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Notes

α,ω-Bis(trichlorostannyl)alkanes as Bis(monodentate) Lewis Acids toward Halide Ions

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Summary: The reactions between $X_3Sn(CH_2)_nSnX_3$ *(X* = *Cl, Br; n* = *1, 3, 4, 8) and halide in solution are described.* ^{119}Sn *NMR spectroscopy* (CD_2Cl_2) *indicates formation of five-coordinate dinuclear 1:2 adducts,* $[X_4Sn(CH_2)_nSnX_4]^{2-}$*, with chloride and bromide. A trigonal-bipyramidal geometry has been confirmed in the solid state for the compound having X* = *Cl and n* = *4. In contrast, fluoride reacts with* $X_3Sn(CH_2)_nSnX_3$ *to give six-coordinate tin species,* $[F_5Sn(CH_2)_nSnF_5]^{4-}$ *There was no evidence indicating that the tin atoms could act as a bidentate acid.*

Introduction

Selective complexation of anions using Lewis acids has became a focus of attention in recent years.[1] The strong Lewis acidity of organotin(IV) halides, $R_{4-n}SnX_n$, which increases significantly with the increasing number of halides attached to tin,[2] make them particularly good candidates for this kind of study. As a consequence, we have been interested for some time in the Lewis acid behavior of bridged ditin compounds toward halide ions.[3] It has been demonstrated that these compounds show a strong affinity toward halides, a property that is enhanced by their ability to form chelate complexes. Tin-containing macrocycles have also been shown to be good Lewis acid hosts.[4] A large number of Lewis acid−Lewis base complexes, e.g. $[R_3SnX_2]^-$, $[R_2SnX_3]^-$, and $[RSnX_4]^-$, is known for mononuclear organotin halides.[5] However, for alkylene-bridged ditin compounds, only the equivalents to triorganotin halides, $R_2XSn(CH_2)_nSnR_2X$, have so far been investigated.[3b] To redress this, we now report on the reaction of various polymethylene-bridged ditin hexahalides,[6] $X_3Sn(CH_2)_nSnX_3$, with fluoride, chloride, and bromide ions. Also reported is the crystal structure of the dianionic complex $[Cl_4Sn(CH_2)_4SnCl_4]^{2-}$, as its benzyltriphenylphosphonium salt.

Results and Discussion

1:2 Adducts of α,ω-Bis(trichlorostannyl)alkanes with Benzyltriphenylphosphonium Chloride (1−4). Addition of 1 mol equiv of benzyltriphenylphosphonium chloride, $[PhCH_2PPh_3]Cl$, to a solution of α,ω-bis(trichlorostannyl)propane, $Cl_3Sn(CH_2)_3SnCl_3$, in CD_2Cl_2 causes the ^{119}Sn NMR signal to shift from −0.9 ppm ($^4J(^{119}Sn-^{117}Sn) = 595$ Hz) to −145.7 ppm ($^4J(^{119}Sn-^{117}Sn) = 642$ Hz). Addition of a second mole equivalent of chloride causes a further low-frequency shift of the ^{119}Sn NMR resonance to −262.1 ppm ($^4J(^{119}Sn-^{117}Sn) = 1526$ Hz). Interestingly, cooling the sample to −80 °C causes the ^{119}Sn chemical shift to move to −269.3 ppm and the coupling constant $^4J(^{117}Sn-^{119}Sn)$ to increase to 1957 Hz. A third equivalent of chloride brings about only a minor further shift (δ −276.4 ppm, $^4J(^{119}Sn-^{117}Sn) = 1700$ Hz). These observations are consistent with the formation of the stable 1:2 chloride adduct $[Cl_4Sn(CH_2)_3SnCl_4]^{2-}$ (**1**), in which both tin atoms are five-coordinate. Stepwise additions of chloride to $Cl_3Sn(CH_2)_4SnCl_3$ results in a similar behavior, the ^{119}Sn NMR resonances moving successively from 6.3 to −165.7 to −262.9 to −274.3 ppm, consistent with the formation of $[Cl_4Sn(CH_2)_4SnCl_4]^{2-}$

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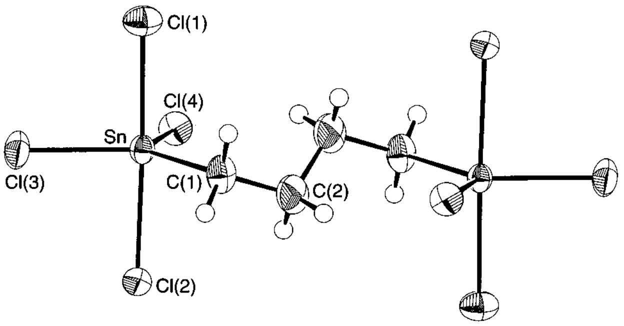

Figure 1. Molecular structure and atomic numbering scheme for the dianion in $[PhCH_2PPh_3]_2[Cl_4Sn(CH_2)_4SnCl_4]$ (**2**).

(**2**). In contrast to **1**, no $J(^{119}Sn-^{117}Sn)$ coupling was observed for **2**.

The 1:2 chloride adducts of the methylene- and octamethylene-bridged ditin compounds were also prepared according to eq 1.

$$Cl_3Sn(CH_2)_nSnCl_3 + 2[PhCH_2PPh_3]Cl \xrightarrow{CHCl_3} [PhCH_2PPh_3]_2[Cl_4Sn(CH_2)_nSnCl_4] \quad (1)$$

1−**4**

1, $n = 3$; **2**, $n = 4$; **3**, $n = 1$; **4**, $n = 8$

Addition of 1 equiv of $[PhCH_2PPh_3]Cl$ to a solution of $BuSnCl_3$ in $CDCl_3$ gave the five-coordinate complex $[PhCH_2PPh_3][BuSnCl_4]$ with a ^{119}Sn chemical shift of −258.0 ppm.[7] Addition of a further equivalent of chloride to the solution did not afford any significant change in the ^{119}Sn chemical shift (δ −266.3). Comparison of the ^{119}Sn chemical shifts of complexes **1** (δ −262.1), **2** (δ −262.9), and **4** (δ −256.7) with that of $[BuSnCl_4]^-$ (δ −258.0) indicates that the tin atoms in **1**, **2**, and **4** are five-coordinate in $CDCl_3$ solution.

The ^{119}Sn chemical shift (δ −363.9) of the 1:2 chloride adduct with the methylene-bridged species **3** indicates a higher coordination number at tin than in **1**, **2**, and **4**. This could be due to the close proximity of the tin atoms in **3**, allowing additional, bridging, intramolecular $Sn-Cl\rightarrow Sn$ interactions, which effectively increase the coordination numbers of tin beyond 5. Addition of a third equivalent of $[PhCH_2PPh_3]Cl$ to **3** and **4**, respectively, did not lead to any substantial shifts in ^{119}Sn NMR spectra (**3** + Cl^- δ −366.2; **4** + Cl^- δ −266.7).

Crystal Structure of 2. The crystal structure determination of **2** shows a unit cell which comprises a centrosymmetric dianion and two $[PhCH_2PPh_3]^+$ cations. A view of the dianion in **2** is shown in Figure 1, and selected interatomic parameters are listed in Table 1. The dinuclear dication features two tin centers bridged by a tetramethylene group. The coordination geometry about each tin atom is completed by four chlorides, leading to distorted-trigonal-bipyramidal geometry. In this description the tin atom lies 0.0798(2) Å out of the CCl_2 plane in the direction of the Cl(1) atom. There are no close intra- or intermolecular Sn···Cl interactions that may indicate an increase in the coordination number about tin. As expected, the two axial Sn−Cl bond distances are significantly longer than the equatorial Sn−Cl bonds. However, whereas the equatorial Sn−Cl distances are equal within experimental error, a significant disparity is noted between the axial Sn−Cl distances. Thus, the Sn−Cl(2) distance of 2.543(2) Å is significantly longer than the Sn−Cl(1) distance of 2.463(2) Å. This difference is readily explained in terms of Cl···H interactions.[8] Hence, while the Cl(1) atom is involved in only one intermolecular Cl···H contact less than 3.0 Å, i.e., 2.95 Å to H(25) (symmetry operation: x, y, $1 + z$), the Cl(2) atom is involved in an intramolecular (2.99 Å to H(2b)) and five intermolecular contacts less than 3.0 Å, i.e., 2.84 Å (H(21b); x, $-1 + y$, $1 + z$), 2.87 Å (H(21a); $-1 - x$, $-y$, $-z$), 2.90 Å (H(14); x, $-1 + y$, $1 + z$), 2.90 Å (H(11); x, $-1 + y$, z) and 2.93 Å (H(8); $-1 - x$, $-y$, $-z$).

Table 1. Selected Interatomic Parameters (Distances in Å and Angles in deg) for $[PhCH_2PPh_3]_2[Cl_4Sn(CH_2)_4SnCl_4]$ (2)[a]

Sn−Cl(1)	2.463(2)	Sn−Cl(2)	2.543(2)
Sn−Cl(3)	2.345(2)	Sn−Cl(4)	2.342(2)
Sn−C(1)	2.143(3)	C(1)−C(2)	1.534(5)
C(2)−C(2)^i	1.495(6)		
Cl(1)−Sn−Cl(2)	177.83(3)	Cl(1)−Sn−Cl(3)	90.44(5)
Cl(1)−Sn−Cl(4)	92.41(5)	Cl(1)−Sn−C(1)	93.1(1)
Cl(2)−Sn−Cl(3)	87.56(5)	Cl(2)−Sn−Cl(4)	88.97(5)
Cl(2)−Sn−Cl(1)	87.6(1)	Cl(3)−Sn−Cl(4)	106.74(6)
Cl(3)−Sn−C(1)	132.24(9)	Cl(4)−Sn−C(1)	120.6(1)
Sn−C(1)−C(2)	110.7(2)	C(1)−C(2)−C(2)^i	113.8(4)

[a] The superscript letter i indicates an atom related by the symmetry operation $-x$, $-1 - y$, $-z$.

Crystallographically confirmed trigonal-bipyramidal geometries within a donor set defined by one carbon and four chloride atoms, as found in **2**, are relatively rare. The only other structure available for direct comparison is that of the methyltin species found in $[Ph_4As][MeSnCl_4]$.[9] In this structure there are two crystallographically independent anions, each with 2-fold symmetry, which show the same variation in the axial and equatorial Sn−Cl bond distances.

1:2 Bromide Adducts of α,ω-Bis(tribromostannyl)propane (5, 6). Reaction of 2 mole equiv of bromide, as R_4NBr (R = Et, Bu), with $Br_3Sn(CH_2)_3SnBr_3$ resulted in the formation of $[R_4N]_2[Br_4Sn(CH_2)_3SnBr_4]$ (**5**, R = Et; **6**, R = Bu), which were isolated as microcrystalline solids (eq 2). Compound **5** was insufficiently soluble to enable the measurement of a ^{119}Sn NMR spectrum. However, addition of a further equivalent of Bu_4NBr to a solution of **6** (δ −524.3, $^nJ(^{117}Sn-^{119}Sn)$ 1618 Hz) in $CDCl_3/CD_2Cl_2$ caused only a small change in the ^{119}Sn chemical shift (δ −534.2), consistent with formation of the five-coordinate tin complex $[Br_4Sn(CH_2)_3SnBr_4]^{2-}$. At −80 °C the ^{119}Sn

$$Br_3Sn(CH_2)_3SnBr_3 + 2R_4NBr \xrightarrow{CHCl_3} [R_4N]_2[Br_4Sn(CH_2)_3SnBr_4] \quad (2)$$

5, **6**

5, R = Et; **6**, R = Bu

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signal moves to δ −516.5 and the coupling $^nJ(^{117}Sn-^{119}Sn)$ increases to 2400 Hz.

ESMS Data. The electrospray mass spectral data are consistent with adduct formation as deduced from the NMR data. At low cone voltage (10 V) the negative ESMS of compounds **1**−**4** (in acetonitrile) contain the dianionic species $[M]^{2-}$ (m/z 282, 289, 268, 317 for **1**−**4**, respectively) as the most abundant species. The singly charged species $[M - Cl]^-$ (m/z 527, 541, 500, 598 for **1**−**4**, respectively) are present in relative abundance of between 5 and 60%. Increasing the cone voltage causes the relative intensities of $[M]^{2-}$ to decrease while the intensities of $[M - Cl]^-$ increase. Interestingly, the spectra of compounds **2**−**4** contain the species $[SnCl_5]^-$ (m/z 225), which is consistent with the observation that solutions containing these compounds eventually decompose to give $[SnCl_6]^{2-}$ as the tin-containing species (see Experimental Section). The negative ESMS of a sample of $(Bu_4N)_2[SnCl_6]$ in acetonitrile contains $[SnCl_5]^-$ as the only observed species.

The positive ion detection mode indicates the ion-paired species $\{[PhCH_2PPh_3]_3M\}^+$ (m/z 1623, 1637, 1595, 1693 for **1**−**4**, respectively) as the most abundant species.

The negative ion spectrum (30 V) of compound **5** (in acetonitrile) shows the presence of $[M - Br]^-$ (m/z 840) as the dominant species with a minor contribution from $[SnBr_5]^-$ (m/z 518, 10%). The positive ion detection mode is dominated by the ion-paired species $\{[NEt_4]_3M\}^+$ (m/z 1310, 100%) and $\{[NEt_4]_4[M + Br]\}^+$ (m/z 1519, 70%).

Fluoride Adducts. In an effort to gain more information about the nature of the $^{119}Sn-^{117}Sn$ coupling in the trimethylene-bridged complexes, we investigated the reaction of fluoride with $Cl_3Sn(CH_2)_3SnCl_3$. Reaction of $Cl_3Sn(CH_2)_3SnCl_3$ with an excess of KF in water resulted in formation of $K_4[F_5Sn(CH_2)_3SnF_5]$ (**7**) in solution (eq 3).

$$Cl_3Sn(CH_2)_3SnCl_3 \xrightarrow{H_2O/KF} \underset{\mathbf{7}}{K_4[F_5Sn(CH_2)_3SnF_5]} \qquad (3)$$

It is known that reactions of KF with $RSnCl_3$ in water lead to the formation of water-soluble complexes of the type K_2RSnF_5.[10] NMR data for $K_2(BuSnF_5)$ had not been previously reported, and consequently this compound was synthesized for comparative purposes. Whereas the reaction of 5 mol equiv of KF with $BuSnCl_3$ gave $K_2(BuSnF_5)$ in moderate yields (60−70%) (δ −625.1 $^1J(^{19}F-^{119}Sn)$ = 3027 Hz, $^1J(^{19}F-^{119}Sn)$ = 1163 Hz), the successful preparation of **7** required more than 10 equiv of KF. The ^{119}Sn NMR chemical shift for **7** (δ −615.7) as well as the $^1J(^{19}F-^{119}Sn)$ coupling to the cis (to carbon) (3019 Hz) and trans (to carbon) (1167 Hz) fluorine atoms are quite similar to the values recorded for $K_2(BuSnF_5)$. The ^{119}Sn NMR spectrum of **7** also displays $^nJ(^{117}Sn-^{119}Sn)$ = 1375 Hz.

The ^{19}F NMR spectrum of $K_2(BuSnF_5)$ shows a quintet for the cis fluoride (δ −137.1; 1F, $^2J(^{19}F-^{19}F)$ = 7 Hz, $^1J(^{117/119}Sn-^{19}F)$ = 1122/1167 Hz) and a doublet for the trans fluorides (δ −134.2; 4F, $^2J(^{19}F-^{19}F)$ = 7 Hz, $^1J(^{117/119}Sn-^{19}F)$ = 2912/3029 Hz), in very good agreement with the data recorded for **7**.

The ^{19}F NMR signals for **7** comprise a quintet at −137.0 ppm ($^2J(^{19}F-^{19}F)$ = 7 Hz, $^1J(^{117/119}Sn-^{19}F)$ = 1118/1169 Hz) for the cis fluoride and a doublet at −133.9 ppm ($^2J(^{19}F-^{19}F)$ = 7 Hz, $^1J(^{117/119}Sn-^{19}F)$ = 2889/3024 Hz, $^5J(^{117/119}Sn-^{19}F)$ = 42 Hz). There is no evidence for bridging fluorine atoms, which implies that the $^nJ(^{117}Sn-^{119}Sn)$ coupling observed is four-bond coupling that occurs through the bridging trimethylene spacer. These data indicate that the tin atoms in both $K_2(BuSnF_5)$ and **7** are six-coordinate.

The ^{19}F NMR spectrum recorded for **7** at 2 °C also indicates the presence of a second species (ca. 20%, δ −131.9 ppm, −129.8 ppm ($^1J(^{117/119}Sn-^{19}F)$ = 2784/2914 Hz)), believed to be $K_4[XF_4Sn(CH_2)_3SnF_4X]$, where X is OH or Cl, respectively. Increasing the amount of KF in the reaction mixture changes the ratio of **7** to the second product in favor of **7**.

Conclusion

Replacing organo substituents at the tin atoms in alkylidene-bridged ditin species by halides appears to increase the Lewis acidity of each of the two tin centers. Somewhat surprisingly, α,ω-bis(trichlorostannyl)alkanes act only as bis(monodentate) Lewis acids toward halide ions, there being no evidence for the ditin acting as a chelate.

Experimental Section

All reactions were carried out under an atmosphere of dry argon. Solvents were dried and purified under argon by standard procedures. NMR spectra were obtained using a Varian 300 MHz Unity Plus NMR spectrometer. ^1H, ^{13}C, and ^{119}Sn chemical shifts δ are given in ppm and are referenced against Me_4Si and Me_4Sn, respectively. Electrospray mass spectra were obtained with a Platform II single-quadrupole mass spectrometer (Micromass, Altrincham, U.K.) using an acetonitrile mobile phase. Acetonitrile solutions (0.1 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. Pressure in the mass analyzer region was usually about 4×10^{-5} mbar. Typically 10 signal-averaged spectra were collected. Uncorrected melting points were determined on a Kofler hot stage. Microanalyses were performed using a CE 1106 elemental analyzer.

General Procedure for the Synthesis of 1:2 Adducts of α,ω-Bis(trichlorostannyl)alkanes and Benzyltriphenylphosphonium Chloride. A solution of $(PhCH_2PPh_3)Cl$ (500 mg, 1.29 mmol) in 4 mL of $CHCl_3$ was added dropwise into a magnetically stirred solution of the α,ω-bis(trichlorostannyl)alkanes[6] (0.645 mmol) in 4 mL of $CHCl_3$. The reaction mixture was stirred overnight to provide a white suspension. The product was filtered off and washed twice with 2 mL portions of $CHCl_3$ before recrystallizing from CH_2Cl_2 to give the 1:2 adduct $[Cl_4Sn(CH_2)_nSnCl_4][PhCH_2PPh_3]_2$. All the 1:2 complexes of α,ω-bis(trichlorostannyl)alkanes, $[Cl_4Sn(CH_2)_nSnCl_4]^{2-}$, appear to be unstable over extended exposure to the atmosphere, eventually decomposing to give $[PhCH_2PPh_3]_2[SnCl_6]$, as confirmed via ^{119}Sn NMR, elemental analysis, ESMS, and X-ray structural analysis.[11] This instability was particularly evident for **4**.

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3: 720 mg, colorless solid (90% yield). **1**: 780 mg, colorless solid (93% yield); mp 180−185 °C. **2**: 680 mg, colorless crystals (83% yield); mp 181−183 °C. **4**: 545 mg, colorless crystals (63% yield).

^{1}H NMR (299.98 MHz, CD_2Cl_2): **3**, δ 3.49 (s, $^2J(^{117/119}Sn-^1H) = 107/112$ Hz, 1H, CH_2), 4.68 (d, $^2J(^{31}P-^1H) = 14$ Hz, 2H, PCH_2), 6.95−7.96 (mm, 20H, Ph); **1**, δ 2.02−2.16 (m, $^2J(^{117/119}Sn-^1H) = 104$ Hz, 2H, CH_2), 2.26−2.42 (m, $^3J(^{117/119}Sn-^1H) = 138$ Hz, 1H, CH_2), 4.70 (d, $^2J(^{31}P-^1H) = 14.4$ Hz, 2H, PCH_2), 6.92−7.93 (mm, 20H, Ph); **2**, δ 1.77−1.90 (m, $^3J(^{117/119}Sn-^1H) = 154$ Hz, 1H, CH_2), 1.94−2.04 (m, $^2J(^{117/119}Sn-^1H) = 108$ Hz, 1H, CH_2), 4.66 (d, $^2J(^{31}P-^1H) = 14$ Hz, 1H, PCH_2), 6.94−7.93 (mm, 10H, Ph); **4**, δ 1.00−1.19 (m, 1H, CH_2), 1.14−1.36 (m, 1H, CH_2), 1.64−1.67 (m, $^3J(^{117/119}Sn-^1H) = 192$ Hz, 1H, CH_2), 1.99−2.19 (m, $^2J(^{117/119}Sn-^1H) = 106$ Hz, 1H, CH_2), 4.64 (d, $^2J(^{31}P-^1H) = 14$ Hz, 1H, PCH_2), 6.84−7.86 (mm, 10H, Ph).

$^{13}C\{^1H\}$ NMR (75.44 MHz, CD_2Cl_2): **3**, δ 80.32 (s, $^1J(^{117/119}Sn-^{13}C) = 995$ Hz, CH_2); **1**, δ 22.60 (s, $^2J(^{117/119}Sn-^{13}C) = 53$ Hz, CH_2), 45.71 (s, $^1J(^{117/119}Sn-^{13}C) = 873/906$ Hz, $^3J(^{117/119}Sn-^{13}C) = 207$ Hz, CH_2); **2**, δ 28.39 (s, $^2J(^{117/119}Sn-^{13}C) = 62/65$ Hz, $^3J(^{117/119}Sn-^{13}C) = 182/191$ Hz, CH_2), 43.71 (s, $^1J(^{117/119}Sn-^{13}C) = 886/928$ Hz, CH_2); **4**, δ 25.17 (s, $^2J(^{117/119}Sn-^{13}C) = 67$ Hz, CH_2), 28.70 (s, CH_2); 31.98 (s, $^3J(^{117/119}Sn-^{13}C) = 149/155$ Hz, CH_2), 44.51 (s, $^1J(^{117/119}Sn-^{13}C) = 881/924$ Hz, CH_2).

$^{119}Sn\{^1H\}$ NMR (111.85 MHz, CD_2Cl_2): **3**, δ −363.9 (s, $^2J(^{117}Sn-^{119}Sn) = 1274$ Hz); **1**, δ −262.1 (s, $^4J(^{117}Sn-^{119}Sn) = 1526$ Hz); **2**, δ −256.5 (s, $W_{1/2} = 125$); **4**, δ −256.7 (s, $W_{1/2} = 40$);

Anal. Calcd for $C_{53}H_{50}Cl_8P_2Sn_2$ (**1**): C, 50.14; H, 3.97. Found: C, 50.51; H, 4.05. Calcd for $C_{54}H_{52}Cl_8P_2Sn_2$ (**2**): C, 50.51; H, 4.08. Found: C, 50.32; H, 4.09.

Synthesis of 1:2 Adducts of 1,3-Bis(tribromostannyl)propane and R_4NBr (5, R = Et; 6, R = Bu). A solution of the appropriate R_4NBr (0.60 mmol) in 1 mL of $CHCl_3$ was added dropwise into a magnetically stirred solution of 1,3-bis(tribromostannyl)propane (228 mg, 0.30 mmol) in 1 mL of $CHCl_3$. The reaction mixture was stirred overnight to provide a white suspension for **5** and a clear solution for **6**, respectively. In the case of **5** the precipitate was filtered off and washed twice with 2 mL portions of CH_2Cl_2 to give yellowish microcrystalline material (291 mg; 73%): mp 173−175 °C. For **6** the organic solvent was removed in vacuo. Recrystallization of the resulting solid from CH_2Cl_2/hexane (2:1) at −30 °C afforded within several days colorless crystals (286 mg, 69%): mp 157−158 °C.

Anal. Calcd for $C_{19}H_{46}Br_8N_2Sn_2$ (**5**): C, 19.35; H, 3.93; N, 2.37. Found: C, 19.38; H, 3.71; N, 2.40. Calcd for $C_{35}H_{78}Br_8N_2Sn_2$ (**6**): C, 29.95; H, 5.60; N, 1.99. Found: C, 29.89; H, 5.51; N, 2.05.

^{1}H NMR (299.98 MHz, acetone-d_6): **5**, δ 1.47 (t, $^3J(^1H-^1H) = 7$ Hz, 12H, CH_3), 2.42−2.57 (m, 1H, CH_2), 2.57−2.69 (m, $^2J(^{117/119}Sn-^1H) = 91$ Hz, 2H, CH_2), 3.53 (q, $^3J(^1H-^1H) = 7$ Hz, 8H, CH_2).; **6** ($CDCl_3$), δ 1.04 (t, $^3J(^1H-^1H) = 7$ Hz, 12H, CH_3), 1.41−1.60 (m, 8H, CH_2), 1.60−1.81 (m, 8H, CH_2), 2.36−2.53 (m, $^3J(^{117/119}Sn-^1H) = 164$ Hz, 1H, CH_2), 2.54−2.67 (m, $^2J(^{117/119}Sn-^1H) = 88$ Hz, 2H, CH_2), 3.18−3.27 (m, 8H, CH_2).

$^{13}C\{^1H\}$ NMR (75.44 MHz, $CDCl_3/CD_2Cl_2$): **6**, δ 13.46 (s, 8C, CH_3), 19.53 (s, CH_2), 23.12 (s, $^2J(^{117/119}Sn-^{13}C) = 53$ Hz, CH_2), 23.83 (s, 8C, CH_2), 49.35 (s, $^1J(^{117/119}Sn-^{13}C) = 753/788$ Hz, $^3J(^{117/119}Sn-^{13}C) = 215/215$ Hz, CH_2), 58.71 (s, NCH_2).

$^{119}Sn\{^1H\}$ NMR (111.85 MHz, $CDCl_3/CD_2Cl_2$): **6**, δ −524.3 (s, $^nJ(^{117}Sn-^{119}Sn) = 1618$ Hz).

Tetrapotassium 1,3-Bis(pentafluorostannyl)propane (7). $Cl_3Sn(CH_2)_3SnCl_3$ (48 mg, 0.0975 mmol) and KF (113 mg, 1.95 mmol) were dissolved in D_2O, and the mixture was analyzed by NMR spectroscopy.

$^{13}C\{^1H\}$ NMR (75.4 MHz, D_2O): δ 21.43 (s, $^2J(^{117/119}Sn-^{13}C) = 56$ Hz, CH_2), 26.21 (quin, $^2J(^{19}F-^{13}C) = 31$ Hz, $^1J(^{117/119}Sn-^{13}C) = 1397$ Hz, CH_2).

$^{19}F\{^1H\}$ NMR (254.2 MHz, D_2O, 2 °C): δ −137.0 (quin, $^2J(^{19}F-^{19}F) = 7$ Hz, $^1J(^{117/119}Sn-^{19}F) = 1118/1169$ Hz, 1F, SnF), −133.9 (d, $^2J(^{19}F-^{19}F) = 7$ Hz, $^1J(^{117/119}Sn-^{19}F) = 2889/3024$ Hz, $^5J(^{117/119}Sn-^{19}F) = 42$ Hz, 4F, SnF), −122.1 (excess of KF).

$^{119}Sn\{^1H\}$ NMR (111.85 MHz, $CDCl_3$): δ −615.7 (d, quin, $^1J(^{19}F-^{119}Sn) = 3019$ Hz, $^1J(^{19}F-^{119}Sn) = 1167$ Hz, $^nJ(^{117}Sn-^{119}Sn) = 1375$ Hz).

X-ray Crystallography. Data for **2** were collected at 173 K employing graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å) on a Rigaku AFC7R diffractometer. Corrections were made for Lorentz and polarization effects[12] but not for absorption.

Crystal data for **2**: $C_{54}H_{52}Cl_8P_2Sn_2$, $M_r = 1284.0$, triclinc, $P\bar{1}$, $a = 11.506(4)$ Å, $b = 13.516(8)$ Å, $c = 10.228(6)$ Å, $\alpha = 77.59(5)°$, $\beta = 73.25(4)°$, $\gamma = 69.47(5)°$, $V = 1415(2)$ Å^3, $Z = 1$ (dinuclear unit and two cations), $D_x = 1.507$ g cm^{-3}, $T = 173$ K, μ(Mo Kα) = 13.51 cm^{-1}, 6814 reflections measured, $\theta_{max} = 27.5°$, 6491 unique ($R_{int} = 0.030$), 4963 with $I \geq 3.0\sigma(I)$.

The structure was solved by direct methods[13] and refined by a full-matrix least-squares procedure based on F.[12] Non-hydrogen atoms were refined with anisotropic displacement parameters, and H atoms were included in the model in their calculated positions (C−H = 0.95 Å). The refinement was continued until convergence with the application of a weighting scheme of the form $w = 1/[\sigma^2(F_o) + 0.00003|F_o|^2]$ when $R = 0.031$ and $R_w = 0.035$. Figure 1 shows a diagram of the dianion that was drawn with ORTEP[14] at the 50% probability level.

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Supporting Information Available: Tables giving positional and thermal parameters and all bond distances and angles for **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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