Bis(halodiphenylstannyl)alkanes as Bidentate Lewis Acids toward Halide Ions[†]

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¹¹⁹Sn and ¹⁹F NMR spectroscopies were used to study reaction of bis(halodiphenylstannyl)alkanes $(Ph_2XSn)_2(CH_2)_n$ (X = F, Cl, Br, I; n = 1, 2, 3) with various halide ions in dichloromethane solution. All three series of bis(halodiphenylstannyl)alkanes, (Ph₂XSn)₂- $(CH_2)_n$ (X = F, Cl, Br, I; n = 1, 2, 3), exhibit chelate ability toward halide, forming anionic 1:1 adducts $[(Ph_2XSn)_2(CH_2)_nX]^-$ which are static at -100 °C on the NMR time scale. The bis(halodiphenylstannyl)alkanes always preferentially chelate fluoride ion over chloride or bromide. Endocyclic Sn-CH₂ rotation brings about intramolecular exchange between bridging and terminal fluorine atoms at higher temperature. For n = 1, and 1:1 adducts $[(Ph_2XSn)_2(CH_2)X]^-$ react with additional fluoride (but not chloride or bromide) eventually to give $[(Ph_2F_2Sn)_2(CH_2)]^{2-}$ in which both tin atoms are five-coordinated. For n = 2, the 1:1 adducts $[(Ph_2XSn)_2(CH_2)_2X]^-$ appear particularly stable and there is no evidence for formation of 1:2 adducts $[(Ph_2X_2Sn)_2(CH_2)_2]^2$. Propylene-bridged 1:1 adducts, $[(Ph_2XSn)_2(CH_2)_3X]^-$, react with both fluoride and chloride to give 1:2 adducts, $[(Ph_2F_2Sn)_2(CH_2)_3]^{2-}$ and $[(Ph_2Cl_2Sn)_2(CH_2)_3]^{2-}$, respectively, in which the tin atoms remain five-coordinated. The crystal structures of $[(Ph_2FSn)_2CH_2F]^-(1), [(Ph_2BrSn)_2CH_2F]^-(4), [(Ph_2ISn)_2CH_2F]^-(8), and$ [(Ph₂ClSnCH₂)₂F]⁻ (11), as their tetraethylammonium salts (1a, 4a, 8a, and 11a, respetively), are described. Colorless crystals of **1a** are monoclinic, space group $P2_1/n$, with a = 11.695(4)Å, b = 14.667(2) Å, c = 18.956(2) Å, $\beta = 103.33(1)^\circ$, V = 3164(1) Å³, and Z = 4. Colorless crystals of 4a are monoclinic, space group Cc, with a = 11.758(1) Å, b = 14.880(2) Å, c =19.316(2) Å, $\beta = 93.981(9)^{\circ}$, V = 3371.3(6) Å³, and Z = 4. Colorless crystals of **8a** are monoclinic, space group $P2_1/n$, with a = 10.032(1) Å, b = 16.923(3) Å, c = 20.523(3) Å, $\beta = 16.923(3)$ Å, $\beta = 16.923$ $99.65(1)^\circ$, V = 3434.9(8) Å³, and Z = 4. Colorless crystals of **11a** are monoclinic, space group $P2_1$, with a = 9.562(2) Å, b = 15.529(4) Å, c = 11.359(4) Å, $\beta = 95.51(2)^\circ$, V = 1678.9(9) Å³, and Z = 2. The structures were refined to final R = 0.027, 0.029, 0.033, and 0.029 for 4661, 2647, 3843, and 3457 reflections with $I \ge 3.0\sigma(I)$, respectively.

Introduction

Organotin(IV) halides exhibit strong Lewis acidity, and the complexation chemistry of organotin(IV) halides has been the subject of study for many years.¹ Compounds containing two tin atoms which are bridged through carbon behave as bifunctional Lewis acids, and derivatives with Lewis bases such as chloride ion, dimethyl sulfoxide, and hexamethylphosphonic amide have been described.²⁻¹³ Most earlier studies were concerned with the solid state properties of these complexes, there being only a few $^{119}\mathrm{Sn}$ NMR investigations^{11,12} on the chelating ability of bis(haloorganostannyl)alkanes toward chloride ion in solution. We now report on the reaction of bidentate Lewis acids bis-(halodiphenylstannyl)alkanes $(Ph_2XSn)_2(CH_2)_n$ (X = F, Cl, Br, I; n = 1, 2, 3) with fluoride, chloride, and bromide ions in dichloromethane solution. Also reported are the crystal structures of [(Ph₂FSn)₂CH₂F]⁻, [(Ph₂BrSn)₂- $CH_2F]^-$, [(Ph₂ISn)₂CH₂F]⁻, and [(Ph₂ClSnCH₂)₂F]⁻ as their tetraethylammonium salts.

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Table 1. NMR Data (at -100 °C in Dichloromethane Solution) for Species Formed by Reaction of Bis(haloorganoyl)alkanes, (Ph₂SnXSn)₂(CH₂)_n, with Halide Ion

species	$\delta(^{119}\text{Sn})$	$\delta(^{19}\text{F})$	$J(^{119}{\rm Sn}-^{19}{\rm F})$	J(F-F)	$^{2}J(^{119}\mathrm{Sn}-^{117}\mathrm{Sn})$
		n = 1		·	
(Ph ₂ ClSn) ₂ CH ₂	21.0				220
$(Ph_2BrSn)_2CH_2$	3.2				223
1 ^{<i>a</i>}	-184.8	$-172.1 (F_a)$	2178	62	325
		-97.4 (F _b)	879	62	
2	-244.4	-141.9	1840		
3	-137.0				
4	-152.1	-98.1	787		288
5 ^b	-188.6 (Sn _a)	-175.3 (F _a)	2211	59	271
	-147.4 (Sn _b)	-98.7 (F _b)	852	59	271
6	-154.8	-96.8	806		276
7 ^c	-190.0 (Sn _a)	-174.4 (F _a)	2202	59	273
	-149.8 (Snb)	-97.6 (F _b)	850	59	273
8	-100.1		780		
		n = 2			
(Ph ₂ ClSnCH ₂) ₂	1.8				
$(Ph_2ISnCH_2)_2$	-40.4				
9	-230.0	-165.1^{f} (F _a)	2100	81	350
		-159.3^{f} (F _b)	1260	81	
10	-177.8	-153.2^{g}	1128		
11	-191.2	-155.3	1180		
12 ^d	-222.8 (Sn _a)	-169.7 (F _a)	2080	80	
	-199.8 (Sn _b)	-159.0 (F _b)	1251		
		<i>n</i> = 3			
(Ph ₂ ClSnCH ₂) ₂ CH ₂	10.3				
13	-142.8				
14	-200.0				
15	-172.7	-142.3	1204		
16 ^e	-209.6 (Sn _a)	-168.8 (F _a)	2042	79	
	-180.7 (Sn _b)	$-140.2 (F_b)$	1250	79	
17	-214.9	-164.9 (F _a)	2030	88	
		-139.4 (F _b)	1264	88	
18	-267.8	-152.0	1880		

 ${}^{a} {}^{3}J(Sn-F_{b}-Sn-F_{a}) = 140 \text{ Hz}. {}^{b} {}^{3}J(Sn_{b}-F_{a}) = 144 \text{ Hz}; J(Sn_{a}-F_{b}) = 815 \text{ Hz}. {}^{c} {}^{3}J(Sn_{b}-F_{a}) = 145 \text{ Hz}; J(Sn_{a}-F_{b}) = 827 \text{ Hz}. {}^{d} J(Sn_{a}-F_{b}) = 1204 \text{ Hz}. {}^{c} J(Sn_{a}-F_{b}) = 1204 \text{ Hz}. {}^{f}Measured at -55 {}^{\circ}C. {}^{s}Measured at -80 {}^{\circ}C. {}^{h}Measured at -35 {}^{\circ}C.$

Results and Discussion

Reaction of Bis(halodiphenylstannyl)methane with Halide Ion. The compound (Ph₂FSn)₂CH₂ has too low solubility in common organic solvents to allow measurement of its ¹¹⁹Sn or ¹⁹F NMR spectrum. However, addition of 1 mol equiv of fluoride ion (Bu₄NF·3H₂O) to $(Ph_2FSn)_2CH_2$ in dichloromethane solubilizes the system and gives rise to a doublet of doublets of doublets resonance at -184.8 ppm, accompanied by ¹¹⁷Sn satellites, in the ¹¹⁹Sn NMR spectrum recorded at -100 °C. The corresponding ¹⁹F NMR spectrum comprises a doublet and a triplet resonance, of relative intensity 2:1, at -172.1 and -97.4 ppm, J(F-F) = 62 Hz. These data (Table 1) are consistent with formation of the anionic species $[(Ph_2FSn)_2CH_2F]^-$ (1) (Chart 1) which contains two apical fluorine atoms and a fluorine atom chelated by two tin atoms to form a four-membered SnCSnF ring. The ¹⁹F NMR chemical shift of the bridging fluorine atom is at considerably higher frequency than that for the two apical fluorine atoms, in line with the trend reported for comparable silicon systems.^{14,15} The magnitude of J(Sn-F) coupling of the terminal fluorides (2178 Hz) is appreciably larger than that of the bridging fluoride (879 Hz) similar to the trend observed in $[(Me_3SnF)_2F]^-$ and in a ditin macrocycle.^{2,16,17}

Variable-temperature NMR spectra indicate that 1 is labile above -100 °C. The two ¹⁹F resonances show loss

of J(F-F) coupling at -30 °C although coupling to ^{117/119}Sn is still evident. Raising the temperature causes the two ¹⁹F resonances to broaden, and at about 0 °C coupling to ^{117/119}Sn is no longer evident. Lack of solubility in an appropriate solvent precluded measurements at significantly higher temperature.

These data are consistent with an intramolecular exchange of the terminal and chelated fluorine atoms resulting from rotation about a $Sn-CH_2$ bond in the methylene bridge. At -30 °C the rate of intramolecular fluorine atom exchange is sufficient such that observation J(F-F) is no longer possible. At 24 °C the two ¹⁹F resonances coalesce, presumably because the rate of rotation about each $Sn-CH_2$ has increased sufficiently to effectively exchange all three fluorine atoms within structure **1**. A similar intramolecular exchange process has been reported recently for some related organosilicon systems.¹⁴



The variable-temperature ¹¹⁹Sn NMR spectra (Figure 1) appear more complex but nevertheless consistent with this intramolecular exchange process. At -30 °C the spectrum appears as a doublet of doublets in which the central two components are significantly broader than the outer two lines. Raising the temperature to 24 °C causes further broadening of all the components. This somewhat complex spectral pattern appears to be

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Addition of a second 1 mol equiv of fluoride to $(Ph_2FSn)_2CH_2$ results in the appearance of a triplet resonance at -244.4 ppm in the ¹¹⁹Sn NMR spectrum at -100 °C. This resonance is assigned to the doubly-charged anionic species $[(Ph_2F_2Sn)_2CH_2]^{2-}$ (2) (Chart 1). The corresponding ¹⁹F NMR spectrum is consistent with this assignment. Furthermore, the ¹⁹F NMR spectrum this doubly-charged anionic species is intact at 24 °C. It appears that $(Ph_2FSn)_2CH_2$ may behave either as a bidentate or as a bismonodentate ligand toward fluoride ion, depending on the concentration of fluoride ion. NMR data are summarized in Table 1. Identical NMR spectra are obtained when Bu₄NF·3H₂O was replaced by the anhydrous fluoride source $[Ph_3SnF_2]^-[Bu_4N]^+$.

The reaction of (Ph₂ClSn)₂CH₂ with chloride ion to give a solid 1:1 adduct [(Ph₂ClSn)₂CH₂·Cl]⁻ has been described previously.¹² Similarly, we find that reaction of chloride with (Ph₂ClSn)₂CH₂ in 1:1 or 2:1 molar ratio leads only to formation of [(Ph₂ClSn)₂CH₂·Cl]⁻ in dichloromethane solution. Reaction of 1 mol equiv of bromide ion (Bu₄NBr) with (Ph₂BrSn)₂CH₂ in dichloromethane solution gives rise to a 119 Sn NMR singlet at -137.0 ppm in the temperature range -100 to 24 °C which is assigned to the bromide chelated anionic species $[(Ph_2BrSn)_2CH_2Br]^-$ (3). Addition of a second 1 mol equiv of bromide causes no apparent change in the ¹¹⁹Sn NMR spectrum at -100 °C, and apparently no new species is formed. In contrast to the case for X = Fwhere a dianion is formed, it appears that $[(Ph_2 XSn_2CH_2$ (for X = Cl or Br) are not sufficiently acidic to add two additional halides.

The addition of 1 mol equiv of fluoride ion to $(Ph_2-BrSn)_2CH_2$ in dichloromethane solution leads to a doublet at -152.1 ppm in the ¹¹⁹Sn NMR spectrum and a singlet, with ^{117/119}Sn satellites, at -98.11 ppm in the ¹⁹F NMR spectrum at -100 °C. These spectra are assigned to formation of a fluoride-chelated species $[(Ph_2BrSn)_2CH_2\cdot F]^-$ (4). It appears that fluoride is preferentially chelated by the two tin atoms of

Figure 1. Tin-119 NMR spectrum of $[(Ph_2SnFSn)_2CH_2F)]^$ in dichloromethane solution at (A) -100 °C and (B) at -30 °C.

-165 -170 -175 -180 -185 -190 -195 -200

(B)

on the pathway to becoming a triplet resonance where the two broad central resonances will eventually collapse to form the central component.

The ¹⁹F NMR spectra at -15 °C show no variation as a function of concentration, which suggests that the observed exchange process is not intermolecular in nature.

As a comparison, the monodentate Lewis acid Ph₂FSnCH₂SiMe₃ was synthesized and its reaction with fluoride examined. The ¹⁹F NMR spectrum at -75 °C of a 1:1 solution of Ph₂FSnCH₂SiMe₃ and Bu₄NF·3H₂O in dichloromethane solution shows a single sharp resonance at -145.5 ppm, accompanied by ^{117/119}Sn satellites (1897 and 1823 Hz, respectively). The ¹¹⁹Sn spectrum at the same temperature shows a triplet at -260.2 ppm with J(Sn-F) = 1897 Hz. Raising the temperature to -35 °C causes the ¹⁹F resonance to

Scheme 1



 $(Ph_2BrSn)_2CH_2$. Significantly, the ¹¹⁹Sn doublet resonance and the ¹⁹F singlet resonance (with ^{117/119}Sn satellites) of 4 remain unchanged as the temperature is raised from -100 to 24 °C, indicating no appreciable exchange between Br and F thereby indicating that fluoride is a better bridging ligand than is bromide.

Addition of 2 mol equiv of fluoride ion to (Ph₂- $BrSn)_2CH_2$ in dichloromethane results in a complex ¹¹⁹Sn NMR spectrum at -100 °C. In addition to the resonances attributed to 4 and 1, there are two doublets of doublets at -147.4 and -188.6 ppm, respectively. The corresponding ¹⁹F spectrum contains two doublets at -98.72 and -175.31 ppm (J(F-F) = 59 Hz). These resonances are assigned to the mixed halide species $[(Ph_2FSn)CH_2(Ph_2BrSn)F]^-$ (5) in which one fluoride is chelated and the other is termianly bound to tin. Variable-temperature ¹⁹F NMR spectra indicate the onset of exchange between bridging and terminal fluorine atoms in 5 at about -30 °C. The reaction of 3 mol equiv of fluoride ion with (Ph2BrSn)2CH2 results in displacement of all the bromide, and only species 1 is observed in the ¹¹⁹Sn and ¹⁹F spectra at -100 °C.

Addition of 1 mol equiv of fluoride ion to $[(Ph_2BrSn)_2CH_2\cdot Br]^-$ (3) results in identical ¹⁹F and ¹¹⁹Sn spectra as were observed for $[(Ph_2BrSn)_2CH_2\cdot F]^-$ (4); i.e. the fluoride displaces the bromide as bridging ligand, demonstrating the superior bridging capacity of the fluoride ion.

The reactions of fluoride ion with $(Ph_2ClSn)_2CH_2$ at molar ratios 1:1, 2:1, and 3:1 give very similar results to those observed for reactions of the bromo analogue. The ¹¹⁹Sn NMR spectrum measured at -100 °C of a dichloromethane solution containing fluoride and $(Ph_2ClSn)_2CH_2$ at molar ratio 2:1 shows the presence of two chloride-fluoride mixed species $[(Ph_2ClSn)_2CH_2\cdot F]^-$ (6) and $[(Ph_2FSn)CH_2(Ph_2ClSn)\cdot F]^-$ (7) as well as 1. The dynamic behavior of species 6 in solution is similar to that of its bromide analogue, 4; i.e. the ¹⁹F and ¹¹⁹Sn spectra do not change significantly in the temperature range -100 to 24 °C. Addition of 1 mol equiv of fluoride to $(Ph_2ISn)_2CH_2$ gives rise to a ¹⁹F spectrum consistent with the formation of $[(Ph_2ISn)_2CH_2F]^-$ (8) in which the fluoride is chelated by the two tin atoms (Table 1). Compound 8 is not sufficiently soluble to allow determination of its ¹¹⁹Sn spectrum. Addition of further mole equivalents of fluoride causes extensive precipitation.

The chelating reactions of bis(halodiphenylstannyl)methane with halide ion are summarized in Scheme 1.

Reaction of Bis(halodiphenylstannyl)ethane with **Halide Ion.** The compound $(Ph_2FSnCH_2)_2$ is not sufficiently soluble in common solvents to allow determination of its ¹⁹F or ¹¹⁹Sn spectra. However, addition of 1 mol equiv of fluoride ion to $(Ph_2FSnCH_2)_2$ in dichloromethane solubilizes the system and gives rise to a doublet of doublets resonance at -230 ppm in the ¹¹⁹Sn NMR spectrum at -100 °C. The ¹⁹F NMR resonances at -100 °C are a little broad but sharpen at -55 °C, and a doublet at -165.1 ppm and a triplet at -159.3ppm with relative intensity of 2:1 are clearly observed. The above data are consistent with formation of an anionic fluoride-chelated species ($[Ph_2FSnCH_2)_2 \cdot F]^-$ (9) which contains a five-membered SnCCSnF ring. The one-bond coupling due to the bridging fluorine is larger than that observed for $[(Ph_2FSn)_2CH_2\cdot F]^-$ (1). These differences appear to result from steric strain in the four-membered ring of $1 (Sn-F-Sn = 97.4^{\circ})$ compared to the more suitable geometry possible in the fivemembered ring of $9 (Sn-F-Sn = 120.5^{\circ})$.

Variable-temperature ¹⁹F NMR spectra of $[(Ph_2-FSnCH_2)_2\cdot F]^-$ (9) indicate an endocyclic Sn-C rotation resulting in intramolecular ligand exchange between bridging and terminal fluorine atoms. The ¹⁹F NMR triplet and doublet resonances lose their J(F-F) coupling at about 10 °C, but coupling to tin is still evident for both resonances at 30 °C. It appears that the energy barrier of endocyclic Sn-C bond rotation is higher for $[(Ph_2FSnCH_2)_2\cdot F]^-$ (9) than for $[(Ph_2FSn)_2CH_2\cdot F]^-$ (1) indicating that the five-membered SnFSnCC ring is more stable than the four-membered SnFSnC ring.

Addition of a second 1 mol equiv of fluoride ion to a solution of $[(Ph_2FSnCH_2)_2 \cdot F]^-$ (9) gives rise to additional, somewhat broad ($W_{1/2} = 120$ Hz), ¹¹⁹Sn resonance at -263.3 ppm. This resonance is only observed in the narrow temperature range of -40 to 10 °C where it appears as a triplet (J(Sn-F) = 1890 Hz) with some additional fine structure. Also present is a weak doublet resonance at -261 ppm, J(Sn-F) = 1980 Hz. The ¹⁹F spectrum of this solution shows a sharp ¹⁹F resonance at -151.2 ppm with very sharp ^{117/119}Sn satelites, J(Sn-F) = 1890 Hz. It was subsequently shown that these additional peaks arose from interactions of the water from the fluoride source, Bu₄NF·3H₂0. Both ¹⁹F and ¹¹⁹Sn spectra of a solution made from the addition of 2 mol equiv of the anhydrous fluoride source [Ph3- SnF_2]Bu₄N] show only formation of **9** and unreacted [Ph₃SnF₂]Bu₄N]. There was some precipitation which was subsequently identified as Ph₃SnF by elemental analysis. We are continuing work on the hydrolysis products of these and other related systems.

Apparently species **9** is particularly stable, there being no evidence for formation of the dianion $[(Ph_2FSnCH_2)_2F_2]^{2-}$. Earlier work¹² reported that the addition of chloride ion to $[(Ph_2ClSnCH_2)_2\cdotCl]^-$ does not change the value of ¹¹⁹Sn chemical shift of the complex, indicating that the doubly-charged anionic complex $[(Ph_2Cl_2SnCH_2)_2]^{2-}$ is probably not formed to any appreciable degree in solution. These results indicate the particular stability of 1:1 halide adducts of bis(halodiphenylstannyl)ethane, possibly due to the favorable formation of five-membered SnCH₂CH₂SnX rings.

Addition of 1 mol equiv of fluoride to $(Ph_2ISnCH_2)_2$ results in formation of the fluoride-chelated species $[(Ph_2ISnCH_2)_2 \cdot F]^-$ (10) (Chart 2), which is identified by the appearance of a doublet at -177.8 ppm in the ¹¹⁹Sn NMR spectrum and a singlet, with ^{119/117}Sn satellites, at -153.22 ppm in the ¹⁹F NMR spectrum at -80 °C. There is no evidence for ligand exchange between fluoride and iodide at room temperature. Addition of a second 1 mol equiv of fluoride to $(Ph_2ISnCH_2)_2$ results in a precipitate which may be due to the formation of $(Ph_2FSnCH_2)_2$. However, the addition of a third mole of fluoride dissolves the precipitate and forms $[(Ph_2FSnCH_2)_2 \cdot F]^-$ (9) which is identified by both ¹¹⁹Sn and ¹⁹F NMR spectra at -80 °C.

Addition of 1 mol equiv of chloride ion to (Ph2- $FSnCH_2$ in dichloromethane results in formation of mixed chloro-fluoro complexes, $[(Ph_2ClSnCH_2)_2 F]^-$ (11) and $[(Ph_2FSnCH_2CH_2SnClPh_2)\cdot F]^-$ (12), as well as $[(Ph_2FSnCH_2)_2 F]^-$ (9). The ¹⁹F resonances which arise from the bridging and the terminal fluorine atoms of [(Ph₂FSnCH₂CH₂SnClPh₂)·F]⁻ (12) do not collapse until 24 °C, again indicating that the barrier to intramolecular exchange of fluorides as a result of rotation about the Sn-C bond is higher in a five-membered SnC₂SnF ring than in a four-membered SnCSnF ring. On the other hand, the ¹⁹F resonance due to [(Ph₂ClSnCH₂)₂·F]⁻ (11) remains sharp, with $^{119/117}$ Sn satellites, at 24 °C which indicates that exchange between chloride and bridging fluoride does not occur on the NMR time scale. Addition of a second chloride to (Ph₂FSnCH₂)₂ does not change either the ¹¹⁹Sn or the ¹⁹F NMR spectrum. That the chelated halide ion is always fluoride indicates the superior bridging capability of fluoride ion over chloride ion.



Reaction of Bis(chlorodiphenylstannyl)propane with Halide Ion. The reaction of chloride ion with $(Ph_2ClSnCH_2)_2CH_2$ at molar ratio 1:1 in dichloromethane solution at -100 °C gives rise to a ¹¹⁹Sn NMR singlet at -142.8 ppm and at molar ratio 2:1 a singlet at -200.0ppm. These data are assigned to the chloride chelated species $[(Ph_2ClSnCH_2)_2CH_2 \cdot Cl]^-$ (13) and the doublycharged species $[(Ph_2Cl_2SnCH_2)_2CH_2]^{2-}$ (14).

Addition of 1 mol equiv of fluoride to $(Ph_2ClSnCH_2)_2$ -CH₂ in dichloromethane gives rise to two doublets of relative intensity of approximately 5:1, at -172.7 and -156.7 ppm, in the ¹¹⁹Sn NMR spectrum recorded at -100 °C. The major resonance is assigned to $[(Ph_2ClSnCH_2)_2CH_2\cdotF]^-$ (15). The addition of a second 1 mol equiv of fluoride to $(Ph_2ClSnCH_2)_2CH_2$ does not cause precipitation but results in formation of the two new species $[Ph_2FSn(CH_2)_3SnClPh_2\cdotF]^-$ (16) and $[(Ph_2FSnCH_2)_2CH_2\cdotF]^-$ (17), in addition to $[(Ph_2 ClSnCH_2)_2CH_2\cdotF]^-$ (17), in addition to $[(Ph_2 ClSnCH_2)_2CH_2\cdotF]^-$ (15). Variable-temperature ¹⁹F NMR spectra of 17 indicate the onset of endocyclic Sn-C rotation, bringing about intramolecular exchange between bridging and terminal fluorine atoms at about -30 °C.

As expected, the addition of a third 1 mol equiv of fluoride to $(Ph_2ClSnCH_2)_2CH_2$ results only in the formation of $[(Ph_2FSnCH_2)_2CH_2\cdot F]^-$ (17) and the addition of fourth fluoride gives rise to both $[(Ph_2FSnCH_2)_2CH_2\cdot F]^-$ (17) and doubly-charged $[(Ph_2F_2SnCH_2)_2CH_2]^{2-}$ (18), in the ratio of approximately 1:4. NMR data are summarized in Table 1.

Table 2. Selected Interatomic Bond Distances (Å) and Angles (deg) for 1a, 4a, 8a, and 11a

$ \begin{array}{l} 1a (X = F(2), \\ Y = F(3)) \end{array} $	4a (X = Br(1), Y = Br(2))	8a (X = I(1), Y = I(2))	11a (X = Cl(1), Y = Cl(2))
2.204(2)	2.274(5)	2.248(4)	2.197(4)
2.004(2)	2.609(1)	2.8558(8)	2.5044(9)
2.095(4)	2.09(1)	2.103(7)	2.107(7)
2.104(4)	2.125(9)	2.115(7)	2.114(7)
2.114(4)	2.128(9)	2.117(7)	2.100(6)
2.249(2)	2.212(5)	2.231(4)	2.178(4)
1.995(2)	2.613(1)	2.8604(8)	2.511(2)
2.097(4)	2.08(1)	2.114(7)	$2.109(7)^a$
2.112(4)	2.125(8)	2.097(7)	2.106(7)
2.097(4)	2.09(1)	2.126(7)	2.113(7)
175.51(9)	171.5(1)	169.6(1)	174.5(1)
78.9(1)	76.1(3)	77.8(2)	82.9(3)
87.8(1)	85.5(3)	85.8(2)	88.9(2)
89.1(1)	87.3(3)	89.1(2)	88.1(2)
97.0(1)	95.5(3)	92.7(2)	91.9(2)
92.8(1)	97.2(2)	96.0(2)	95.4(2)
94.4(1)	98.4(3)	99.1(2)	92.9(2)
119.0(2)	115.9(4)	121.9(3)	122.5(3)
118.6(2)	121.3(4)	117.1(3)	118.2(3)
120.4(1)	118.3(3)	117.9(3)	118.2(3)
176.27(9)	172.1(1)	172.0(1)	173.5(1)
77.8(1)	77.7(3)	77.9(2)	$82.8(2)^{a}$
87.7(1)	88.4(3)	89.5(2)	88.6(2)
86.8(1)	88.6(3)	87.4(2)	88.8(2)
98.7(1)	94.4(3)	94.2(2)	91.1(2) ^a
95.2(1)	96.3(2)	95.2(2)	93.0(2)
93.9(1)	95.4(3)	95.9(2)	96.1(2)
118.9(2)	124.5(4)	114.3(3)	$122.1(3)^{a}$
119.4(2)	119.9(4)	124.5(3)	$121.4(3)^{a}$
118.5(2)	113.1(4)	118.8(3)	115.5(3)
	1a (X = F(2), Y = F(3)) 2.204(2) 2.004(2) 2.095(4) 2.104(4) 2.114(4) 2.249(2) 1.995(2) 2.097(4) 2.112(4) 2.097(4) 175.51(9) 78.9(1) 87.8(1) 89.1(1) 97.0(1) 92.8(1) 94.4(1) 119.0(2) 118.6(2) 120.4(1) 176.27(9) 77.8(1) 87.7(1) 86.8(1) 98.7(1) 95.2(1) 93.9(1) 118.9(2) 119.4(2) 118.5(2)	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $

^{*a*} For C(1) substitute C(2).

Molecular Structures of 1a, 4a, 8a, and 11a. The X-ray crystal structures of 1, 4, 8, and 11, characterized as their NEt_4^+ salts (1a, 4a, 8a, and 11a), confirm the stoichiometries of the compounds and provide detailed information on the molecular geometries; Table 2 lists pertinent interatomic parameters. The lattice of 1a comprises discrete anions of 1 and NEt_4^+ cations, there being no significant interionic contacts; the closest contact in the lattice of 3.271(6) Å occurs between the F(2) and C(62) atoms. The structure of the anion in **1a** is shown in Figure 2 and comprises two Sn atoms linked by a F and a CH_2 bridge leading to the formation of a skewed rhombus; the deviations of the Sn(1), Sn(2), F(1), and C(1) atoms from the four-membered ring are 0.0002(3), 0.0003(3), -0.013(2), and -0.060(4) Å, respectively. Whereas the two Sn-C(1) bond distances are equivalent within experimental error, there is a significant difference between the Sn-F(1) distances, i.e. 2.204(2) cf. 2.249(2) Å. Each Sn atom is also coordinated by a terminal F atom and two phenyl groups. The Sn(1)...Sn(2) separation of 3.3446(6) Å is too long to be considered a significant interaction. The geometry about each of the Sn atoms is distorted trigonal bipyramidal with the equatorial plane being defined by the C atoms in each case; the F(1)-Sn-F(2)and F(1)-Sn(2)-F(3) axial angles are 175.51(9) and $176.27(9)^\circ$, respectively. Sn(1) and Sn(2) lie respectively 0.1733(3) and -0.2170(3) Å out of the trigonal planes in the direction of the terminal F atoms which form the shorter of the Sn-F interactions as expected. The gross geometric features found in the structure of 1a are also observed in the structures of 4a and 8a.

The closest non-H contact in the lattice of 4a is 3.19(1) Å found between the F(1) and C(61)' atoms (symmetry operation: x, 1 - y, -0.5 + z). The deviations of the



Figure 2. Molecular structure and crystallographic numbering scheme for 1a.

Sn(1), Sn(2), F(1), and C(1) atoms from the central fourmembered ring (see Figure 3) are 0.0000(1), 0.0000(1), 0.031(6), and 0.12(1) Å, respectively. As for 1a, the Sn-C(1) bridges are symmetrical and the F(1) bridges are not; the Sn(1)...Sn(2) separation is 3.3777(8) Å. The Sn(1) lies 0.2593(1) Å out of the trigonal plane defined by the three C donors in the direction of the Br(1) atom, and the corresponding value for the Sn(2) atom is 0.1949(1) Å (i.e. in the direction of the Br(2) atom). In the lattice of **8a**, the closest non-H contact occurs



Figure 3. Molecular structure and crystallographic numbering scheme for 4a.



Figure 4. Molecular structure and crystallographic numbering scheme for 8a.

between the F(1) and C(71)' atoms (symmetry operation: -x, 1 - v, 1 - z; the molecular structure of the anion in 8a is shown in Figure 4. The deviations from the four-membered ring of the Sn(1), Sn(2), F(1), and C(1) atoms are 0.0000(5), 0.0000(5), 0.001(4), and 0.005(7)Å, respectively. In contrast to that observed in 1a and 4a, both the methylene and F(1) bridges are symmetrical in 8a; the Sn(1)...Sn(2) separation is 3.3776(7)A. As with **1a** and **4a**, the Sn atoms lie out of the trigonal planes in the directions of the iodide to which they are bonded; the deviations out of the planes for the Sn(1) and Sn(2) atoms are 0.2155(5) and 0.1888(5) Å, respectively. Crystals were not obtained for the analogous Cl structure; however, those for the derivative in which the Sn atoms are linked by a ethylene bridge were obtained and subjected to an X-ray study.



Figure 5. Molecular structure and crystallographic numbering scheme for 11a.

Table 3.	Analytical and	d Melting	Point Data	for Compounds
	1a, 4a,	6a, 8a, 9a	h, and 11a ^a	

			anal. (%): found (calcd)		
compd	formula	mp (°C)	C	Н	N
1a 4a 6a 8a 9a	$\begin{array}{c} C_{33}H_{42}F_3NSn_2\\ C_{33}H_{42}Br_2FNSn_2\\ C_{33}H_{42}Cl_2FNSn_2\\ C_{33}H_{42}Fl_2NSn_2\\ C_{34}H_{44}F_3NSn_2 \end{array}$	192-193 165-167 155 192-196 198-200	53.10 (53.05) 45.77 (45.62) 50.84 (50.81) 41.25 (41.16) 53.64 (53.65)	5.76 (5.67) 4.90 (4.87) 5.46 (5.43) 4.43 (4.40) 5.80 (5.83)	1.80 (1.87) 1.40 (1.61) 1.71 (1.80) 1.41 (1.45) 1.84 (1.84)
11a	$C_{34}H_{44}Cl_2FNSn_2 \\$	192-196	51.48 (51.43)	5.52 (5.58)	1.72 (1.76)

^a $(Ph_2XSn)_2CH_2F^-Et_4N^+$: 1a, X = F; 6a, X = Cl; 4a, X = Br; 8a, X = I. $(Ph_2XSnCH_2)_2F^-Et_4N^+$: 9a, X = F; 11a, X = Cl.

The structure of the anion in **11a** is illustrated in Figure 5. The closest intermolecular contact in the lattice occurs between the C(13) and C(82) atoms (symmetry operation: -1 + x, y, z) at 3.21(4) Å. The essential features of the anion in 11a are as described above for 1a, 4a, and 8a except that, as a result of a bridging ethylene group, the molecule is constructed about a central five-membered ring. This ring is puckered somewhat as seen in the F(1)/Sn(1)/C(1)/C(2)and F(1)/Sn(2)/C(2)/C(1) torsion angles of 38.1(5) and $40.5(5)^{\circ}$, respectively. The Sn atoms exist in distorted trigonal bipyramidal geometries and lie 0.1250(1) and 0.1232(4) Å out of their respective trigonal planes in the directions of the terminal Cl atoms. In 11a, the F(1)bridge is symmetrical within experimental error as are the two Sn-C(ethylene) separations and the Sn(1)...Sn(2)separation is the longest of the four anions at 3.799(1)A. Of the four structures investigated, the shortest Sn-F(1) bond distances are found in 11a, although it is noted the errors associated with some of these distances are relatively high. The availability of several closely related structures enables a systematic comparison of their derived interatomic parameters.

As noted above, each of the Sn atoms exists in a distorted trigonal bipyramidal geometry and the distortion of the axial F(1)-Sn-X angles increases in the sequence F < Br < I for the methylene-bridged compounds; the distortion for X = Cl species, for which there

Table 4.	Crystallographic	: Data
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	compd			
	1a	4a	8a	11a
formula	$C_{33}H_{42}F_3NSn_2$	C ₃₃ H ₄₂ Br ₂ FNSn ₂	C ₃₃ H ₄₂ FI ₂ NSn ₂	C ₃₄ H ₄₄ Cl ₂ FNSn ₂
fw	747.1	868.9	962.9	794.0
cryst size, mm	0.37 diameter	$0.32 \times 0.32 \times 0.40$	$0.05 \times 0.15 \times 0.15$	$0.10 \times 0.27 \times 0.42$
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	Cc	$P2_1/n$	P21
a, Å	11.695(4)	11.758(1)	10.032(1)	9.562(2)
b, Å	14.667(2)	14.880(2)	16.923(3)	15.529(4)
c, Å	18.956(2)	19.316(2)	20.523(3)	11.359(4)
β , deg	103.33(1)	93.981(9)	99.65(1)	95.51(2)
$V, Å^3$	3164(1)	3371.3(6)	3434.9(8)	1678.9(9)
Ζ	4	4	4	2
$Q_{\text{calcd}}, \text{g cm}^{-3}$	1.568	1.712	1.862	1.571
F(000)	1496	1704	1848	796
μ , cm ⁻¹	16.18	38.86	32.79	16.75
transm factors	0.938-1.033	0.956-1.035	0.973-1.043	0.899-1.063
data colled	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$	$+h,+k,\pm l$
no. of data collcd	6322	3391	6919	4394
no. of unique data	6013	3223	6528	4161
no, of unique data with $I \ge 3.0\sigma(I)$	4661	2647	3843	3457
R	0.027	0.029	0.033	0.029
R _w	0.032	0.032	0.032	0.033
residual density, e Å ⁻³	0.43	0.47	0.57	0.40

Table 5. Fractional Atomic Coordinates and Their Estimated Standard Deviations for 1a

Table 6. Fractional Atomic Coordinates and Their Estimated Standard Deviations for 4a

atom	<i>x</i>	у	Z	atom	x	у	z
Sn(1)	-0.03538(2)	0.28032(2)	0.13340(2)	Sn (1)	0.4276(-)	0.28438(4)	0.1766(-)
Sn(2)	-0.07784(3)	0.07290(2)	0.19610(2)	Sn(2)	0.35522(6)	0.30725(4)	0.34188(4)
F(1)	-0.0850(2)	0.1431(1)	0.0897(1)	Br (1)	0.4519(1)	0.14142(8)	0.10078(8)
F(2)	0.0049(2)	0.4024(2)	0.1800(1)	Br(2)	0.3117(1)	0.18531(8)	0.43375(7)
F(3)	-0.0652(2)	0.0175(2)	0.2937(1)	F(1)	0.3978(5)	0.3947(3)	0.2548(3)
N(1)	-0.0307(3)	0.6687(2)	0.1842(2)	N(1)	0.3742(7)	0.3392(5)	0.8439(5)
C(1)	-0.0378(4)	0.2081(3)	0.2284(2)	C(1)	0.3977(11)	0.2145(6)	0.2673(6)
C(11)	-0.1949(3)	0.3279(3)	0.0684(2)	C(11)	0.2808(7)	0.3366(6)	0.1199(5)
C(12)	-0.2345(4)	0.3001(3)	-0.0015(3)	C(12)	0.2722(9)	0.4237(7)	0.1051(5)
C(13)	-0.3395(5)	0.3310(4)	-0.0432(3)	C(13)	0.1737(10)	0.4600(8)	0.0743(7)
C(14)	-0.4057(5)	0.3895(4)	-0.0140(4)	C(14)	0.0833(10)	0.4047(11)	0.0572(7)
C(15)	-0.3695(5)	0.4158(4)	0.0554(4)	C(15)	0.0907(9)	0.3172(9)	0.0722(7)
C(16)	-0.2638(4)	0.3861(3)	0.0958(3)	C(16)	0.1901(9)	0.2817(7)	0.1029(6)
C(21)	0.1168(3)	0.2731(3)	0.0914(2)	C(21)	0.5880(7)	0.3455(6)	0.1628(5)
C(22)	0.1922(4)	0.3462(3)	0.0981(2)	C(22)	0.6678(8)	0.3036(8)	0.1260(5)
C(23)	0.2940(4)	0.3413(4)	0.0741(3)	C(23)	0.7714(10)	0.3405(11)	0.1183(6)
C(24)	0.3225(5)	0.2634(5)	0.0447(3)	C(24)	0.7965(11)	0.4227(12)	0.1457(7)
C(25)	0.2495(5)	0.1903(4)	0.0366(3)	C(25)	0.7174(12)	0.4666(9)	0.1787(7)
C(26)	0.1474(4)	0.1959(3)	0.0608(3)	C(26)	0.6127(9)	0.4272(8)	0.1877(7)
C(31)	-0.2554(4)	0.0359(3)	0.1555(2)	C(31)	0.1955(7)	0.3741(5)	0.3421(5)
C(32)	-0.3268(4)	0.0870(3)	0.1025(3)	C(32)	0.1429(8)	0.4063(7)	0.2822(5)
C(33)	-0.4435(5)	0.0650(4)	0.0794(3)	C(33)	0.0434(9)	0.4545(8)	0.2818(6)
C(34)	-0.4091(5)	-0.0061(5)	0.1077(3)	C(34)	-0.0049(9)	0.4665(8)	0.3440(8)
C(35)	-0.4207(5)	-0.0570(4)	0.1597(3)	C(35)	0.0422(11)	0.4337(8)	0.4021(6)
C(36)	-0.3035(4)	-0.0356(3)	0.1835(3)	C(36)	0.1428(8)	0.3873(7)	0.4013(5)
C(41)	0.0533(3)	-0.0104(3)	0.1714(2)	C(41)	0.4842(8)	0.3711(6)	0.4040(6)
C(42)	0.1487(4)	-0.0378(3)	0.2234(2)	C(42)	0.5822(9)	0.4005(8)	0.3753(7)
C(43)	0.2372(4)	-0.0881(3)	0.2059(3)	C(43)	0.6685(12)	0.4418(10)	0.4178(10)
C(44)	0.2307(4)	-0.1117(3)	0.1357(3)	C(44)	0.6542(15)	0.4568(10)	0.4842(10)
C(45)	0.1365(4)	-0.0861(3)	0.0829(2)	C(45)	0.5618(15)	0.4291(11)	0.5131(7)
C(46)	0.0494(4)	-0.0360(3)	0.1010(2)	C(46)	0.4751(10)	0.3875(8)	0.4716(7)
C(51)	-0.1387(5)	0.6137(3)	0.1869(3)	C(51)	0.2879(14)	0.2750(9)	0.8685(8)
C(52)	-0.2498(5)	0.6467(5)	0.1395(3)	C(52)	0.1953(13)	0.3206(14)	0.9060(11)
C(61)	-0.0130(4)	0.6703(3)	0.1082(3)	C(61)	0.3208(12)	0.4104(9)	0.8010(8)
C(62)	0.0040(6)	0.5807(4)	0.0762(3)	C(62)	0.2658(15)	0.3761(12)	0.7305(9)
C(71)	0.0710(5)	0.6235(3)	0.2356(3)	C(71)	0.4489(13)	0.2836(10)	0.8061(9)
C(72)	0.1867(6)	0.6668(4)	0.2406(4)	C(72)	0.5533(14)	0.3394(12)	0.7790(9)
C(81)	-0.0433(4)	0.7660(3)	0.2047(3)	C(81)	0.4304(11)	0.3883(9)	0.9037(8)
C(82)	-0.0657(5)	0.7803(4)	0.2785(3)	C(82)	0.4791(14)	0.3212(13)	0.9611(8)

is an ethylene bridge between the Sn atoms, falls neatly between X = F and Br compounds, but this may be coincidental. Estimates of the Sn-X single bond distances have been listed in literature and are 1.96, 2.345, 2.49, and 2.72 Å for X = F to I, respectively.¹⁸ The average differences between Sn-X(axial) observed in the present study and the ideal values follow the sequence $F \ll Br < I < Cl$. For the first three compounds, this sequence follows the order found for the series of $Me_2SnX(C_6H_4-2-C(O)OMe)$ structures,¹⁸ and the result for **11a** reflects, again, the steric relieving effect of the five-membered ring.

⁽¹⁸⁾ Kolb, U.; Dräger, M.; Jousseaume, B. Organometallics **1991**, 10, 2737.

 Table 7.
 Fractional Atomic Coordinates and Their Estimated Standard Deviations for 8a

atom	x	У	z
Sn (1)	0.06294(5)	0.73970(3)	0.90483(2)
Sn(2)	0.01233(5)	0.74580(3)	0.73801(2)
I(1)	0.22443(6)	0.63344(4)	0.99310(3)
I(2)	0.13729(6)	0.65920(4)	0.64480(3)
F(1)	-0.0627(4)	0.8061(2)	0.8215(2)
N(1)	0.4445(6)	0.0941(4)	0.2661(3)
C(1)	0.1242(7)	0.6886(4)	0.8212(3)
C(11)	-0.1230(7)	0.7102(5)	0.9343(3)
C(12)	-0.1604(9)	0.6358(5)	0.9428(4)
C(13)	-0.2875(11)	0.6178(7)	0.9560(5)
C(14)	-0.3741(11)	0.6758(9)	0.9635(5)
C(15)	-0.3370(10)	0.7511(8)	0.9580(5)
C(16)	-0.2131(10)	0.7692(6)	0.9424(5)
C(21)	0.1560(8)	0.8475(5)	0.9396(3)
C(22)	0.0851(9)	0.9172(6)	0.9305(4)
C(23)	0.1420(11)	0.9881(5)	0.9520(4)
C(24)	0.2731(11)	0.9896(6)	0.9812(4)
C(25)	0.3447(10)	0.9222(7)	0.9906(5)
C(26)	0.2871(8)	0.8515(5)	0.9705(4)
C(31)	-0.1814(7)	0.6990(4)	0.7070(3)
C(32)	-0.2538(8)	0.6694(5)	0.7534(4)
C(33)	-0.3794(9)	0.6368(6)	0.7366(4)
C(34)	-0.4382(8)	0.6354(6)	0.6721(5)
C(35)	-0.3702(9)	0.6641(6)	0.6254(4)
C(36)	-0.2417(8)	0.6951(5)	0.6428(4)
C(41)	0.0578(7)	0.8598(4)	0.7041(3)
C(42)	0.0948(8)	0.9207(5)	0.7472(4)
C(43)	0.1239(8)	0.9944(5)	0.7253(4)
C(44)	0.1120(8)	1.0084(5)	0.6604(5)
C(45)	0.0751(9)	0.9493(5)	0.6167(4)
C(46)	0.0492(8)	0.8750(5)	0.6382(4)
C(51)	0.4475(12)	0.0261(6)	0.2232(5)
C(52)	0.3396(14)	0.0249(7)	0.1629(5)
C(61)	0.4520(10)	0.1700(6)	0.2290(5)
C(62)	0.5715(12)	0.1799(9)	0.1971(6)
C(71)	0.3132(9)	0.0979(6)	0.2920(5)
C(72)	0.2847(11)	0.0309(7)	0.3339(5)
C(81)	0.5615(10)	0.0865(7)	0.3202(5)
C(82)	0.5762(10)	0.1492(8)	0.3699(5)

Experimental Section

NMR Spectroscopy. NMR spectra were recorded on a JEOL GX270 FT NMR spectrometer with broad band proton decoupling of ¹¹⁹Sn at 100.75 MHz and ¹⁹F at 254.19 MHz, using an external deuterium lock, and referenced against external Me₄Sn and CFCl₃, respectively. Temperatures were maintained using a JEOL GTV3 control system. Complexes for NMR investigation were generally prepared in situ by reaction of bis(halodiorganostannyl)alkanes with appropriate mole ratios of tetrabutylammonium halide in dichloromethane solution. The concentration of bis(halodiorganostannyl)-alkanes was typically about 0.1 M.

General Methods. Tetrabutylammonium fluoride trihydrate, $Bu_4NF\cdot 3H_2O$, tetrabutylammonium chloride, Bu_4NCl , tetrabutylammonium bromide, Bu_4NBr , and tetraethylammonium fluoride dihydrate, $Et_4NF\cdot 2H_2O$, were obtained from Aldrich, Sigma, and Fluka, respectively. The bis(haloorganostannyl)alkanes and $[Ph_3SnF_2]^-[Bu_4N]^+$ were synthesized as described elsewhere.^{7,8,12,19}

Synthesis of Diphenyl(trimethylsilylmethyl)fluorostannane, $Ph_2FSnCH_2SiMe_3$. Ph_3SnCl (70.0 g, 0.18 mol) dissolved in 150 mL of thf was added dropwise to a magnetically stirred solution of Me_3SiCH_2MgCl prepared from Me_3SiCH_2Cl (27.50 g, 0.20 mol) and Mg (4.80 g, 0.20 mol) in 150 mL of thf. The reaction mixture was refluxed for 3 h. Twothirds of the thf was distilled off, and 150 mL of ether was added. The reaction mixture was then hydrolyzed under ice cooling with diluted HCl. The organic layer was separated, washed with water, and dried over Na_2SO_4 . Filtration and evaporation of solvent yielded 63 g of crude $Ph_3SnCH_2SiMe_3$

 Table 8. Fractional Atomic Coordinates and Their Estimated Standard Deviations for 11a^a

atom	x	у	z
Sn(1)	0.07970(5)	1/4	0.38261(4)
Sn(2)	0.19871(4)	0.06704(4)	0.19393(4)
Cl(1)	0.1040(2)	0.4074(2)	0.4280(2)
Cl(2)	0.3591(2)	0.0293(2)	0.0392(2)
F (1)	0.0703(4)	0.1141(2)	0.3286(3)
N(1)	0.6451(7)	0.1801(5)	0.7778(6)
C(1)	0.2495(7)	0.2531(6)	0.2775(6)
C(2)	0.2294(7)	0.1997(5)	0.1659(6)
C(11)	0.1022(8)	0.2095(6)	0.5611(6)
C(12)	0.1070(16)	0.1258(7)	0.5898(8)
C(13)	0.1281(20)	0.0978(9)	0.7082(10)
C(14)	0.1454(13)	0.1542(10)	0.7930(9)
C(15)	0.1361(10)	0.2370(8)	0.7688(8)
C(16)	0.1161(9)	0.2669(6)	0.6519(7)
C(21)	-0.1243(6)	0.2647(5)	0.2985(6)
C(22)	-0.1646(7)	0.3380(5)	0.2388(7)
C(23)	-0.2993(8)	0.3483(6)	0.1863(7)
C(24)	-0.3958(8)	0.2859(7)	0.1925(8)
C(25)	-0.3599(9)	0.2137(7)	0.2500(10)
C(26)	-0.2241(8)	0.1999(6)	0.3031(9)
C(31)	0.3199(7)	-0.0021(5)	0.3268(6)
C(32)	0.2559(9)	-0.0450(7)	0.4123(7)
C(33)	0.3387(14)	-0.0894(8)	0.5000(9)
C(34)	0.4814(14)	-0.0903(8)	0.5001(10)
C(35)	0.5415(10)	-0.0505(7)	0.4175(8)
C(36)	0.4640(9)	-0.0062(5)	0.3298(7)
C(41)	0.0205(7)	0.0018(4)	0.1135(6)
C(42)	-0.1002(9)	-0.0004(7)	0.1663(9)
C(43)	-0.2206(9)	-0.0415(8)	0.1119(11)
C(44)	-0.2178(9)	-0.0766(6)	0.0072(8)
C(45)	-0.0991(9)	-0.0766(7)	-0.0459(8)
C(46)	0.0187(9)	-0.0377(6)	0.0075(7)
C(51)	0.6220(30)	0.2838(18)	0.7878(25)
C(51')	0.5351(23)	0.1974(16)	0.8652(19)
C(52)	0.5169(47)	0.3050(29)	0.8496(36)
C(52')	0.4949(32)	0.2902(21)	0.8817(27)
C(61)	0.7750(24)	0.2389(18)	0.8085(19)
C(61')	0.6913(26)	0.1477(17)	0.9065(21)
C(62)	0.8430(25)	0.2228(18)	0.9419(22)
C(62')	0.8144(22)	0.1782(15)	0.9606(19)
C(71)	0.5673(35)	0.2094(24)	0.6611(30)
C(71')	0.5043(30)	0.1376(21)	0.7361(24)
C(72)	0.4759(28)	0.1759(18)	0.5893(22)
C(72')	0.5628(21)	0.0241(14)	0.7702(17)
C(81)	0.6836(30)	0.0868(21)	0.7735(25)
C(81')	0.7591(34)	0.1789(24)	0.6982(30)
C(82)	0.7905(34)	0.0988(23)	0.6820(28)
C(82')	0.6761(37)	0.1734(26)	0.5764(33)
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^a Atoms C(51)-C(82') have 50% site occupancy factors.

as an oil which was not further analyzed. It was dissolved in 150 mL of CH₂Cl₂. Iodine (36.5 g, 0.14 mol) was added in small portions to this magnetically stirred solution, and stirring was continued over night. The solvent was then removed in vacuo and the oily residue dissolved in 50 mL of acetone. This solution was added dropwise to a magnetically stirred solution of KF (21.00 g, 0.36 mol) in water. Immediate precipitation took place. Stirring was continued overnight. The precipitate was filtered off, washed twice with water, and dried. Recrystallization from hot acetone yielded 49 g (72% with respect to Ph₃SnCl) of Ph₂FSnCH₂SiMe₃ as colorless crystals, mp 225 °C.

¹H NMR (CDCl₃): 0.12 (s, 9 H, SiMe₃), 0.67, ²J(¹⁹Sn⁻¹H) = 83.9 Hz (2 H, SnCH₂), 7.60 (m, 4 H, o-Ph), 7.45 ppm (m, 6 H, m,p-Ph). ¹¹⁹Sn NMR (CDCl₃) 24.9 ppm, ¹J(¹¹⁹Sn⁻¹⁹F) = 2380 Hz. Anal. Found: C, 50.43; H, 5.30. Calcd for C₁₆H₂₁-FSiSn (MW 379.14): C, 50.69; H, 5.58.

Synthesis of Bis(diphenylfluorostannyl)methane, $(Ph_2FSn)_2CH_2$. $(Ph_2BrSn)_2CH_2$ (3 g, 4.2 mmol) and potassium fluoride (0.6 g, 10.3 mmol) were stirred in 20 mL of acetone and 5 mL of water for 24 h. The colorless precipitate formed was filtered off, washed with water, methanol, and diethyl ether, and then dried to give 2.3 g (92%) of $(Ph_2FSn)_2CH_2$ as a colorless amorphous solid, mp >360 °C dec. Anal. Found: C, 49.67; H, 3.78. Calcd for $C_{25}H_{22}F_2Sn_2$: C, 50.22; H, 3.71.

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Synthesis of 1,2-Bis(diphenylfluorostannyl)ethane, (Ph₂FSnCH₂)₂. (Ph₃SnCH₂)₂ (11 g, 0.015 mol) was dissolved in 150 mL of CH₂Cl₂. Iodine (7.6 g, 0.03 mol) was added in small portions to the magnetically stirred solution. The iodine color disappeared. The reaction mixture was stirred over night followed by evaporation of the solvent. The residue was dissolved in 150 mL of ether and dropped under magnetic stirring into a solution of 5.3 g of potassium fluoride in 20 mL of water. Immediate precipitation took place. Stirring was continued for a further 4 h. The precipitate was filtered off and washed with water, methanol, and ether to give 7 g (76%) of (Ph₂FSnCH₂)₂ as a colorless amorphous solid, mp >250 °C dec. Anal. Found: C, 51.10, H, 3.86. Calcd for C₂₆H₂₄F₂Sn₂: C, 51.05, H, 3.92.

Synthesis of Fluoride Complexes (as Tetraethylammonium Salts) 1a, 4a, 6a, 8a, 9a, and 11a. Bis-(halogenodiphenyl)methanes or -ethanes, respectively (0.3 mmol), and tetraethylammonium fluoride dihydrate (0.3 mmol) were refluxed in 10 mL of methylene chloride under magnetic stirring for 5 min. The resulting solution was carefully filtered. Hexane was added, and the reaction mixture was slowly evaporated to yield the complexes 1a, 4a, 6a, 8a, 9a, and 11a almost quantitatively as colorless crystals. Elemental analyses and melting points are given in Table 3.

Crystallography. Crystals of **1a**, **4a**, **8a**, and **11a** were grown from CH₂Cl₂/hexane solutions by slow evaporation. Intensity data for the colorless crystals were measured at room temperature (20 °C) on a Rigaku AFC6R diffractometer fitted with graphite-monochromatized Mo K α radiation, $\lambda = 0.710$ 73 Å. The $\omega - 2\theta$ scan technique was employed to measure data in each case up to a maximum Bragg angle of 25.0° (27.5° for **11a**) in each case. The data sets were corrected for Lorentz and polarization effects,²⁰ and an empirical absorption correction was applied.²¹ Relevant crystal data are given in Table 4.

The structures were solved by direct methods²² and refined by a full-matrix least-squares procedure based on F^{20} Non-H atoms were refined with anisotropic thermal parameters, and H atoms were included in the models in their calculated positions (C-H = 0.97 Å) for 1a, 4a, and 8a. In the refinement of 11a, the anion atoms were refined as for the remaining structures and with H atoms in calculated positions; however, the NEt₄⁺ cation was found to be disordered. The disorder was modeled by assigning two sites for each of the eight C atoms, and these were refined isotropically with 50% site occupancy factors; H atoms were not included for the disordered atoms. The refinements were continued until convergence employing σ weights; the analysis of variance showed no special features indicating that an appropriate weighting scheme had been applied in each case. The absolute configurations of both 4a and 11a were determined by reversing the signs of the reflections in each data set and comparing the refinements. Final refinement details are collected in Table 4. Fractional atomic coordinates are listed in Table 5-8, and the numbering schemes employed are shown in Figures 2-5 (drawn with ORTEP²³ at 25, 25, 30, and 20% probability ellipsoids, respectively). The teXsan²⁰ package, installed on an Iris Indigo workstation, was employed for all calculations.

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Supplementary Material Available: Tables of anisotropic thermal parameters, H positional and thermal parameters, and bond distances and angles (23 pages). Ordering information is given on any current masthead page.

OM940639+

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