(10)
C(22)	598(16)	833(10)	2049(8)

(2) *TsSnPh₂F* (II)

Crystal data: $C_{22}H_{37}FSi_3Sn$, $M = 523.5$, monoclinic, a 9.043(4), b 15.699(3), c 18.330(5) Å, β 90.88(3), U 2601.9 Å³, Z 4, D_c 1.34 g cm⁻³, $F(000)$ 1080. Monochromated Mo- K_α radiation, λ 1.71069 Å, μ 11.3 cm⁻¹. Space group $P2_1/c$ from systematic absences of $h0l$ for l odd and $0k0$ for k odd.

A crystal of ca. 0.25 × 0.3 × 0.3 mm was used. The details of the data collection and structure refinement were as described for I except that: (i) the maximum $I/\sigma(I)$ was 20; (ii) 3670 reflections were used for the structure analysis; (iii) hydrogen atoms were placed at calculated positions and were not refined; (iv) refinement converged at $R = 0.058$, $R' = 0.119$; and (v) a final difference map had peaks of up to 0.9 eÅ⁻³.

Atomic coordinates are listed in Table 3, and bond lengths and angles in Table 4.

TABLE 4

INTRAMOLECULAR DISTANCES (Å) AND ANGLES (°) IN *TsSnPh₂F* (II) (with estimated standard deviations in parentheses)

Sn-F	1.965(8)	Sn-C(1)	2.179(10)
Sn-C(11)	2.156(12)	Sn-C(17)	2.122(12)
Si(1)-C(1)	1.860(10)	Si(1)-C(2)	1.882(13)
Si(1)-C(3)	1.857(14)	Si(1)-C(4)	1.895(13)
Si(2)-C(1)	1.937(10)	Si(2)-C(5)	1.85(2)
Si(2)-C(6)	1.813(14)	Si(2)-C(7)	1.895(15)
Si(3)-C(1)	1.922(10)	Si(3)-C(8)	1.88(2)
Si(3)-C(9)	1.85(2)	Si(3)-C(10)	1.87(2)
C(11)-C(12)	1.39(2)	C(11)-C(16)	1.38(2)
C(12)-C(13)	1.39(2)	C(13)-C(14)	1.33(2)
C(14)-C(15)	1.37(2)	C(15)-C(16)	1.40(2)
C(17)-C(18)	1.33(2)	C(17)-C(22)	1.41(2)
C(18)-C(19)	1.42(3)	C(19)-C(20)	1.39(3)
C(20)-C(21)	1.27(3)	C(21)-C(22)	1.37(2)
F-Sn-C(1)	104.6(3)	F-Sn-C(11)	98.9(4)
F-Sn-C(17)	99.5(4)	C(1)-Sn-C(11)	119.2(4)
C(1)-Sn-C(17)	119.5(4)	C(11)-Sn-C(17)	110.4(4)
C(1)-Si(1)-C(2)	111.8(5)	C(1)-Si(1)-C(3)	115.3(6)
C(1)-Si(1)-C(4)	112.9(5)	C(2)-Si(1)-C(3)	106.3(7)
C(2)-Si(1)-C(4)	102.9(6)	C(3)-Si(1)-C(4)	106.8(7)
C(1)-Si(2)-C(5)	109.9(6)	C(1)-Si(2)-C(6)	114.6(5)
C(1)-Si(2)-C(7)	110.7(5)	C(5)-Si(2)-C(6)	105.8(7)
C(5)-Si(2)-C(7)	108.2(7)	C(6)-Si(2)-C(7)	107.4(7)
C(1)-Si(3)-C(8)	112.3(6)	C(1)-Si(3)-C(9)	114.1(6)
C(1)-Si(3)-C(10)	111.5(6)	C(8)-Si(3)-C(9)	105.8(8)
C(8)-Si(3)-C(10)	105.4(8)	C(9)-Si(3)-C(10)	107.1(8)
Sn-C(1)-Si(1)	107.9(5)	Sn-C(1)-Si(2)	106.1(4)
Sn-C(1)-Si(3)	107.2(5)	Si(1)-C(1)-Si(2)	113.3(5)
Si(1)-C(1)-Si(3)	112.3(5)	Si(2)-C(1)-Si(3)	109.7(5)
Sn-C(11)-C(12)	122.3(9)	Sn-C(11)-C(16)	118.4(9)
C(12)-C(11)-C(16)	119(1)	C(11)-C(12)-C(13)	118(1)
C(12)-C(13)-C(14)	125(1)	C(13)-C(14)-C(15)	116(1)
C(14)-C(15)-C(16)	122(1)	C(11)-C(16)-C(15)	119(1)
Sn-C(17)-C(18)	127(1)	Sn-C(17)-C(22)	117.5(9)
C(18)-C(17)-C(22)	115(1)	C(17)-C(18)-C(19)	122(2)

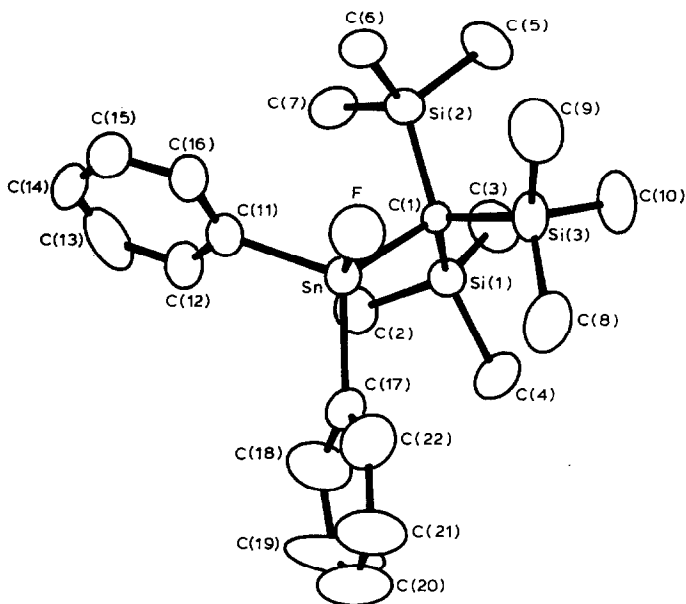


Fig. 2. Molecular structure of $(\text{Me}_3\text{Si})_3\text{CSnPh}_2\text{F}$ (II) with atom numbering scheme.

The molecular structure with atom numbering is shown in Fig. 2. Supplementary data are available from the authors.

(3) $\text{TsiSnMe}_2\text{F}$ (III)

Crystal data: $\text{C}_{11}\text{H}_{33}\text{FSi}_3\text{Sn}$. M 399.4, cubic, a 12.850(3) Å, space group $Pa\bar{3}$.

Of 2153 reflections measured for $+h+k+l$ for $2 < \theta < 20^\circ$, there were only 466 with $I > \sigma(I)$, and only 151 of these were unique. If the density is assumed to be ca. 1.3 g cm^{-3} , as for compounds I and II, there must be 4 molecules in the unit cell and each molecule must be on a site of 3-fold symmetry and so be extensively disordered. No attempt was made to locate the atom positions.

Results and discussion

The compound $\text{TsiSnMe}_2\text{F}$ was made from $\text{TsiSnMe}_2\text{Cl}$ and AgBF_4 in CH_2Cl_2 . When the reaction mixture was stirred for 30 min the product isolated was apparently the tetrafluoroborate, but when the stirring was carried on for 3 h the fluoride $\text{TsiSiMe}_2\text{F}$ was obtained in 75% yield.

It is noteworthy that Me_3SnBF_4 was isolated by Clark and O'Brien from the reaction of Me_3SnCl with AgBF_4 in liquid SO_2 ; it was described as stable but hygroscopic, and shown to have a polymeric structure involving five-coordinate tin [11]. It is not clear whether $\text{TsiSnMe}_2\text{BF}_4$, which evidently loses BF_3 fairly readily, is less stable. The apparent melting point observed for the solid, 313°C , was identical with that of $\text{TsiSnMe}_2\text{F}$, which suggests that BF_3 was lost from the solid before melting, even though the sample was in a sealed capillary tube.

Compound II was obtained similarly from $\text{TsiSnPh}_2\text{Cl}$ and AgBF_4 in CH_2Cl_2 ;

the initial product was assumed to be $\text{TsiSnPh}_2\text{BF}_4$, but recrystallization from MeOH gave II in 80% yield.

When $\text{TpsiSnMe}_2\text{Cl}$ was treated with AgBF_4 in CH_2Cl_2 , the ^1H NMR spectrum of the solution showed that the product was not the fluoride I since the signal from the SnMe_2 protons (at δ 0.60) was a singlet, and it was assumed to be the tetrafluoroborate $\text{TpsiSnMe}_2\text{BF}_4$. Addition of a few drops of MeOH and evaporation of the solution then gave a 90% yield of the fluoride I (which showed a doublet at δ 0.55 for the SnMe_2 resonance).

We first tried to determine the structure of $\text{TsiSnMe}_2\text{F}$ but could not measure enough reflections of adequate quality to permit full structural analysis. The data established beyond doubt, however, that the molecules have site symmetry $\bar{3}$, and thus are either fully free to rotate about their centres in the lattice (as are the molecules of solid $(\text{Me}_3\text{Si})_4\text{C}$ at room temperature) or, more likely, are randomly rotationally disordered. This means that the crystal is made up of discrete $\text{TsiSnMe}_2\text{F}$ molecules, with no intermolecular $\text{F} \cdots \text{Sn}$ interactions, in accord with the observations on I and II discussed below.

We next examined compound II, in the expectation that the presence of the two Ph groups on the tin atom would, by destroying the quasi-spherical shape associated with the molecule of $(\text{Me}_3\text{Si})_3\text{CSnMe}_2\text{F}$, result in a less disordered crystal. We were, in fact, able to determine the structure of the molecule and show beyond doubt that the crystal consisted of discrete molecules of II, the shortest intermolecular $\text{Sn} \cdots \text{F}$ distance being 7.8 Å. Since the structural parameters ($R = 0.058$; $R^1 = 0.119$) were less precise than those for I, the structure of the latter is discussed first.

In our experience compounds containing the less symmetrical Tpsi ligands give more satisfactory diffraction data than the corresponding species containing Tsi ligands, and I did, indeed, give better results than either II or III. Again the most significant feature of the structure is that the crystal is made up of discrete molecules, the closest intermolecular $\text{F} \cdots \text{Sn}$ distance being 7.6 Å; thus the presence of the single bulky Tpsi ligand along with two Me ligands on tin is sufficient to inhibit five-coordination. The configuration about the four-coordinate tin atom is however, markedly distorted from the tetrahedral, the Me groups being bent away from the Tpsi group (the mean Tpsi-Sn-Me angle is $120.3(4)^\circ$), and both the Tpsi and Me groups lying over towards the small F ligand (the Tpsi-Sn-F angle is $103.37(8)^\circ$ and the mean Me-Sn-F angle is $99.7(1)^\circ$). The Me-Sn-Me angle ($108.6(1)^\circ$) is close to tetrahedral. The Sn-Me bonds (mean $2.130(2)$ Å) appear to be significantly shorter than the Sn-Tpsi bond ($2.185(2)$ Å). The overall geometry around Sn is fairly close to that in $(\text{C}_6\text{H}_{11})_3\text{SnF}$ [1] when account is taken of the presence of three equivalent alkyl groups in the latter. It is relevant to note that there is no intramolecular $\text{F} \cdots \text{Si}$ interaction, the shortest $\text{F} \cdots \text{Si}$ distance being 3.5 Å, only 0.1–0.2 Å below the sum of the Van der Waals radii. The Sn-F bond length ($1.965(2)$ Å) is startlingly smaller than that reported for $(\text{C}_6\text{H}_{11})\text{SnF}$, viz. $2.45(1)$ Å, but the latter value was considered by the authors concerned to be an artefact arising from the inaccuracy of the structure determination [1]. The value we report appears to represent the first accurate measure of the Sn-F bond length in a four-coordinate tin compound, and is appreciably less than the sum (2.11 Å) of the covalent radii. The Sn-F bond is also significantly shorter than the non-bridging bonds in the five-coordinate tin species $[\text{Et}_4\text{N}][\text{Me}_2\text{Sn}(\text{F})\text{O}_6\text{H}_4\text{S}-2]$ ($2.041(5)$ Å) [7] and $(\text{t-Bu}_2\text{Sn}(\text{OH})\text{F}_2)$ [5] ($2.049(6)$ Å), but substantially longer than the non-

bridging Sn–F bonds in the hexa-coordinate tin species $(\text{SnF}_4)_4$ (1.88) [12]. The lengths of the bridging Sn–F bonds in the latter are 2.02 Å [12], those in Me_2SnF_2 2.12 ± 0.01 Å [2], and those in Me_3SnF are 2.2–2.6 Å [3].

Features of the structure within the Tpsi ligand resemble those in this ligand and the related Tsi ligand in a range of compounds (see, e.g., ref. 13), viz:

- (a) The C(1)–Si bonds (1.903(3), 1.926(2), and 1.930(2) Å) are significantly longer than the Si–Me (mean 1.874(4) Å) and Si–Ph bonds (1.890(2) Å).
- (b) The internal C–C–C angles at the *ipso* carbon atoms [116.5(2), 116.6(2), and 115.6(2)°] are distinctly smaller than the 120° associated with a regular hexagon.
- (c) The strain is mainly accommodated by opening of the Si–C(1)–Si angles (mean 111.8(34)°) towards the tin atom and corresponding closing of the Me–Si–Me and Me–Si–Ph angles (overall mean 105.7(21)°).

The structure of fluoride II is closely similar to that of I, and the configuration around tin is distorted from tetrahedral in a very similar way. The features of the geometry within the $(\text{Me}_3\text{Si})_3\text{C}$ ligand correspond to those outlined for I in (a)–(c) above, but are less clear cut because of the poorer precision. The shortest intramolecular F···Si distance is 3.6 Å.

Mössbauer and NMR spectra

The Mössbauer spectra of fluorides I and III were determined by Dr. P.J. Smith (International Tin Research Institute), and showed asymmetric doublets; the relevant data are shown in Table 5.

The data for the two compounds are very similar, confirming the similarity of the solid state structures. The values of the isomer shifts, δ , are in the range observed for other trialkyltin halides [14], but somewhat lower than that (viz. 1.55 mm s^{-1}) for $(\text{C}_6\text{H}_{11})_3\text{SnF}$ [1]. The values of the quadrupole splitting, ΔE_q , are (possibly fortuitously) close to those calculated for the point charge model [15] and fall in the upper end of the range (1.00 – 2.40 mm s^{-1}) usually associated with regular tetrahedral triorganotin compounds R_3SnX [16], but they are markedly lower than those for polymeric trialkyltin fluorides (e.g. 3.82 mm s^{-1} for Me_3SnF [16]) and also than those for $(\text{C}_6\text{H}_{11})_3\text{SnF}$ (3.96 mm s^{-1}) [1] and $(\text{Me}_2\text{PhCCH}_2)_3\text{SnF}$ (2.79 mm s^{-1}) [17], in both of which intermolecular F···Sn interactions are weak.

The values of $^1J(^{119}\text{Sn}-^{19}\text{F})$ for compounds I–III (2374, 2463, and 2376 Hz, respectively) are of interest, since most trialkyltin fluorides are polymeric and so insufficiently soluble to give the relevant NMR spectra. The values are close to that (2298 Hz) quoted for $(\text{Me}_2\text{PhCCH}_2)_3\text{SnF}$ [18].

TABLE 5
 $^{119\text{m}}\text{Sn}$ MÖSSBAUER SPECTRA ^a

Compound	δ (mm s^{-1})	ΔE_q (mm s^{-1})	Γ_1^b (mm s^{-1})	Γ_2^b (mm s^{-1})
TsiSnMe ₂ F (I)	1.26	2.35	0.86	1.19
TpsiSnMe ₂ F (III)	1.31	2.12	1.17	2.01

^a Relative to Ba $^{119\text{m}}\text{SnO}_3$. ^b Γ_1 and Γ_2 are widths at half height at higher and lower energies, respectively.

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