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Methylene-Bridged Tri- and Tetratin Compounds as Lewis Acids

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Syntheses of a series of trinuclear tin compounds, $(Ph_2XSnCH_2)_2SnXPh$ (**2**, X = Ph; **6**, X = F; **8**, X = Cl) and $(PhCl_2SnCH_2)_2SnCl_2$ (**10**) and tetranuclear tin compounds $(Ph_2XSnCH_2SnXPh)_2CH_2$ (**3**, X = Ph; **7**, X = F; **9**, X = Cl) are reported, and the crystal structure of $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-[C_{12}H_{24}O_6{\cdot}K]^+$ (**6b**) is described. Variable temperature ^{119}Sn and ^{19}F NMR studies indicate that the structure observed for the anion in **6b** in the solid state is retained in solution. There is no NMR evidence for the formation of 1:2 adducts with fluoride ion, although such species are identified in acetonitrile solutions from electrospray mass spectrometry (ESMS). ^{119}Sn NMR spectral data indicate that reaction of trinuclear tin compound **8** with $[(Ph_3P)_2N]^+Cl^-$ and HMPA results in formation of the 1:1 complexes $[(Ph_2ClSnCH_2)_2SnClPh{\cdot}Cl]^-[(Ph_3P)_2N]^+$ (**8a**) and $(Ph_2ClSnCH_2)_2SnClPh{\cdot}[(CH_3)_2N]_3PO$ (**8b**), respectively. In contrast, ^{19}F and ^{119}Sn NMR data show that the tetranuclear tin compound **7** reacts with fluoride ion to give a stable 1:2 adduct $[(Ph_2FSnCH_2SnFPh)_2CH_2{\cdot}2F]^{2-}2[Bu_4N]^+$ (**7b**) in solution, being no NMR evidence for formation of a 1:1 adduct. However, ESMS indicates the presence of both 1:1 and 1:2 adducts in acetonitrile solution.

Introduction

In recent years molecular recognition of anions has become a very popular topic in host−guest chemistry.[1] The complexation chemistry of Lewis acid organotin(IV) halides has also been intensively studied.[2−7] Reaction of alkyl-bridged di- and polystannanes with Lewis bases results in formation of the corresponding adducts.[2,5−9] Although the trinuclear tin compound $Me_2Sn(CH_2SnMe_3)_2$[10a] has been described, there is only one report[10b] on the complexation behavior of alkyl-bridged chains containing three tin atoms and no report on alkyl-bridged systems containing four tin atoms. We now report the syntheses of methylene-bridged tri- and tetrastannanes $(Ph_2XSnCH_2)_2SnXPh$ (**2**, X = Ph; **6**, X = F; **8**, X = Cl), $(Ph_2XSnCH_2SnXPh)_2CH_2$ (**3**, X = Ph; **7**, X = F; **9**, X = Cl), and $(PhCl_2SnCH_2)_2SnCl_2$ (**10**) and their complexation behavior toward fluoride ions, chloride ions, and HMPA.

Results and Discussion

Synthetic Aspects. Ph_3SnCH_2Br (**1**) was prepared according to the method of Seyferth and Andrews[10c] by reaction of Ph_3SnBr with bromomethylzinc bromide. Reaction of the Grignard reagent **1a** with Ph_2SnCl_2 or $(Ph_2FSn)_2CH_2$[2a] afforded the perphenylated methylene-bridged tri- and tetratin chains $(Ph_3SnCH_2)_2SnPh_2$ (**2**) and $(Ph_3SnCH_2SnPh_2)_2CH_2$ (**3**), respectively (eqs 1 and 2). Compounds **2** and **3** were transformed into their iodo

$$\underset{\mathbf{1a}}{2Ph_3SnCH_2MgBr} + Ph_2SnCl_2 \xrightarrow[-2MgBrCl]{thf} \underset{\mathbf{2}}{Ph_2Sn(CH_2SnPh_3)_2} \quad (1)$$

$$\underset{\mathbf{1a}}{2Ph_3SnCH_2MgBr} + (Ph_2FSn)_2CH_2 \xrightarrow[-2MgBrF]{thf} \underset{\mathbf{3}}{(Ph_3SnCH_2SnPh_2)_2CH_2} \quad (2)$$

derivatives $(Ph_2ISnCH_2)_2SnIPh$ (**4**) and $(Ph_2ISnCH_2SnIPh)_2CH_2$ (**5**), respectively, by reaction with iodine in CH_2Cl_2 solution (eqs 3 and 4). Treatment of **4** and **5** in diethyl ether with aqueous potassium fluoride yielded $(Ph_2FSnCH_2)_2SnFPh$ (**6**) and $(Ph_2FSnCH_2SnFPh)_2CH_2$ (**7**) as colorless amorphous solids which are almost insoluble in common organic solvents (eqs 3 and 4).

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$$\mathbf{2} + 3I_2 \xrightarrow[-3PhI]{CH_2Cl_2} \underset{\mathbf{4}}{(Ph_2ISnCH_2)_2SnIPh} \xrightarrow[-3KI]{3KF} \underset{\mathbf{6}}{(Ph_2FSnCH_2)_2SnFPh} \quad (3)$$

$$\mathbf{3} + 4I_2 \xrightarrow[-4PhI]{CH_2Cl_2} \underset{\mathbf{5}}{(Ph_2ISnCH_2SnIPh)_2CH_2} \xrightarrow[-4KI]{4KF} \underset{\mathbf{7}}{(Ph_2FSnCH_2SnFPh)_2CH_2} \quad (4)$$

When **4** and **5** were stirred with silver chloride in acetonitrile for 14 days, $(Ph_2ClSnCH_2)_2SnClPh$ (**8**) and $(Ph_2ClSnCH_2SnClPh)_2CH_2$ (**9**) were formed, respectively, as colorless solids (eqs 5 and 6). Compounds **8** and **9** are soluble in common organic solvents such as CH_2Cl_2, $CHCl_3$, toluene and thf. Reaction of **2** with $HgCl_2$ afforded $(PhCl_2SnCH_2)_2SnCl_2$ (**10**) (eq 7). Compound **10** is soluble in diethyl ether, acetone, and acetonitrile.

$$\mathbf{4} + 3AgCl \xrightarrow[\text{14 days}]{CH_3CN} \underset{\mathbf{8}}{(Ph_2ClSnCH_2)_2SnClPh} + 3AgI \quad (5)$$

$$\mathbf{5} + 4AgCl \xrightarrow[\text{14 days}]{CH_3CN} \underset{\mathbf{9}}{(Ph_2ClSnCH_2SnClPh)_2CH_2} + 4AgI \quad (6)$$

$$\mathbf{2} + 6HgCl_2 \xrightarrow[-6PhHgCl]{\text{acetone, 0 °C}} \underset{\mathbf{10}}{(PhCl_2SnCH_2)_2SnCl_2} \quad (7)$$

Reaction of **6** with $Et_4NF{\cdot}2H_2O$ gives the anionic fluoride adduct $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-$ as crystalline $[Et_4N]^+$ salt **6a** (eq 8), which was of insufficient quality for X-ray analysis. Better quality crystals of anionic $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-$ were obtained as the potassium salt $[K{\cdot}18\text{-crown-}6]^+$, **6b**, from reaction between **6** and equimolar quantities of potassium fluoride and 18-crown-6 (eq 9).

$$\mathbf{6} + Et_4NF{\cdot}2H_2O \xrightarrow[-2H_2O]{CH_2Cl_2} \underset{\mathbf{6a}}{[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-[Et_4N]^+} \quad (8)$$

$$\mathbf{6} + KF{\cdot}18\text{-crown-}6 \xrightarrow{CH_2Cl_2} \underset{\mathbf{6b}}{[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-[K{\cdot}18\text{-crown-}6]^+} \quad (9)$$

Reaction of Bis((diphenylfluorostannyl)methyl)phenylfluorostannane (6) with Fluoride Ions. The trinuclear tin compound **6** is insufficiently soluble for NMR measurements. However, addition of 1 mol equivalent of $Bu_4NF{\cdot}3H_2O$ to **6** in CH_2Cl_2 gives a clear solution for which no ^{119}Sn NMR signal could be detected at room temperature. However, after cooling to −80 °C, a ^{119}Sn NMR spectrum is observed and shows a triplet of triplets resonance at −62.9 ppm (assigned to Sn(I)) and a doublet of doublet of doublets resonance at −158.9 ppm (assigned to Sn(II)) with an integral ratio of 1:2, consistent with the *in situ* formation of the 1:1 adduct $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-[Bu_4N]^+$, hereafter referred to as **6c** (Table 1). As previously observed,[2a] the couplings to the bridging fluorides F_b are smaller than the couplings to the terminal fluorides F_a (Chart 1). The ^{19}F NMR spectrum of **6c** at −95 °C shows two signals of equal intensity at −100.9 ppm (F_b) and −181.9 ppm (F_a) with ^{119}Sn satellites, the magnitudes of which correspond to the $^nJ(^{119}Sn-^{19}F)$ observed in the ^{119}Sn NMR spectrum (Table 1).

The NMR data for **6c** are consistent with the retention in solution of the monoanionic structure $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-$ observed in the solid state for **6b**. The coalescence phenomena observed in the NMR spectra are consistent with an intra- and/or intermolecular exchange process involving tin−fluoride bond rupture and rotation about the Sn−C bond, making F_a and F_b equivalent at higher temperature.[2a] There are no significant changes after addition of further mole equivalents of $Bu_4NF{\cdot}3H_2O$ to the solution of **6c**, and consequently we have no NMR evidence for the formation of higher fluoride adducts.

The negative-ion ES mass spectrum of a solution of **6** in acetonitrile shows an isotopic cluster pattern centered at $m/z = 845$, which is consistent with self-ionization to give the monoanion $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-$. There is also a weaker cluster pattern (approximately 10% relative abundance) centered at $m/z = 787$ consistent with the presence of $[\mathbf{6} - Ph + 2F]^-$ and small amounts of dinuclear tin species $[Ph_2FSnCH_2SnF_3Ph]^-$ ($m/z = 559$) and $[Ph_2FSnCH_2SnF_2Ph_2]^-$ ($m/z = 617$). Interestingly, also present are significant quantities of dianionic species $[\mathbf{6} + 2F]^{2-}$ ($m/z = 432$), $[\mathbf{6} - Ph+3F]^{2-}$ ($m/z = 403$), and $[\mathbf{6} - 2Ph + 4F]^{2-}$ ($m/z = 374$). The positive-ion ESMS carries very little ion current and contains weak signals consistent with the presence of $[Ph_3Sn]^+$ ($m/z = 351$), $[Ph_3Sn(\text{acetonitrile})]^+$ ($m/z = 392$), and $[(Ph_3Sn)_2F]^+$ ($m/z = 719$). The observation in the ESMS of phenyl loss was confirmed in a macroscale experiment by benzene detection using GC. Addition of up to 3 mol equiv of $Bu_4NF{\cdot}3H_2O$ brings about no significant changes in the negative-ion ESMS, whereas in the positive-ion mode ion-pair species such as $[\mathbf{6} + (Bu_4N)_2F]^+$ ($m/z = 1330$), $[\mathbf{6} + (Bu_4N)_3F_2]^+$ ($m/z = 1591$), $[(\mathbf{6} - F + Ph)(Bu_4N)_2F]^+$ ($m/z = 1388$), and $[(\mathbf{6} - F + Ph)(Bu_4N)_3F_2]^+$ ($m/z = 1533$) appear.

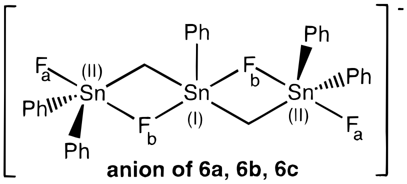
Reaction of Bis[((diphenylfluorostannyl)methyl)phenylfluorostannyl]methane (7) with Fluoride Ions. Addition of 1 mol equiv of $Bu_4NF{\cdot}3H_2O$ to the tetranuclear tin compound **7** in CH_2Cl_2 does not give a clear solution, and no ^{119}Sn NMR signal was observed between room temperature and −95 °C. The ^{19}F NMR spectrum at −95 °C displays broad and unresolved resonances between −120 and −165 ppm, and there is no clear NMR evidence for the formation of a monoanionic adduct $[(Ph_2FSnCH_2SnFPh)_2CH_2{\cdot}F]^-[Bu_4N]^+$, **7a** (Chart 2). One hypothesis is that the broad signals result from an intramolecular exchange of the bridging and terminal fluorine atoms in the 1:1 adduct, **7a**, which still remains rapid on the NMR time scale, even at low temperature.

Addition of a second mole equivalent of $Bu_4NF{\cdot}3H_2O$ to **7** in CH_2Cl_2 results in a clear solution. The ^{119}Sn NMR spectrum of this solution at −95 °C contains two equally intense resonances at −96.7 ppm ($W_{1/2} = 330$ Hz, Sn(I), doublet of doublets) and −196.5 ppm ($W_{1/2} = 170$ Hz, Sn(II), doublet of doublets) (Table 1). The signals were too broad to enable observation of ^3J(Sn−

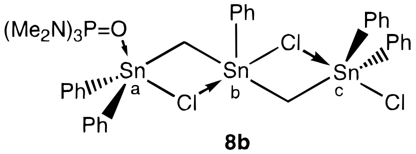
Table 1. ^{119}Sn (−80 °C) and ^{19}F (−95 °C) NMR Data in CD_2Cl_2 of $[(Ph_2FSnCH_2)_2SnFPh\cdot F]^-[Bu_4N]^+$ (6c) and $[(Ph_2FSnCH_2SnFPh)_2CH_2\cdot 2F]^{2-}2[Bu_4N]^+$ (7b)

	^{119}Sn NMR		^{19}F NMR	
anion	(^{119}Sn) [ppm]	$^nJ(^{119}Sn_x{-}^{19}F_y)$ [Hz]	$\delta(^{19}F_y)$ [ppm]	$^nJ(^{19}F_y{-}^{119}Sn_x)$ [Hz]
6c	−62.9 (tt, $Sn_{(I)}$)	$^1J(^{119}Sn_{(I)}{-}^{19}F_b) = 1234$	−100.9 (F_b)	$^1J(^{19}F_b{-}^{119}Sn_{(I)}) = 1224/1174$
		$^3J(^{119}Sn_{(I)}{-}^{19}F_a) = 124$		$^1J(^{19}F_b{-}^{119}Sn_{(II)}) = 573$
	−158.9 (ddd, $Sn_{(II)}$)	$^1J(^{119}Sn_{(II)}{-}^{19}F_a) = 2216$	−181.9 (F_a)	$^1J(^{19}F_a{-}^{119}Sn_{(II)}) = 2163$
		$^1J(^{119}Sn_{(II)}{-}^{19}F_b) = 582$		
		$^3J(^{119}Sn_{(II)}{-}^{19}F_b) = 116$		
7b	−96.7 (dd, $Sn_{(I)}$)	$^1J(^{119}Sn_{(I)}{-}^{19}F_c) = 1908$	−122.0 (F_b)	$^1J(^{19}F_b{-}^{119}Sn) = 1171$
		$^1J(^{119}Sn_{(I)}{-}^{19}F_b) = 1171$		$^2J(^{19}F_b{-}^{19}F_{a/c}) = 81$
	−196.5 (dd, $Sn_{(II)}$)	$^1J(^{119}Sn_{(II)}{-}^{19}F_a) = 1978$	−145.6 (F_c)	$^1J(^{19}F_c{-}^{119}Sn_{(I)}) = 1826$
		$^1J(^{119}Sn_{(II)}{-}^{19}F_b) = 1415$		$^2J(^{19}F_c{-}^{19}F_b) = 76$
			−151.5 (F_a)	$^1J(^{19}F_a{-}^{119}Sn_{(II)}) = 1906$
				$^2J(^{19}F_a{-}^{19}F_b) = 73$

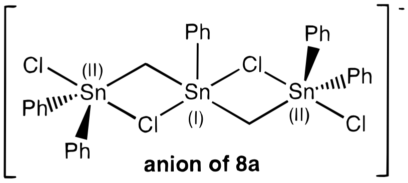
Chart 1



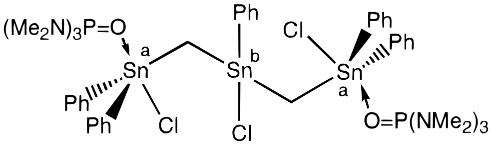
anion of 6a, 6b, 6c



8b

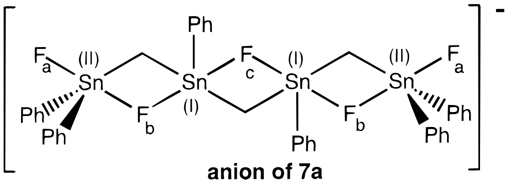


anion of 8a

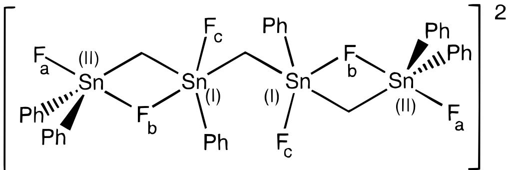


8c

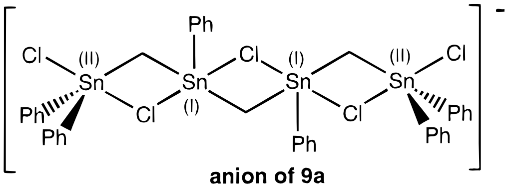
Chart 2



anion of 7a



anion of 7b



anion of 9a

F) couplings. The corresponding ^{19}F NMR spectrum at −95 °C displays three equally intense resonances at −122.0, −145.6, and −151.5 ppm (Table 1). Both the number of signals and the coupling patterns support the formation of the 1:2 fluoride adduct $[(Ph_2FSnCH_2SnFPh)_2CH_2\cdot 2F]^{2-}2[Bu_4N]^+$, **7b** (Chart 2), whose solution structure has been postulated on the basis that the more electronegative fluorides would occupy axial positions in trigonal-bipyramidal geometries about five-coordinate tin atoms.[10d] The rather broad resonances may again be a result of residual exchange between bridging and terminal fluorine atoms. Addition of a third mole equivalent of fluoride ion to **7** causes no change to the ^{119}Sn and ^{19}F NMR spectra.

The negative-ion ES mass spectrum of **7** in acetonitrile indicates self-ionization to give [**7** + F]$^-$ (m/z = 1075). After the addition of 1 mol equiv of fluoride ion, the ESMS shows an additional isotope cluster (centered at m/z = 617) consistent with presence of the ditin species $[Ph_2FSnCH_2SnFPh_2\cdot F]^-$. After the addition of a second mole equivalent of fluoride ion, the ESMS gives clear evidence for the presence of dianionic species [**7** − Ph + 3F]$^{2-}$ (m/z = 518) and [**7** + 2F]$^{2-}$ (m/z = 547) as well as for the tritin species $(Ph_2FSnCH_2SnF_2CH_2SnFPh_2\cdot F)^-$ (m/z = 789) and $(Ph_2FSnCH_2SnFPhCH_2SnFPh_2\cdot F)^-$ (m/z = 845).

Reaction of Bis((diphenylchlorostannyl)methyl)phenylchlorostannane (8), Bis[((diphenylchlorostannyl)methyl)phenylchlorostannyl]methane (9), and Bis((phenyldichlorostannyl)methyl)dichlorostannane (10) with Chloride Ions. Addition of chloride ions to solutions of the trinuclear tin species **8** and **10** or the tetranuclear species **9** causes changes in the position of the ^{119}Sn NMR chemical shifts (Figure 1). For **8**, both the geminal and terminal tin atoms reach their maximum low-frequency shifts upon addition of 1 mol equiv chloride ion, indicating formation of the monoanionic species **8a** (Chart 1).

The negative-ion ESMS of **8** in acetonitrile solution shows isotopic m/z clusters consistent with the self-ionization of **8** to give [**8** + Cl]$^-$ (m/z = 911) and [**8**-Ph + 2Cl]$^-$ (m/z = 869). After the addition of an equimolar quantity of chloride ion (as a triphenylbenzylphosphonium salt), the main isotopic m/z cluster can be assigned

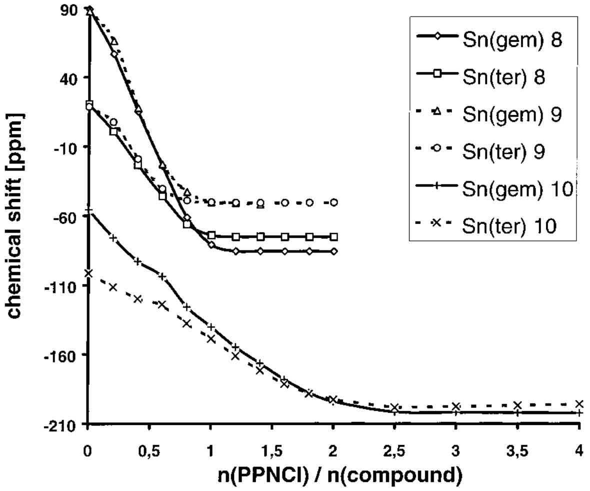


Figure 1. Plot of ^{119}Sn chemical shift (ppm) versus molar ratio of $[(Ph_3P)_2N]^+Cl^-$/tin compound.

to $[\mathbf{8} + Cl]^-$. Further additions of chloride ions bring about no significant change in the ESMS.

Somewhat surprisingly, the data in Figure 1 indicate that **9** also forms a 1:1 adduct $[(Ph_2ClSnCH_2SnClPh)_2CH_2{\cdot}Cl]^-[(Ph_3P)_2N]^+$, **9a** (Chart 2), with chloride ion rather than a 1:2 complex. We attribute this result to the lower coordinating power of chloride ion toward tin(IV) in comparison to that of fluoride ion.

Because of the very poor solubility of **10** in CH_2Cl_2, the ^{119}Sn NMR measurements of **10** to which chloride ions have been added (Figure 1) were performed in CD_3CN. They indicate formation of both 1:1 and 1:2 adducts in solution.

The ^{13}C NMR data for the 1:1 adduct ($\delta(CH_2)$ 46.1 ppm, $^1J(^{119}Sn-^{13}C) = 775, 691$ Hz; $\delta(C_i)$ 147.3 ppm, $^1J(^{119}Sn-^{13}C_i) = 1072$ Hz) indicate hexacoordinate tin atoms with the carbon atoms *trans*.[11,12] The sixth coordination side is very likely occupied by acetonitrile.

The ^{13}C NMR data for the 1:2 adduct ($\delta(CH_2)$ 56.1 ppm, $^1J(^{119}Sn-^{13}C) = 861, 765$ Hz; $\delta(C_i)$ 150.2 ppm, $^1J(^{119}Sn-^{13}C_i) = 1143$ Hz) are also in agreement with hexacoordination. The slight difference in comparison with the 1:1 adduct is a result of replacement of acetonitrile by chloride.

The negative-ion ESMS of **10** in acetonitrile solution contains an *m/z* cluster as the most abundant species, consistent with the 1:1 adduct $[\mathbf{10} + Cl]^-$ ($m/z = 787$). No additional species are observed after addition of up to 2 mol equiv of chloride ion.

Reaction of Bis((diphenylchlorostannyl)methyl)phenylchlorostannane (8) with HMPA. HMPA complexes of bis(halodiphenylstannyl)methane and -ethane have been reported and showed HMPA to be a nonbridging donor toward these ditin species.[7,13,14]

The ^{119}Sn NMR spectrum at room temperature of an equimolar solution of **8** and HMPA in CH_2Cl_2 shows an extremly broad signal at −49.9 ppm, indicative of a fast exchange process. At −80 °C, the ^{119}Sn NMR spectrum displays three equally intense resonances at −35.9 (Sn_c), −50.8 (Sn_b), and −162.9 (Sn_a) ppm (d, $^2J(^{119}Sn-^{31}P) = 155$ Hz). In addition, there are three equal but very low intensity signals (7% of the major resonances) at −80.0, −117.0, and −130.0 ppm for which no assignment is made. The ^{31}P NMR spectrum at room temperature shows a signal at 27.0 ppm with no $^{119/117}$Sn satellites, indicating fast exchange. At −88 °C, the signal shifts to 25.6 ppm and shows an unresolved $^2J(^{31}P-^{119/117}Sn)$ coupling of 147 Hz.

The formation of **8b** (Chart 1) at low temperature is evidenced by (i) the observation of three equally intense ^{119}Sn resonances with considerable low-frequency shifts with respect to the signals at 20.5 and 89.1 ppm observed for **8**, (ii) the observation of a $^2J(^{119}Sn_a-^{31}P)$ coupling in the low-temperature ^{119}Sn NMR, and (iii) the observation of two resonances for the methylene carbons (14.4, 15.9 ppm) and three resonances for the ipso carbons (143.9, 143.3, 142.5 ppm) of the phenyl groups in the ^{13}C NMR spectrum at −80 °C. It is interesting to notice that the structural change in **8b** imposed on Sn_a upon coordination of HMPA is transmitted via chlorine bridges to Sn_b and even to Sn_c.

The ^{119}Sn NMR spectrum of a dichloromethane solution of **8** to which 2 mol equiv of HMPA have been added shows no signal at room temperature but two signals with an integral ratio of 1:2 at −13.9 and −186.7 ppm (d, $^2J(^{119}Sn-^{31}P) = 143$ Hz) at −88 °C. In addition, low-intensity signals appear at −45.2, −82.6, −147.5, and −208.7 ppm for which no assignment is made. The ^{31}P NMR spectrum at −88 °C shows a single resonance at 24.1 ppm ($^2J(^{119}Sn-^{31}P) = 148$ Hz). Both ^{119}Sn (two major signals) and ^{31}P NMR are consistent with the formation of **8c** (Chart 1). No change of the ^{119}Sn NMR is observed upon addition of a third mole equivalent HMPA, i.e., no $(Ph_2ClSnCH_2)_2SnClPh{\cdot}3HMPA$ is formed. This is also confirmed by the observation of two ^{31}P NMR resonances at 25.9 and 24.8 ppm ($^2J(^{119}Sn-^{31}P) = 153$ Hz) with an integral ratio of 1:2 at −88 °C, representing noncoordinated and coordinated HMPA.

The negative-ion ESMS of **8**, to which 1 mol equiv of HMPA has been added, shows the presence of peaks consistent with the species $[\mathbf{8} + Cl]^-$ ($m/z = 911$) and $[\mathbf{8} - Ph + 2Cl]^-$ ($m/z = 869$). The positive-mode ESMS of the same solution gives spectra consistent with $[\mathbf{8} - Cl + HMPA]^+$ ($m/z = 1120$) and $[\mathbf{8}\text{-}Cl + 2HMPA]^+$($m/z = 1199$).

All structures shown in this paper are postulated on the basis that pentacoordinate triorganotin(IV) derivatives exhibit trigonal-bipyramidal configurations with the electronegative substituents occupying the axial positions.[4,10d,13]

Molecular Structure of $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-[C_{12}H_{24}O_6{\cdot}K]^+$ (6b). The molecular structure of **6b** is illustrated in Figure 2 showing the crystallographic numbering scheme. Unit cell data and refinement details are given in Table 2. Selected interatomic parameters are listed in Table 3. Each of the three tin atoms exhibit a slightly distorted trigonal bipyramid with two phenyl and one methylene groups in equatorial and two fluorines in axial positions. The axial F(1)−Sn(1)−F(2) and F(1)−Sn(2)−F(1a) angles are 175.7(2)° and 177.1(2)°, respectively. Sn(1) lies 0.228 Å out of the C(7), C(21), C(31) trigonal plane in direction of F(2). There is no deviation of Sn(2) from the C(7), C(7a), C(11) plane. The asymmetry of the Sn(1)−F(1)−Sn(2) bridge

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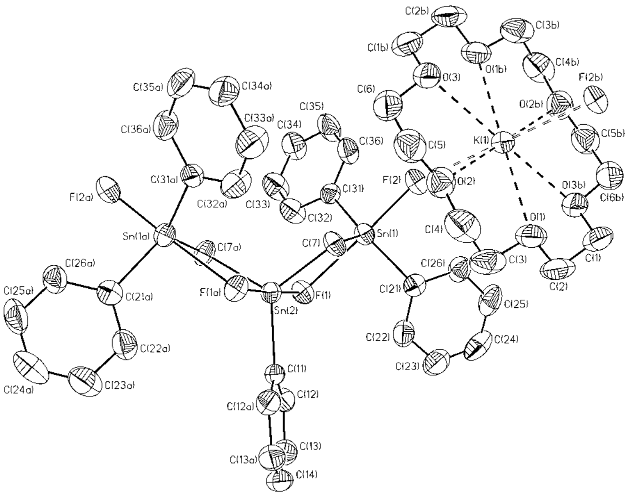

Figure 2. General view (SHELXTL-PLUS) of **6b** showing 30% probability displacement ellipsoids and the atom numbering. Symmetry transformations used to generate equivalent atoms: (a) $= -x + 1, y, -z + {}^{1}/_{2}$; (b) $= -x + {}^{3}/_{2}, -y + {}^{3}/_{2}, -z + 1$.

Table 2. Crystallographic Data for Compound 6b

empirical formula	$C_{44}H_{53}F_4KO_6Sn_3$
fw	1149.03
temperature	298(2) K
wavelength	0.710 69
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimens	
$a = 28.535(10)$ Å	$\alpha = 90°$
$b = 10.212(2)$ Å	$\beta = 120.23(2)°$
$c = 19.015(6)$ Å	$\gamma = 90°$
volume	4787(2) Å^3
Z	4
density (calcd)	1.594 Mg/m^3
density (measd)	1.597(5) Mg/m^3
abs coeff	1.698 mm^{-1}
F(000)	2280
cryst size	0.54 0.32 0.12 mm
θ range for data collection	1.6−29.96°
no. of index ranges	$0 < h < 40, -14 < k < 0, -26 < l < 22$
no. of reflns colld	6968
no. of indep reflns	6968 [R(int) = 0.0000]
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	6967/0/267
goodness-of-fit on F^2	1.004
final *R* indices	R1 = 0.0683 ($F > 4\sigma(F)$); wR2 = 0.0871
largest diff peak and hole	0.525 and −0.438 e Å^{-3}

with Sn(1)−F(1) 2.342(4) and Sn(2)−F(1) 2.154(4) Å is higher in comparison with the related compound $[(Ph_2FSn)_2CH_2{\cdot}F]^-[NEt_4]^+$.[2a] The Sn(1)−F(2) of 2.020(4) Å is close to a Sn−F single bond of 1.96 Å.[15a−c] The Sn−C bond lengths are as expected and comparable with the corresponding values found in $[(Ph_2FSn)_2CH_2{\cdot}F]^-[NEt_4]^+$.[2a] The Sn(1)−F(1)−Sn(2)−C(7) four-membered ring is almost planar; the deviations of Sn(1), C(7), Sn(2), and F(1) from the plane are −0.052(2), 0.059(3), −0.056(2), and 0.050(2) Å, respectively. The torsion angle between the symmetry-related four-membered rings amounts to 72.57(16)°.

The anionic $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-$ units are linked via F(2)···[K·18-crown-6]$^+$ bridges of 2.767 Å to form an infinite chain. The bridging capacity of [K·18-crown-6]$^+$ [15d−20] as well as [Na·15-crown-5]$^+$ [21] was previously observed for related anionic tin and silicon compounds.

Experimental Section

General Methods. All reactions were carried out under a dry nitrogen atmosphere. The solvents were purified by distillation under nitrogen from the appropriate drying agents. The tetraalkylammmonium fluorides, HMPA, PPNCl, and 18-crown-6 were commercial products. Bromotriphenylstannane, dichlorodiphenylstannane, and bis(diphenylfluorostannyl)methane were synthesized as described in the literature.[2a,22,23] The experimental density of the crystals of **6b** was measured using a Micromeritics Accu Pyc 1330.

NMR Spectroscopy. NMR spectra were recorded on Bruker DRX400, Bruker DPX300, and JEOL GX270 FT NMR spectrometers with broad-band decoupling of ^{119}Sn at 149.21, 111.92, and 100.75 MHz, respectively, ^{19}F at 254.19 MHz, and ^{13}C at 100.61 MHz, using external and internal deuterium lock, and referenced against external Me_4Sn (^{119}Sn), $CFCl_3$ (^{19}F), and Me_4Si (^{13}C, ^{1}H). Temperatures were maintained using a JEOL GTV3 control system. The complexes for the NMR investigations were generally prepared *in situ*. The fluoride complexes were prepared by reaction of $(Ph_2FSnCH_2)_2SnFPh$ (**6**) or $(Ph_2FSnCH_2SnFPh)_2CH_2$ (**7**) with the appropriate mole ratios of $Bu_4NF{\cdot}3H_2O$ in dichloromethane solution. The HMPA complexes of bis((diphenylchlorostannyl)methyl)phenylchlorostannane, $(Ph_2ClSnCH_2)_2SnClPh{\cdot}n[(CH_3)_2N]_3PO$ (**8b**, $n = 1$; **8c**, $n = 2$), were generated *in situ* by reaction of 1:1, respectively, 1:2 mol ratios of $(Ph_2ClSnCH_2)_2SnClPh$ (**8**) and HMPA in dichloromethane. The concentrations of the stannyl fluorides were typically about 0.1 M.

Electrospray Mass Spectrometry. Electrospay mass spectra were obtained with a Platform II single-quadrupole mass spectrometer (Micromass, Altrincham, U.K.) using an acetonitrile mobile phase. Acetonitrile solutions (1 mM) of the compounds were injected directly into the spectrometer via a Rheodyne injector equipped with a 50 μL loop. A Harvard 22 syringe pump delivered the solutions to the vaporization nozzle of the electrospray ion source at a flow rate of 10 μL min^{-1}. Nitrogen was used as both a drying gas and for nebulization with flow rates of approximately 200 and 20 mL min^{-1}, respectively. The pressure in the mass analyzer region was usually about 4×10^{-5}. Typically, 10 signal-averaged spectra were collected.

Synthesis of (Bromomethyl)triphenylstannane, Ph_3SnCH_2Br (1). A solution of Ph_3SnBr (95.89 g, 223 mmol) in 150 mL of thf was added dropwise at 40 °C to a solution of $BrZnCH_2Br$ prepared from Zn (58.34 g, 892 mmol), dibromomethane (155.21 g, 892 mmol) and cupric acetate monohydrate (1.00 g, 5.01 mmol) in 400 mL of thf. The reaction mixture was stirred overnight at 40 °C, and most of the thf was distilled off. After addition of 300 mL of hexane and 100 mL of 3% hydrochloric acid, the organic layer was separated and washed with diluted HCl. The solvent was evaporated, and the resulting yellow oil was dissolved in 200 mL of ether.

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Table 3. Selected Bond Distances (Å), Angles (deg), and Torsion Angles (deg) for 6b

Bond Distances			
Sn(1)−F(2)	2.020(4)	Sn(2)−C(11)	2.136(11)
Sn(1)−C(21)	2.117(8)	Sn(2)−F(1)	2.154(4)
Sn(1)−C(7)	2.119(6)	K(1)−O(2)	2.761(6)
Sn(1)−C(31)	2.133(8)	K(1)−F(2)	2.767(4)
Sn(1)−F(1)	2.342(4)	K(1)−O(1)	2.773(7)
Sn(2)−C(7)	2.110(6)	K(1)−O(3)	2.865(6)
Bond Angles			
F(2)−Sn(1)−C(21)	94.3(3)	C(7)−Sn(2)−C(7a)	113.8(4)
F(2)−Sn(1)−C(7)	99.4(2)	C(7)−Sn(2)−C(11)	123.1(2)
C(21)−Sn(1)−C(7)	118.8(3)	C(7)−Sn(2)−F(1a)	97.5(2)
F(2)−Sn(1)−C(31)	94.6(3)	C(7)−Sn(2)−F(1)	80.9(2)
C(21)−Sn(1)−C(31)	114.1(3)	C(11)−Sn(2)−F(1)	91.45(11)
C(7)−Sn(1)−C(31)	123.7(3)	F(1a)−Sn(2)−F(1)	177.1(2)
F(2)−Sn(1)−F(1)	175.7(2)	F(2b)−K(1)−F(2)	180.0
C(21)−Sn(1)−F(1)	88.9(3)	Sn(2)−F(1)−Sn(1)	96.70(14)
C(7)−Sn(1)−F(1)	76.5(2)	Sn(1)−F(2)−K(1)	153.3(2)
C(31)−Sn(1)−F(1)	86.7(2)	Sn(2)−C(7)−Sn(1)	105.3(3)
Torsion Angles			
C(7)−Sn(2)−F(1)−Sn(1)	−5.6(2)	F(1)−Sn(1)−F(2)−K(1)	74(2)
C(7a)−Sn(2)−F(1)−Sn(1)	107.4(2)	F(2b)−K(1)−F(2)−Sn(1)	115(100)
C(11)−Sn(2)−F(1)−Sn(1)	−128.91(11)	C(7a)−Sn(2)−C(7)−Sn(1)	−87.9(3)
F(1a)−Sn(2)−F(1)−Sn(1)	51.09(11)	C(11)−Sn(2)−C(7)−Sn(1)	92.1(3)
F(2)−Sn(1)−F(1)−Sn(2)	−13(2)	F(1a)−Sn(2)−C(7)−Sn(1)	−171.2(3)
C(21)−Sn(1)−F(1)−Sn(2)	125.6(2)	F(1)−Sn(2)−C(7)−Sn(1)	6.4(3)
C(7)−Sn(1)−F(1)−Sn(2)	5.7(2)	F(2)−Sn(1)−C(7)−Sn(2)	172.7(3)
C(31)−Sn(1)−F(1)−Sn(2)	−120.2(2)	C(21)−Sn(1)−C(7)−Sn(2)	−87.1(4)
C(21)−Sn(1)−F(2)−K(1)	−64.9(5)	C(31)−Sn(1)−C(7)−Sn(2)	70.7(4)
C(7)−Sn(1)−F(2)−K(1)	55.2(5)	F(1)−Sn(1)−C(7)−Sn(2))	−5.9(3)

While stirring, a solution of KF (10.00 g, 172 mmol) in 50 mL of water was added to convert unreacted Ph_3SnBr to insoluble Ph_3SnF. After 3 h, the precipitate was filtered off and the organic layer was separated and dried over Na_2SO_4. Addition of 40 mL of ethanol and slow evaporation of the ether yielded 30 g (30%) of Ph_3SnCH_2Br as colorless crystals, mp 80−82 °C. ^{119}Sn NMR (CH_2Cl_2) δ: −129.4 [$^1J(^{119}Sn-^{13}C_i)$ 544 Hz] [$^1J(^{119}Sn-^{13}CCH_2)$ 368 Hz]. ^{1}H NMR ($CDCl_3$) δ: 3.14 (s, 2H, CH_2) [$^2J(^{119}Sn-^1H)$ 18 Hz], 7.3−7.6 (m, 15H, Ph_3Sn). ^{13}C NMR ($CDCl_3$, [$^nJ(^{119}Sn-^{13}C)$ Hz]) δ: 8.2 (CH_2) [370], 128.7 (C_m) [54], 129.4 (C_p) [12], 137.0 (C_o) [36], 136.9 (C_i) [542]. Anal. Calcd for $C_{19}H_{17}BrSn$ (443.94): C, 51.40; H, 3.86. Found: C, 51.71; H, 3.92.

Synthesis of Bis((triphenylstannyl)methyl)diphenylstannane, ($Ph_3SnCH_2)_2SnPh_2$ (2). A solution of Ph_2SnCl_2 (7.56 g, 22 mmol) in 25 mL of thf was added dropwise to a magnetically stirred solution of Ph_3SnCH_2MgBr prepared from Ph_3SnCH_2Br (22.25 g, 50 mmol) and Mg (1.30 g, 54 mmol) in 70 mL of thf. The reaction mixture was refluxed overnight, and two-thirds of the thf was distilled off, followed by addition of 150 mL of ether. The reaction mixture was hydrolyzed under ice-cooling with diluted HCl, and the organic layer was separated, dried over Na_2SO_4, and filtered. Addition of 40 mL of ethanol and fractional crystallization yielded 10.80 g (49%) of $(Ph_3SnCH_2)_2SnPh_2$ as colorless crystals, mp 118−119 °C. ^{119}Sn NMR ($CDCl_3$) δ: −25.0 (^{gem}Sn, 1Sn) [$^2J(^{119}Sn-^{117}Sn)$ 246 Hz] [$^1J(^{119}Sn-^{13}C_i)$ 488 Hz], −79.0 (^{ter}Sn, 2Sn) [$^2J(^{119}Sn-^{117}Sn)$ 244 Hz] [$^1J(^{119}Sn-^{13}C_i)$ 509 Hz]. ^{1}H NMR ($CDCl_3$) δ: 0.56 (s, 4H, CH_2) [$^2J(^{119}Sn-^1H)$ 62 Hz], 7.2−7.4 (m, 40H, PhSn). ^{13}C NMR ($CDCl_3$, [$^nJ(^{119/117}Sn-^{13}C)$ Hz]) δ: −14.4 (CH_2) [283], ^{ter}SnPh: 128.9 (C_m) [50], 129.3 (C_p) [11], 137.4 (C_o) [38], 140.0 (C_i) [509/488], ^{gem}SnPh: 128.7 (C_m) [48], 129.1 (C_p) [14], 137.1 (C_o) [37], 141.3 (C_i). Anal. Calcd for $C_{50}H_{44}Sn_3$ (1001.03): C, 59.99; H, 4.43. Found: C, 60.21; H, 4.42.

Synthesis of Bis[((triphenylstannyl)methyl)diphenylstannyl]methane, $(Ph_3SnCH_2SnPh_2)_2CH_2$ (3). $(Ph_2FSn)_2CH_2$ (2.99 g, 5 mmol) was added in small portions to a magnetically stirred and filtered solution of Ph_3SnCH_2MgBr prepared from Ph_3SnCH_2Br (4.60 g, 10.3 mmol) and Mg (250 mg, 11.1 mmol) in 50 mL of thf. The reaction mixture was refluxed overnight. Two-thirds of the thf was distilled off, and 50 mL of ether was added. The reaction mixture was hydrolyzed under ice-cooling with diluted HCl, and the organic layer was separated, dried over Na_2SO_4, and filtered. Addition of 20 mL of ethanol and fractional crystallization yielded 1.80 g (28%) of $(Ph_3SnCH_2SnPh_2)_2CH_2$ as a colorless solid, mp 84−86 °C. ^{119}Sn NMR (CH_2Cl_2) δ: −25.9 (^{gem}Sn, 2Sn) [$^2J(^{119}Sn-^{117}Sn)$ 241 Hz] [$^1J(^{119}Sn-^{13}C_i)$ 492 Hz], −79.8 (^{ter}Sn, 2Sn) [$^2J(^{119}Sn-^{117}Sn)$ 241 Hz] [$^1J(^{119}Sn-^{13}C_i)$ 508 Hz]. ^{1}H NMR ($CDCl_3$) δ: 0.19 (s, 2H, $^{gem}SnCH_2{}^{gem}Sn$) [$^2J(^{119}Sn-^1H)$ 60 Hz], 0.48 (s, 4H, $^{ter}SnCH_2{}^{gem}Sn$) [$^2J(^{119}Sn-^1H)$ 62 Hz], 7.0−7.4 (m, 50H, PhSn). ^{13}C NMR ($CDCl_3$, [$^nJ(^{119/117}Sn-^{13}C)$ Hz]) δ: −15.1 ($^{ter}SnCH_2{}^{gem}Sn$) [280], −13.4 ($^{gem}SnCH_2{}^{gem}Sn$) [270], ^{ter}SnPh: 128.2 (C_m) [51], 128.7 (C_p) [11], 136.8 (C_o) [45], 139.4 (C_i) [510/484], ^{gem}SnPh: 128.1 (C_m) [51], 128.5 (C_p) [11], 136.5 (C_o) [40], 140.9 (C_i) [494/470]. Anal. Calcd for $C_{63}H_{56}Sn_4$ (1287.98): C, 58.75; H, 4.38. Found: C, 58.65; H, 4.62.

Synthesis of Bis((diphenyfluorostannyl)methyl)phenylfluorostannane, $(Ph_2FSnCH_2)_2SnFPh$ (6). Iodine (2.74 g, 10.8 mmol) was added in small portions under ice-cooling to a magnetically stirred solution of $(Ph_3SnCH_2)_2SnPh_2$ (3.60 g, 3.6 mmol) in 20 mL of dichloromethane. The reaction mixture was stirred overnight. The solvent and iodobenzene were removed in vacuo. Addition of 10 mL of dichloromethane, filtration and evaportion of the solvent afforded 3.80 g (92%) of $(Ph_2ISnCH_2)_2SnIPh$ (**4**) as an oil. ^{119}Sn NMR (CH_2Cl_2) δ: −12.9 (^{gem}Sn, 1Sn) [$^2J(^{119}Sn-^{117}Sn)$ 283 Hz] [$^1J(^{119}Sn-^{13}C_i)$ 568 Hz], −66.5 (^{ter}Sn, 2Sn) [$^2J(^{119}Sn-^{117}Sn)$ 281 Hz] [$^1J(^{119}Sn-^{13}C_i)$ 560 Hz]. ^{1}H NMR ($CDCl_3$) δ: 1.60 (s, 4H, CH_2) [$^2J(^{119}Sn-^1H)$ 61 Hz], 7.0−7.7 (m, 25H, PhSn). ^{13}C NMR ($CDCl_3$, [$^nJ(^{119}Sn-^{13}C)$ Hz]) δ: 0.2 (CH_2) [268], ^{ter}SnPh: 128.8 (C_m) [64], 130.1 (C_p), 135.8 (C_o) [52], 137.9 (C_i), ^{gem}SnPh: 128.6 (C_m) [64], 129.9 (C_p), 135.4 (C_o) [52].

A solution of $(Ph_2ISnCH_2)_2SnIPh$ (3.80 g, 3.30 mmol) in 10 mL of ether was added dropwise to a magnetically stirred solution of KF (1.72 g, 29.73 mmol) in 15 mL of water, and stirring was continued overnight. The colorless precipitate was filtered off and washed twice with water, methanol, and ether to give 2.32 g (85%) of $(Ph_2FSnCH_2)_2SnFPh$ as a colorless amorphous solid, mp > 250 °C. Anal. Calcd for $C_{32}H_{29}Sn_3F_3$ (826.71): C, 46.49; H, 3.54. Found: C, 45.48; H, 3.58.

Synthesis of Bis[((diphenylfluorostannyl)methyl)phenylfluorostannyl]methane, $(Ph_2FSnCH_2SnFPh)_2CH_2$ (7). $(Ph_3SnCH_2SnPh_2)_2CH_2$ (600 mg, 0.47 mmol) was dissolved in 10 mL of dichloromethane, and iodine (473 mg, 1.86 mmol) was added in small portions under ice-cooling and magnetic stirring. The reaction mixture was stirred overnight. The solvent and iodobenzene were removed in vacuo. Addition of 10 mL of dichloromethane, filtration, and evaporation of the solvent afforded 620 mg (89%) of $(Ph_2ISnCH_2SnIPh)_2CH_2$ (**5**) as an oil. ^{119}Sn NMR (CH_2Cl_2) δ: -11.4 (^{gem}Sn, 2Sn) [$^2J(^{119}Sn-^{117}Sn)$ 286 Hz], -67.1 (^{ter}Sn, 2Sn) [$^2J(^{119}Sn-^{117}Sn)$ 269 Hz]. ^{1}H NMR ($CDCl_3$) δ: 1.74 (s, 2H, $^{gem}SnCH_2{}^{gem}Sn$), 1.80 (s, 4H, $^{ter}SnCH_2{}^{gem}Sn$), 7.0−7.7 (m, 30H, PhSn). ^{13}C NMR ($CDCl_3$) δ: 0.2 ($^{ter}SnCH_2{}^{gem}Sn$), 1.5 ($^{gem}SnCH_2{}^{gem}Sn$), ^{ter}SnPh: 128.8 (C_m), 130.1 (C_p), 135.8 (C_o), 136.8 (C_i), ^{gem}SnPh: 128.7 (C_m), 130.0 (C_p), 135.4 (C_o), 137.9 (C_i).

A solution of $(Ph_2ISnCH_2SnIPh)_2CH_2$ (600 mg, 0.4 mmol) in 15 mL of ether was added dropwise to a magnetically stirred solution of KF (374 mg, 6.46 mmol) in 15 mL of water, and stirring of the suspension was continued overnight. The colorless precipitate was filtered off and washed twice with water, methanol, and ether to give 378 mg (89%) of $(Ph_2FSnCH_2SnFPh)_2CH_2$ as a colorless amorphous solid, mp > 250 °C. No satisfactory elemental analysis could be obtained.

Synthesis of Bis((diphenylchlorostannyl)methyl)phenylchlorostannane, $(Ph_2ClSnCH_2)_2SnClPh$ (8). Under exclusion of light, to a solution of $(Ph_2ISnCH_2)_2SnIPh$ (3.00 g, 2.61 mmol) in 35 mL of acetonitrile, AgCl (2.24 g, 15.65 mmol) was added and the reaction mixture was stirred for 14 days until the ^{119}Sn NMR showed complete disappearance of $(Ph_2ISnCH_2)_2SnIPh$. The precipitate of AgI was filtered off, and the solvent was removed in vacuo. The resulting oil was dissolved in 30 mL of dichloromethane and filtered. Addition of 10 mL of hexane and slow evaporation of the dichloromethane afforded 2.10 g (93%) of $(Ph_2ClSnCH_2)_2SnClPh$ as a colorless solid, mp 102−103 °C. ^{119}Sn NMR ($CDCl_3$) δ: 89.1 (^{gem}Sn, 1Sn) [$^2J(^{119}Sn-^{117}Sn)$ 267 Hz], 20.5 (^{ter}Sn, 2Sn) [$^2J(^{119}Sn-^{117}Sn)$ 281 Hz]. ^{1}H NMR ($CDCl_3$) δ: 1.39 (s, 4H, CH_2) [$^2J(^{119}Sn-^1H)$ 63 Hz], 7.2−7.7 (m, 25H, PhSn). ^{13}C NMR ($CDCl_3$, [$^nJ(^{119/117}Sn-^{13}C)$ Hz]) δ: 2.6 (CH_2) [321/304], ^{ter}SnPh: 129.0 (C_m) [66], 130.4 (C_p) [14], 135.6 (C_o) [52], 138.3 (C_i) [623/595], ^{gem}SnPh: 128.8 (C_m), 130.2 (C_p), 135.1 (C_o), 139.7 (C_i). Anal. Calcd for $C_{32}H_{29}Cl_3Sn_3$ (876.06): C, 43.87; H, 3.34. Found: C, 43.10; H, 3.50.

Synthesis of Bis[((diphenylchlorostannyl)methyl)phenylchlorostannyl]methane, $(Ph_2ClSnCH_2SnClPh)_2CH_2$ (9). Under exclusion of light, to a solution of $(Ph_2ISnCH_2SnIPh)_2CH_2$ (600 mg, 0.4 mmol) in 10 mL of acetonitrile, AgCl (462 mg, 3.22 mmol) was added and the reaction mixture was stirred for 14 days until the ^{119}Sn NMR showed complete disappearence of $(Ph_2ISnCH_2SnIPh)_2CH_2$. The precipitate of AgI was filtered off and the solvent was removed in vacuo. The resulting oil was dissolved in 30 mL of dichloromethane and filtered. Addition of 10 mL of hexane and slow evaporation of the dichloromethane afforded 400 mg (83%) of $(Ph_2ClSnCH_2SnClPh)_2CH_2$ as a solid, mp 58−63 °C. ^{119}Sn NMR ($CDCl_3$) δ: 85.0 (^{gem}Sn, 2Sn), 17.4 (^{ter}Sn, 2Sn) [$^2J(^{119}Sn-^{117}Sn)$ 234 Hz]. ^{1}H NMR (CD_2Cl_2) δ: 1.33 (s, 4H, $^{ter}SnCH_2Sn^{gem}$) [$^2J(^{119}Sn-^1H)$ 62 Hz], 1.47 (s, 2H, $^{gem}SnCH_2Sn^{gem}$) [$^2J(^{119}Sn-^1H)$ 62 Hz], 7.0−7.8 (m, 30H, PhSn). ^{13}C NMR (CD_2Cl_2, [$^nJ(^{119/117}Sn-^{13}C)$ Hz]) δ: 3.4 ($^{ter}SnCH_2Sn^{gem}$) [321], 5.9 ($^{gem}SnCH_2Sn^{gem}$) [327],^{ter}SnPh: 129.4 (C_m), 130.8 (C_p), 136.1 (C_o), 138.9 (C_i), ^{gem}SnPh: 129.2 (C_m), 130.6 (C_p), 135.6 (C_o), 140.4 (C_i). No satisfactory elemental analysis could be obtained.

Synthesis of Bis((phenyldichlorostannyl)methyl)dichlorostannane, $(PhCl_2SnCH_2)_2SnCl_2$ (10). A solution of $HgCl_2$ (4.07 g, 15 mmol) in 20 mL of acetone was added dropwise to an ice-cooled and magnetically stirred solution of $(Ph_3SnCH_2)_2SnPh_2$ (2.50 g, 2.5 mmol) in 25 mL of acetone. The reaction mixture was stirred overnight at room temperature. The precipitate of PhHgCl was filtered off, and the solvent was removed in vacuo. A 30 mL portion of ether was added to the residue, and the rest of PhHgCl was filtered off. Addition of 10 mL of toluene and evaporation of the ether afforded 1.10 g (59%) of $(PhCl_2SnCH_2)_2SnCl_2$ as a colorless amorphous solid, mp 145−147 °C. ^{119}Sn NMR (concentration dependent; 150.13 mg in 2 mL of CH_3CN) δ: -55.8 (^{gem}Sn, 1Sn), -101.3 (^{ter}Sn, 2Sn). ^{1}H NMR (CD_3CN) δ: 2.45 (s, 4H, CH_2) [$^2J(^{119}Sn-^1H)$ 89 Hz], 7.4−8.0 (m, 10H, PhSn). ^{13}C NMR (CD_3CN, [$^nJ(^{119/117}Sn-^{13}C)$ Hz]) δ: 34.5 (CH_2) [606], ^{ter}SnPh: 129.6 (C_m) [101], 131.4 (C_p) [20], 135.3 (C_o) [67], 143.0 (C_i). Anal. Calcd for $C_{14}H_{14}Cl_6Sn_3$ (751.05): C, 22.39; H, 1.88. Found: C, 22.53; H, 2.01.

Synthesis of Potassium-18-crown-6-bis((diphenylfluorostannyl)methyl)phenyldifluorostannate, $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-[C_{12}H_{24}O_6{\cdot}K]^+$ (6b). A suspension of $(Ph_2FSnCH_2)_2SnFPh$ (817 mg, 0.988 mmol), KF (58 mg, 0.988 mmol), and 18-crown-6 (261 mg, 0.988 mmol) in 20 mL of dichloromethane was refluxed under magnetic stirring. After 2 days, the solution became almost clear and was filtered. Hexane was added to the filtrate, and slow evaporation of the dichloromethane yielded 650 mg (57%) of **6b** as colorless crystals, mp 186−187 °C. ^{119}Sn NMR (−80 °C, CD_2Cl_2) δ: -61.1 (tt, ^{gem}Sn, 1Sn) [$^1J(^{119}Sn-^{19}F_b)$ 1234 Hz] [$^3J(^{119}Sn-^{19}F_a)$ 129 Hz], -159.5 (ddd, ^{ter}Sn, 2Sn) [$^1J(^{119}Sn-^{19}F_a)$ 2216 Hz] [$^1J(^{119}Sn-^{19}F_b)$ 592 Hz] [$^3J(^{119}Sn-^{19}F)$ 110 Hz]. ^{1}H NMR ($CDCl_3$) δ: 1.58 (s, 4H, $SnCH_2Sn$) [$^2J(^{119}Sn-^1H)$ 75 Hz], 3.46 (s, 24H, OCH_2CH_2O), 7.2−8.0 (m, 25H, PhSn). ^{13}C NMR ($CDCl_3$, [$^nJ(^{119}Sn-^{13}C)$ Hz]) δ: 7.8 ($SnCH_2Sn$) [494], 71.4 (OCH_2CH_2O), ^{ter}SnPh: 128.3 (C_m) [67], 130.2 (C_p), 137.9 (C_o) [51], 145.5 (C_i) [744], ^{gem}SnPh: 129.3 (C_m) [65], 130.2 (C_p), 137.8 (C_o), 144.6 (C_i). Anal. Calcd for $C_{44}H_{53}F_4O_6K\,Sn_3$ (1149.12): C, 45.99; H, 4.65. Found: C, 45.8; H, 4.9.

Synthesis of Tetraethylammonium Bis((diphenylfluorostannyl)methyl)phenyldifluorostannate $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-[Et_4N]^+$ (6a). A suspension of $(Ph_2FSnCH_2)_2SnFPh$ (1.06 g, 1.28 mmol) and $Et_4NF{\cdot}2H_2O$ (238 mg, 1.28 mmol) in 20 mL of dichloromethane was refluxed for 10 min. The solution was filtered, and 5 mL of hexane was added. After evaporation of the dichloromethane, 900 mg (72%) of the complex was isolated as a colorless solid, mp 134−137 °C. ^{1}H NMR ($CDCl_3$) δ: 0.87 (t, 12H, CH_3CH_2N), 2.65 (q, 8H, CH_3CH_2N), 1.53 (s, 4H, $SnCH_2Sn$) [$^2J(^{119}Sn-^1H)$ 77 Hz], 7.1−8.0 (m, 25H, Ph). ^{13}C NMR ($CDCl_3$, [$^nJ(^{119}Sn-^{13}C)$ Hz]) δ: 5.7 (CH_2) [487], 6.6 ($\mathbf{C}H_3CH_2N$), 51.4 ($CH_3\mathbf{C}H_2N$), ^{ter}SnPh: 127.8 (C_m) [67], 128.7 (C_p), 136.0 (C_o) [50], 143.7 (C_i), ^{gem}SnPh: 127.7 (C_m) [66], 128.7 (C_p), 135.8 (C_o) [52], 142.7 (C_i). Anal. Calcd for $C_{40}H_{49}Sn_3F_4N_1$ (975.90): C, 49.23; H, 5.06; N, 1.44. Found: C, 48.78; H, 5.16; N, 1.31.

Crystallography. Crystals of $[(Ph_2FSnCH_2)_2SnFPh{\cdot}F]^-[C_{12}H_{24}O_6{\cdot}K]^+$ were grown from CH_2Cl_2/hexane solutions by slow evaporation. Intensity data for the colorless crystal were collected with $\omega/2\theta$ scans on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. The lattice parameters were determined from a symmetry-constrained least-squares fit of the angular settings for 25 reflections with $\theta_{max} = 15.0°$. Three standard reflections were recorded every 300 reflections, and an anisotropic intensity loss up to 2.8% was detected during X-ray exposure. The data were corrected for Lorentz−polarization decay but not for absorption effects. The structure was solved by standard Patterson and difference Fourier methods SHELXTL PLUS[24] (Sheldrick, 1987), and refined satisfactorily with space group *C*2/*c* by full-matrix least-squares calculations SHELXL93.[25] The H atoms were placed in geometrically calculated positions and refined with a common isotropic temperature factor for the different C−H types (H_{aryl}, C−H = 0.93 Å, $U_{iso} = 0.081(7)$ Å^2; H_{alkyl}, C−H = 0.97 Å; $U_{iso} = 0.124(10)$ Å^2). Atomic

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scattering factors for neutral atoms and real and imaginary dispersion terms were taken from *International Tables for X-ray Crystallography*.[24] The programs used were SHELXTL PLUS,[25] SHELXL93,[26] PARST,[27] PLATON,[28] and MISSYM.[29] Crystallographic data are given in Table 2.

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Supporting Information Available: Tables of atomic coordinates, anisotropic displacement parameters, bond lengths and angles, and torsion angles for **6b** (9 pages). Ordering information is given on any current masthead page.

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