Organometallics **2005,** *24,* 773−776

The First Dimeric Triorganotin Fluoride: Stabilization by Unsymmetrically Oriented Menthyl Substituents

Jens Beckmann,[†] Dainis Dakternieks, and Andrew Duthie*

Centre for Chiral and Molecular Technologies, Deakin University, Geelong 3217, Australia

Received November 9, 2004

Summary: In the solid state, (−)-tris([1R,2S,5R]-menthyl)tin fluoride, Men_3SnF *(**6**), exhibits a dimeric structure in which one tin atom is four-coordinate and the other five-coordinate. This novel dimeric association mode is attributed to the orientation of the unsymmetrical menthyl groups, which are arranged to allow a minimum Sn⋯Sn separation of 4.84 Å within the dimer. The exocyclic isopropyl groups of the menthyl groups point in opposite directions on each tin atom of the dimer, thus preventing further association (Sn⋯Sn separation outside the dimer 10.49 Å).* ^{119}Sn *and* ^{19}F *MAS NMR spectroscopy were utilized to probe the diverse coordination numbers found by X-ray crystallography for the geometries of the two tin and fluorine sites. In solution, **6** is a monomer at both room temperature and −100 °C. However, upon addition of* Bu_4NF*, **6** is in equilibrium with* $[(Men_3SnF)_2F]^-$ *(**6a**),* $[Men_3SnF_2]^-$ *(**6b**), and noncoordinating fluoride anions.*

Introduction

The degree of association in triorganotin fluorides, R_3SnF (R = alkyl, aryl), is intimately related to the steric bulk of the organic substituents, which confines the space available for intermolecular Sn−F interactions.[1] Triorganotin fluorides with very bulky substituents, e.g. Mes_3SnF (**1**, Sn−F = 1.96 Å; Mes = mesityl),[2] are monomers and possess tetrahedral tin atoms. On the other hand, triorganotin fluorides having small organic groups, e.g. Ph_3SnF (**2**, Sn−F = 2.15 Å),[3] are polymeric and exhibit trigonal-bipyramidal tin atoms. In this geometry, the fluorine atoms occupy the axial positions, where they link adjacent tin atoms within the polymer chain. Between the boundaries of monomers and polymers, a number of triorganotin fluorides, e.g. Me_3SnF (**3**, Sn−F = 2.15/2.45 Å),[4] *c*-Hex_3SnF (**4**, Sn−F = 2.05/2.30 Å),[5] and $(Me_3SiCH_2)_3SnF$ (**5**, Sn−F = 2.03/3.12 and 2.37/2.78 Å),[6] with asymmetric Sn−F bridges are known. In these compounds the geometry lies between the tetrahedral and trigonal-bipyramidal extremes (4 + 1 coordination). There is strong evidence to suggest that all of these intermediate structures are disordered, which for **5** was recently explained by a flip-flop motion of the fluorine atoms between two minimum energy positions separated by a low energy barrier.[6] The structures of triorganotin fluorides and related compounds have been frequently investigated by ^{119}Sn MAS NMR spectroscopy, which is a particularly useful tool for this class of compounds, due to the coupling information provided by the NMR-active ^{19}F nucleus.[7]

We now describe (−)-tris([1*R*,2*S*,5*R*]-menthyl)tin fluoride, (−)-Men_3SnF (**6**), which shows a hitherto unobserved association mode by forming dimers in the solid state.

Results and Discussion

(−)-Tris([1*R*,2*S*,5*R*]-menthyl)tin fluoride, Men_3SnF (**6**), was prepared in good yield by a halide exchange reaction from (−)-tris([1*R*,2*S*,5*R*]-menthyl)tin chloride, Men_3SnCl,[8] and KF in DMF under anhydrous conditions and was obtained as a low-melting crystalline solid (eq 1).[9] Unexpectedly, the X-ray structure analysis has

$$Men_3SnCl \xrightarrow[\text{DMF}]{\text{anhydrous KF}} \underset{\mathbf{6}}{Men_3SnF} \qquad (1)$$

revealed that two molecules of **6** are associated via intermolecular Sn⋯F interactions to give isolated dimers in the solid state. The structure is depicted in Figure 1, and selected bond parameters are collected in the caption of the figure. A useful parameter to classify the degree of association in the solid state is the Sn⋯Sn separation, which increases for the previously reported polymeric and monomeric triorganotin fluorides in the order Ph_3SnF (**2**; 4.29 Å)[3] < Me_3SnF (**3**; 4.32 Å)[4] < *c*-Hex_3SnF (**4**; 4.35 Å)[5] < $(Me_3SiCH_2)_3SnF$ (**5**; 5.15 Å)[6]

---

* To whom correspondence should be addressed. E-mail: aduthie@deakin.edu.au. Fax: ++61-3-5227-1040.

[†] Present address: Institut für Chemie, Freie Universität Berlin, Fabeckstrasse 34-36, 14195 Berlin, Germany.

(1) For reviews see: (a) Ingham, R. K.; Rosenberg, S. D.; Gilman, H. *Chem. Rev.* **1960**, *60*, 459. (b) *Gmelin Handbook of Inorganic Chemistry*; ; Springer: Berlin, 1978; Tin, Part 5 (Organotin Fluorides, Triorganotin Chlorides). (c) Jagirdar, B. R.; Murphy, E. F.; Roesky, H. W. *Prog. Inorg. Chem.* **1999**, *48*, 351.

(2) Reuter, H.; Puff, H. *J. Organomet. Chem.* **1989**, *379*, 223.

(3) Tudela, D.; Gutierrez-Puebla, E.; Monge, A. *J. Chem. Soc., Dalton Trans.* **1992**, 1069.

(4) (a) Clark, H. C.; O'Brien, R. J.; Trotter, J. *J. Chem. Soc.* **1964**, 2332. (b) Clark, H. C.; O'Brien, R. J.; Trotter, J. *Proc. Chem. Soc.* **1964**, 85.

(5) Tudela, D.; Fernandez, R.; Belsky, V. K.; Zavodnik, V. E. *J. Chem. Soc., Dalton Trans.* **1996**, 2123.

(6) Beckmann, J.; Horn, D.; Jurkschat, K.; Rosche, F.; Schürmann, M.; Zachwieja, U.; Dakternieks, D.; Duthie, A.; Lim, A. E. K. *Eur. J. Inorg. Chem.* **2003**, 164.

(7) (a) Harris, R. K.; Packer, K. J.; Reams, P. *Chem. Phys. Lett.* **1985**, *115*, 16. (b) Harris, R. K.; Reams, P.; Packer, K. J. *J. Mol. Struct.* **1986**, *141*, 13. (c) Bai, H.; Harris, R. K.; Reuter, H. *J. Organomet. Chem.* **1991**, *408*, 167. (d) Bai, H.; Harris, R. K. *J. Magn. Reson.* **1992**, *96*, 24. (e) Kim, Y. W.; Labouriau, A.; Taylor, C. M.; Earl, W. L.; Werbelow, L. G. *J. Phys. Chem.* **1994**, *98*, 4919. (f) Cherryman, J. C.; Harris, R. K. *J. Magn. Reson.* **1997**, *128*, 21.

(8) Lucas, C.; Santini, C. C.; Prinz, M.; Cordonnier, M.-A.; Basset, J.-M.; Connil, M.-F.; Jousseaume, B. *J. Organomet. Chem.* **1996**, *520*, 101.

(9) Initial attempts to prepare Men_3SnF in aqueous concentrated KF solution produced impure products. In these cases IR spectroscopy revealed the presence of hydroxy groups: Wharf, I.; Lebuis, A. M.; Roper, G. A. *Inorg. Chim. Acta* **1999**, *294*, 224.

10.1021/om049140y CCC: $30.25

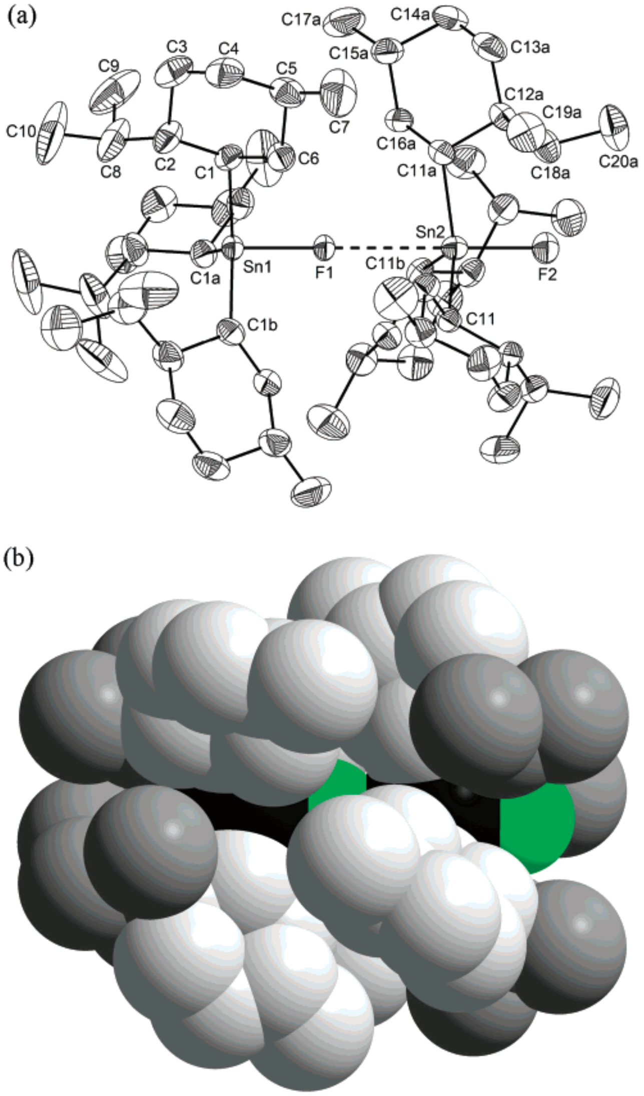

Figure 1. (a) General view of **6** showing 20% probability displacement ellipsoids and the atom-numbering scheme. Selected bond lengths (Å) and angles (deg): Sn1−F1, 1.997(3); Sn2···F1, 2.842(3); Sn2−F2, 1.981(4); Sn1−C1, 2.178(6); Sn2−C11, 2.165(4); Sn1···Sn2, 4.839(1); F1−Sn1−C1, 96.58(2); C1−Sn1−C1a, 118.67(10); F2−Sn2−C11, 100.24(5); C11−Sn2−C11a, 116.88(10); F1···Sn2−F2, 180; Sn1−F1···Sn2, 180. Symmetry operation used to generate equivalent atoms: (a) = $1 - x + y$, $1 - x$, z; (b) = $1 - y$, $x - y$, z. (b) Space-filling model of **6** demonstrating the shielding effect of the isopropyl groups (medium gray) at the ends of the dimer.

< Mes_3SnF (**1**; 6.42 Å).[7] For Men_3SnF (**6**) the Sn···Sn separation within the dimer is 4.839(1) Å and lies between those of *c*-Hex_3SnF (**4**)[5] and $(Me_3SiCH_2)_3SnF$ (**5**),[6] whereas the closest Sn···Sn separation of adjacent dimers is 10.489(1) Å. The dimer comprises an asymmetric Sn1−F1···Sn2 linkage (Sn1−F1 = 1.997(3) Å; Sn2···F1 = 2.842(3) Å) and a terminal (nonbridging) fluorine atom (F2) attached to one tin atom (Sn2−F2 = 1.981(4) Å). The geometry of Sn2 is defined by a primary C_3F donor set and an additional intermolecular Sn···F contact that gives rise to a distorted-trigonal-bipyramidal configuration that is best described as a 4 + 1 coordination (geometrical goodness $\Delta\Sigma(\theta)$ = 49.9°).[10]

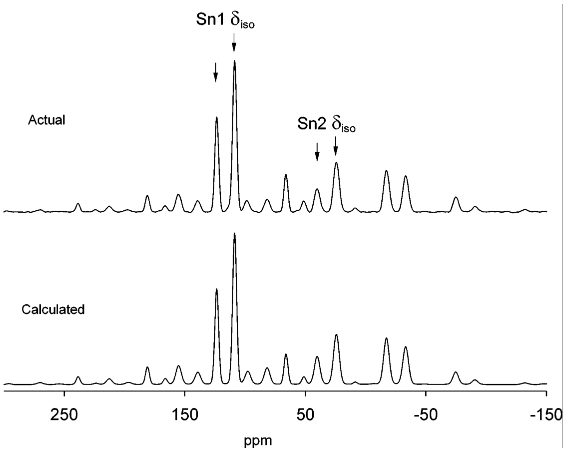

Figure 2. Experimental and iteratively fitted ^{119}Sn MAS NMR spectra (149.03 MHz, ν_{RO} 8570 Hz) of **6**. The two doublets at δ_{iso} 116.1 and 32.2 and are indicated by arrows.

Interestingly, the geometry of Sn1, also defined by a primary C_3F donor set, shows features that closely resemble a distorted trigonal bipyramid, with one deficient axial ligand (geometrical goodness $\Delta\Sigma(\theta)$ = 66.3°),[10] rather than the expected tetrahedron (Figure 1a). The α-carbon atoms of Sn1 and Sn2 adopt orientations that deviate by only 10.3° (dihedral angle around the Sn−Sn vector) from the rather unexpected eclipsed conformation. The most interesting feature of the structure is the conformation of the organic substituents, which provides an explanation as to why the Sn−F association stops at the stage of dimers. The three isopropyl groups belonging to the menthyl groups attached to Sn1 point in the direction opposite to those of Sn2, effectively capping the ends of the dimer and denying further coordination at these points (Figure 1b). In this manner the unsymmetrically shaped menthyl groups allow minimization of the Sn−F···Sn bridge distance within the dimer. Consistent with the crystal structure, the ^{119}Sn MAS NMR spectrum of Men_3SnF (**6**) reveals two doublets centered at δ 116.1 and 32.2 having $^1J(^{119}Sn-^{19}F)$ couplings of 2200 and 2390 Hz, which were unambiguously assigned to Sn1 and Sn2, respectively; the spectrum is depicted in Figure 2. The assignment is based on the relationship between the coordination number of the tin atoms and the ^{119}Sn NMR chemical shift and correlation of the Sn−F bond length with the magnitude of the $^1J(^{119}Sn-^{19}F)$ coupling.[6,7] The two doublets are accompanied by sets of spinning sidebands, which were used to perform tensor analyses according to the method of Herzfeld and Berger (Figure 2); the results are collected in Table 1.[11] The asymmetry (η) is 0.00 for all four components of the two doublets, as is required by the group theory for the 3-fold symmetry axes[12] of Sn1 and Sn2 established by X-ray crystallography. The slightly different geometries of Sn1 and Sn2 are reflected in the average anisotropies ζ of −75 and −170, respectively. As proposed earlier for $(Me_3SiCH_2)_3SnF$ (**5**), this parameter appears to be

---

[10] Kolb, U.; Beuter, M.; Dräger, M. *Inorg. Chem.* **1994**, *33*, 4522.

[11] Herzfeld, J.; Chen, X. In *Encyclopedia of Nuclear Magnetic Resonance*; Grant, D. M., Harris, R. K., Eds.; Wiley: Chichester, U.K., 1996; Vol. 7, p 4362.

[12] (a) Buckingham, A. D.; Malm, S. M. *Mol. Phys.* **1971**, *22*, 1127. (b) Klaus, E.; Sebald, A. *Magn. Reson. Chem.* **1994**, *32*, 679. (c) Sebald, A. In *Advanced Application of NMR to Organometallic Chemistry*; Gielen, M., Willem, R., Wrackmeyer, B., Eds.; Wiley: Chichester, U.K., 1996; p 123.

Table 1. ^{119}Sn MAS NMR Parameters for Men$_3$SnF (6)^a

δ_{iso}	amt, %	ζ	η	σ_{11}	σ_{22}	σ_{33}
123.5	25.2	−103	0.00	−72	−72	−227
108.7	26.3	−46	0.00	−86	−86	−155
40.2	25.2	−195	0.00	57	57	−235
24.2	23.3	−144	0.00	48	48	−168

^{a} Definitions: δ_{iso} (ppm) $= -\sigma_{\mathrm{iso}} = -(\sigma_{11} + \sigma_{22} + \sigma_{33})/3$; ζ (ppm) $= \sigma_{33} - \sigma_{\mathrm{iso}}$ and $\eta = |\sigma_{22} - \sigma_{11}||\sigma_{33} - \sigma_{\mathrm{iso}}|$, where σ_{11}, σ_{22}, and σ_{33} (ppm) are the principal tensor components of the shielding anisotropy (SA), defined as follows: $|\sigma_{33} - \sigma_{\mathrm{iso}}| > |\sigma_{11} - \sigma_{\mathrm{iso}}| > |\sigma_{22} - \sigma_{\mathrm{iso}}|$.

particularly sensitive to weak Sn···F interactions.[6] Additional $^1J(^{119}\mathrm{Sn}{-}^{19}\mathrm{F})$ coupling information associated with the intermolecular Sn···F interaction (e.g. doublets of doublets) was not observed for **5**[6] and **6**. However, the ^{119}Sn MAS NMR signal of Sn2 is somewhat broader than that of Sn1, which is tentatively attributed to the presence of an unresolved $^1J(^{119}\mathrm{Sn}{-}^{19}\mathrm{F})$ coupling. The ^{19}F MAS NMR spectrum of **6** reveals two overlapping signals at δ_{iso} −223.1 and −224.2 with approximately equal intensities.

Compound **6** exhibits good solubility in common organic solvents such as CHCl$_3$, toluene, THF, and MeOH. Consistent with a monomeric structure in solution, the ^{119}Sn NMR spectrum (d_8-toluene) of **6** at room temperature shows a doublet centered at δ 83.4 ($w_{1/2}$ = 30 Hz) with a $^1J(^{119}\mathrm{Sn}{-}^{19}\mathrm{F})$ coupling of 2300 Hz. The ^{19}F NMR spectrum of **6** reveals a singlet at δ −227.8 with resolved tin satellites ($^1J(^{19}\mathrm{F}{-}^{117/119}\mathrm{Sn})$ = 2200/2300 Hz) and an intensity ratio indicative of a monomeric triorganotin fluoride. In an effort to see whether association of the monomers occurs at lower temperatures, the same sample was investigated by low-temperature NMR spectroscopy. At −100 °C the ^{119}Sn and ^{19}F NMR spectra show signals that have shifted to 112.3 and −226.0, respectively, but no qualitative change was observed.

Formation of the fluoride-bridged dimeric anion $[(\mathrm{Me_3SnF})_2\mathrm{F}]^-$ has previously been observed in solution.[13] It was therefore interesting to determine if the steric bulk of the menthyl groups would prohibit a similar observation for Men$_3$SnF (**6**). To investigate its reactivity toward fluoride anions, mixtures of **6** with 0.5, 1.0, and 5.0 equiv of Bu$_4$NF were prepared in toluene. For 0.5 and 1.0 equiv of added Bu$_4$NF the room-temperature ^{119}Sn NMR spectra show one slightly broad doublet signal for **6** at δ 83.0 ($w_{1/2}$ = 80 Hz) and 83.0 ($w_{1/2}$ = 130 Hz), respectively, whereas no reasonable spectrum could be obtained for 5.0 equiv of added Bu$_4$NF. Apart from the increased broadness of the signals assigned to **6**, no evidence for the formation of anionic triorganotin fluorides was found at room temperature. However, when the samples were cooled to −100 °C, new signals evolved that were unambiguously assigned to $[(\mathrm{Men_3SnF})_2\mathrm{F}]^-$ (**6a**) and $[\mathrm{Men_3SnF_2}]^-$ (**6b**) on the basis of the multiplet patterns derived from the various $^1J(^{119}\mathrm{Sn}{-}^{19}\mathrm{F})$ couplings. Apparently, the species **6a** and **6b** are configurationally labile at room temperature, thus having a life span that is short on the ^{19}F and ^{119}Sn NMR time scale. The populations of **6**, **6a**, and **6b** vary with the ratio of the reactants, and the nonstoichiometry of the reaction suggests that these compounds are in equilibrium with noncoordinating fluoride anions. For 0.5 equiv of added Bu$_4$NF, the ^{119}Sn NMR spectrum shows three signals at δ 109.9 (**6**, integral 50%), −114.6 (**6a**, integral 25%) and −212.6 (**6b**, integral 25%), whereas for 1.0 equiv of added Bu$_4$NF the spectrum shows slightly shifted signals at δ 109.6 (**6**, integral 33%), −115.9 (**6a**, integral 33%), and −214.8 (**6b**, integral 33%). At 5.0 equiv of Bu$_4$NF, the ^{119}Sn NMR spectrum shows only one signal at δ −219.1 for **6b**. The ^{119}Sn NMR signal of **6a** at δ −114.6 was observed as a doublet of doublets, giving rise to two inequivalent $^1J(^{119}\mathrm{Sn}{-}^{19}\mathrm{F})$ couplings of 1080 and 2080 Hz, which are associated with the bridging fluorine atom and the terminal fluorine atoms, respectively. The ^{119}Sn NMR signal of **6b** at δ −212.6 was observed as a triplet arising from a $^1J(^{119}\mathrm{Sn}{-}^{19}\mathrm{F})$ coupling of 1700 Hz. Consistent with the ^{119}Sn NMR results at −100 °C, the ^{19}F NMR spectra reveal signals at δ −165.9, −188.6, and −117.6 for **6a** and **6b**, which are accompanied by tin satellites indicating $^1J(^{19}\mathrm{F}{-}^{117/119}\mathrm{Sn})$ couplings of 1050, 2050, and 1650 Hz.

The observation that **6**, **6a**, and **6b** are in equilibrium with noncoordinating fluoride anions is reminiscent of the reactivity of Me$_3$SnF (**3**) under similar conditions.[13] On the other hand, Ph$_3$SnF (**2**) reacts readily with 1.0 equiv of Bu$_4$NF to give high yields of Bu$_4$N[Ph$_3$SnF$_2$] and no evidence for equilibria of the associated anion $[(\mathrm{Ph_3SnF})_2\mathrm{F}]^-$ (**2a**) in solution was found.[14]

Experimental Section

General Remarks. Men$_3$SnCl was prepared according to a literature procedure.[8] Solution NMR spectra were obtained using a JEOL GX 270 spectrometer (at 270.17 MHz (^{1}H), 67.94 (^{13}C), 254.19 (^{19}F), and 100.73 (^{119}Sn)) and were referenced against SiMe$_4$, CFCl$_3$, or SnMe$_4$. Solid-state ^{19}F MAS NMR spectra were acquired on a Varian Inova 300 spectrometer (at 282.27 MHz) using a Doty 5 mm triple-resonance MAS probe. A Hahn spin−echo pulse sequence was used with 0.5 ms echo time, 4.8 μs 90° pulse, 1.5 s recycle delay, and MAS at 6.5 kHz. Spectra were referenced externally to CFCl$_3$ as 0 ppm. The ^{119}Sn CP-MAS NMR spectra were measured with a JEOL Eclipse Plus 400 spectrometer (at 149.05 MHz) equipped with a 6 mm MAS probe, *c*-Hex$_4$Sn (δ −97.35) as a secondary reference, and cross polarization (5 ms contact time, 10 s recycle delay). The isotropic chemical shifts (δ_{iso}) were determined by comparison of two acquisitions measured at sufficiently different spinning frequencies. The tensor analysis was performed using the method of Herzfeld and Berger[11] implemented in DmFit 2002.[15] Optical rotations were measured on a Jasco DIP-1000 digital polarimeter using a 10 mL cell. Elemental analysis was carried out by CMAS, Belmont, Australia.

Synthesis of Men$_3$SnF (6). Under inert conditions, solid Men$_3$SnCl (53.0 g, 92.67 mmol) was added to KF (60.0 g, 1.03 mmol) that had been dried at 150 °C in vacuo. Dry DMF (500 mL) was added, and the mixture was heated overnight at reflux. The reaction mixture was cooled and the solvent removed in vacuo. The residue was dissolved in water (200 mL) and chloroform (500 mL), the organic layer separated, dried over Na$_2$SO$_4$, and filtered, and the solvent removed in vacuo. Crystallization from ethanol gave colorless crystals of **6** (39.5 g, 77% yield): mp 80−81 °C. $[\alpha]^{25}_{\mathrm{D}} = -75.4°$ (c = 1,

---

(13) Dakternieks, D.; Zhu, H. *Inorg. Chim. Acta* **1992**, *196*, 19.

(14) Beckmann, J.; Dakternieks, D.; Duthie, A.; Tiekink, E. R. T. *J. Organomet. Chem.* **2002**, *648*, 204.

(15) Massiot, D.; Fayon, F.; Capron, M.; King, I.; Le Calvé, S.; Alonso, B.; Durand, J.-O.; Bujoli, B.; Gan, Z.; Hoatson, G. *Magn. Reson. Chem.* **2002**, *40*, 70.

$CHCl_3$). ^{1}H NMR ($CDCl_3$): δ 0.75−1.05 (m, 11H), 1.13−1.32 (m, 3H), 1.35−1.50 (m, 1H), 1.60−1.78 (m, 2H), 1.85−2.15 (m, 2H). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 16.46 (CH_3), 21.96 (CH_3), 22.36 (CH_3), 26.87 (CH_2), 35.07 (CH), 35.13 (CH_2), 36.02 (CH), 39.34 (CH_2), 42.57 ($^1J(^{13}C-^{117/119}Sn) = 309/323$ Hz, $^2J(^{13}C-Sn-^{19}F) = 7$ Hz; CH), 45.78 (CH). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −227.8 ($^1J(^{19}F-^{117/119}Sn) = 2200/2300$ Hz). $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): δ 83.4 ($^1J(^{119}Sn-^{19}F) = 2300$ Hz). Anal. Calcd for $C_{30}H_{57}FSn$ (555.48): C, 64.87; H, 10.34. Found: C, 65.18; H, 9.98.

NMR Experiments. To d_8-toluene solutions (0.50 mL) of **6** (50 mg, 0.090 mmol) was added 0.50 equiv (12 mg, 0.045 mmol), 1.00 equiv (24 mg, 0.090 mmol), or 5.00 equiv (118 mg, 0.450 mmol) of tetra-*n*-butylammonium fluoride. ^{19}F and ^{119}Sn NMR measurements on the three samples were performed at 20 and −100 °C.

Crystallography. Single crystals of **6** suitable for X-ray crystallography were obtained from a solution of hexane at −20 °C. Crystal data and structure solution at $T = 293(2)$ K: $C_{30}H_{57}FSn$, $M_r = 555.45$, trigonal, $R3$, crystal dimensions $0.20 \times 0.35 \times 0.45$ mm^3, $a = 12.7120(13)$ Å, $b = 12.7120(13)$ Å, $c = 36.998(8)$ Å, $V = 5177.7(13)$ Å^3, $Z = 6$, $\rho_{calcd} = 1.069$ Mg m^{-3}, $F(000) = 1776$, $\mu = 0.758$ mm^{-1}. Intensity data were collected on a Bruker SMART Apex CCD diffractometer with Mo Kα radiation (graphite crystal monochromator, $\lambda = 0.710\,73$ Å) to a maximum of $\theta_{max} = 27.51°$ via ω scans (completeness 96.4% to θ_{max}). Data were reduced and corrected for absorption using the programs SAINT and SADABS.[16] The structure was solved by direct methods and difference Fourier synthesis using SHELX-97 implemented in the program WinGX 2002.[17] Full-matrix least-squares refinement on F^2 using all data was carried out with anisotropic displacement parameters applied to all non-hydrogen atoms. Hydrogen atoms were included in geometrically calculated positions using a riding model and were refined isotropically. The weighting scheme employed was of the type $w = [\sigma^2(F_o^2) + (0.0445P)^2]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$. R1 = 0.0310 for 3327 ($I > 2\sigma(I)$) reflections and wR2 = 0.0976 for 3590 independent reflections; GOF = 1.072, and the Flack parameter was −0.03(3). The maximum/minimum residual electron densities were +0.566/−0.233 e Å^{-3}.

Acknowledgment. The Australian Research Council (ARC) is thanked for financial support. Associate Profs. Jonathan White and Frances Separovic (The University of Melbourne) are gratefully acknowledged for the crystallographic and ^{19}F MAS NMR data collection.

Supporting Information Available: Tables giving X-ray crystallographic data for **6**. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre (CCDC No. 216651) for **6**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, +44-1223-336033; e-mail, deposit@ccdc.cam.ac.uk; web, http://www.ccdc.cam.ac.uk).

OM049140Y

---

(16) SMART, SAINT and SADABS; Siemens Analytical X-ray Instruments Inc., Madison, WI, 1999.

(17) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *20*, 565.