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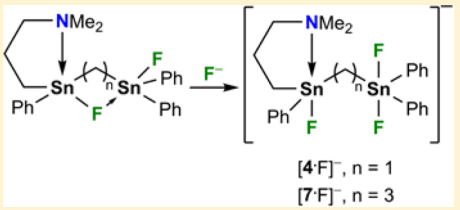
Unsymmetrical Bicentric Organotin Lewis Acids $\{Me_2N(CH_2)_3\}Ph(X)Sn(CH_2)_nSnPh_2X$ (X = F, I; *n* = 1, 3): Syntheses and Structures

Nour Alashkar, Christina Dietz, Samer Baba Haj, Wolf Hiller, and Klaus Jurkschat*

Lehrstuhl für Anorganische Chemie II, Technische Universität Dortmund, 44221 Dortmund, Germany

Supporting Information

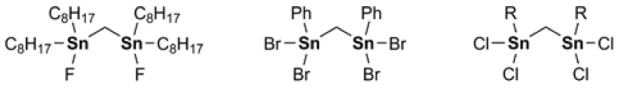
ABSTRACT: The syntheses of the intramolecularly coordinated organotin compounds $\{Me_2N(CH_2)_3\}Ph(X)SnCH_2SnPh_2X$ (**3**, X = I; **4**, X = F) and $\{Me_2N(CH_2)_3\}Ph(F)Sn(CH_2)_3SnPh_2F$ (**7**) are reported. The compounds have been characterized by elemental analysis, electrospray mass spectrometry, ^1H,^1H DOSY (**4**), ^{13}C, ^{19}F, and ^{119}Sn NMR spectroscopy, and single-crystal X-ray diffraction analysis. In the solid state, compound **4** is a head-to-tail dimer as a result of unsymmetrical Sn−F−Sn bridges, whereas compound **7** is a monomer with F→Sn intramolecular coordination, giving a six-membered ring. In solution, both **4** and **7** are monomeric. The reactions of both **4** and **7** with fluoride anion in CD_2Cl_2 have been investigated by variable-temperature ^{19}F and ^{119}Sn NMR spectroscopy.



INTRODUCTION

The selective complexation of anions by all sorts of host molecules remains a hot topic in contemporary chemistry. The progress made in this field is demonstrated in regular reviews.[1a−k] Although the topic is still dominated by organic receptors, organometallic compounds also receive increasing attention in this domain.[2a−m] In this context, we focused on the complexation behavior of spacer-bridged ditin compounds as bicentric Lewic acids toward different anions.[2n] We demonstrated the potential of bis(haloorganylstannyl)methanes of the type $[R_nX_{(3-n)}Sn]_2CH_2$ as ionophores in ion-selective electrodes.[2o] An elegant example is bis(fluorido-di-*n*-octylstannyl)-methane, $[(n\text{-}C_8H_{17})_2SnF]_2CH_2$,[3] **A** (Chart 1), which showed good results as an ionophore for a fluoride-anion-selective electrode. Other examples are bis(dibromidophenylstannyl)-methane, $(PhSnBr_2)_2CH_2$,[4] **B** (Chart 1), which exhibits excellent selectivity toward phosphate anions, and bis-(dichloridoorganostannyl)methane, $\{(RCl_2Sn)_2CH_2$, R = (4-*n*-C_8H_{17}-$C_6H_4)\}$,[5] **C** (Chart 1), which was shown to be a highly selective arsenate ionophore.

Chart 1. Selected Bicentric Tin-Based Lewis Acids Having Potential as Anion Carriers



A **B** **C**, R = 4-*n*-C_8H_{17}-C_6H_4

Previously, we have reported the complexation reactions of bis(halodiphenylstannyl)alkanes, $(Ph_2XSn)_2(CH_2)_n$ (X = I, Br, Cl, F; *n* = 1, 2, 3),[6] with different halide anions and found that bis(fluoridodiphenylstannyl)alkanes always preferentially chelate fluoride anions over chloride or bromide. However, the low solubility of these compounds as with many other fluoridoorganotin compounds precludes their practical applications. One strategy to overcome this problem and to solubilize organotin fluorides is the employment of intramolecularly coordinating *built-in* ligands such as the 3-(dimethylamino)propyl substituent, $[Me_2N(CH_2)_3]$.[7,8] In continuation of our studies mentioned above we report herein the syntheses and molecular structures of the fluorido-substituted organotin compounds $\{Me_2N(CH_2)_3\}Ph(F)SnCH_2SnPh_2F$, **4**, and $\{Me_2N(CH_2)_3\}$-$Ph(F)Sn(CH_2)_3SnPh_2F$, **7**, containing the 3-(dimethylamino)-propyl substituent. Also reported are ^{19}F and ^{119}Sn NMR spectroscopic studies of the reactions of **4** and **7** with tetraethylammonium fluoride dihydrate, $NEt_4F{\cdot}2H_2O$, in CD_2Cl_2 solution.

RESULTS AND DISCUSSION

Syntheses of 1−4 and Molecular Structures in the Solid State. The reaction of the triorganotin iodide $\{Me_2N$-$(CH_2)_3\}Ph_2SnI$[8] with triphenylstannylmethylmagnesium bromide, Ph_3SnCH_2MgBr,[9] in THF gave $\{Me_2N(CH_2)_3\}$-$Ph_2SnCH_2SnPh_3$, **1**, in moderate yield (Scheme 1).

The reactions of compound **1** with 1 or 2 molar equiv of elemental iodine in CH_2Cl_2 afforded the corresponding iodine-substituted compounds $\{Me_2N(CH_2)_3\}Ph(I)SnCH_2SnPh_3$, **2**, and $\{Me_2N(CH_2)_3\}Ph(I)SnCH_2SnPh_2I$, **3**, in good and quantitative yields, respectively (Scheme 1). The reaction of compound **3** with an excess of potassium fluoride (KF) in a mixture of CH_2Cl_2 and water provided the organotin fluoride $\{Me_2N(CH_2)_3\}Ph(F)SnCH_2SnPh_2F$, **4**, in moderate yield (Scheme 1).

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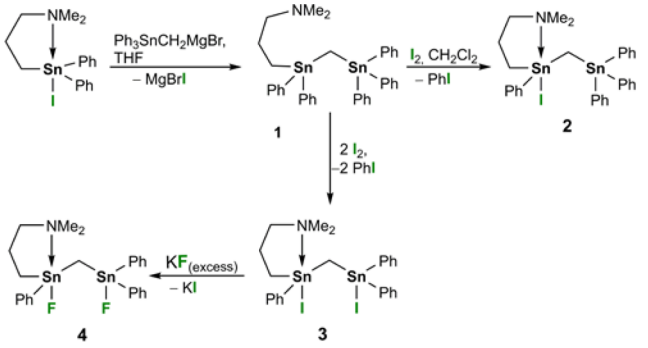
Scheme 1. Syntheses of the Organotin Compounds 1−4



Compounds **2** and **3** are light yellowish solids, whereas compound **4** is a white solid. They show good solubility in $CHCl_3$, CH_2Cl_2, and acetone.

Single crystals of compounds **2** and **3** suitable for X-ray diffraction analyses were each obtained by slow evaporation of the solvent from the corresponding solution in CH_2Cl_2/*n*-hexane at room temperature. Those for **4** were obtained by keeping a solution of the compound in acetone at −5 °C.

Compounds **2**, **3**, and **4** crystallize in the monoclinic space groups $P2_1/c$, $C2/c$, and $P2_1/n$, respectively. The molecular structures of **2**−**4** are presented in Figures 1−3, and selected interatomic distances and angles are listed in Table 1.

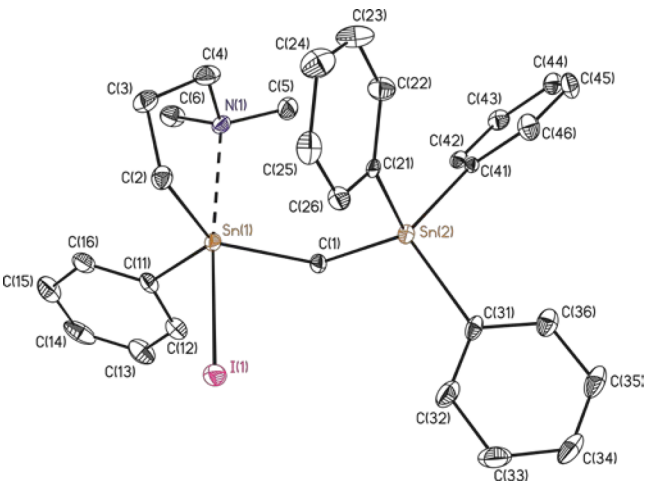


Figure 1. General view (SHELXTL) of a molecule of **2** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. There is a disorder of the phenyl ring C(41) to C(46) with iodine I(2) (I2 is not shown; see Experimental Section) with a ratio of 90:10. Hydrogen atoms are omitted for clarity.

The Sn(1) atoms in compounds **2** and **3** are each pentacoordinated and exhibit a distorted trigonal-bipyramidal environment (geometric goodness $\Delta\Sigma(\theta)$ = 83.1° for **2** and **3**) with C(1), C(2), and C(11) occupying the equatorial and N(1) and I(1) the axial positions. The Sn(1)−N(1) interatomic distances of 2.486(4) (**2**) and 2.433(3) Å (**3**) are shorter than the corresponding distance in compound $Me_2N(CH_2)_3SnPh_2I$ (**A**) of 2.541(5) Å[8] and longer than that in Me_2N-$(CH_2)_3SnMe_2I$ (**B**) of 2.38(1) Å.[10] The Sn(1)−I(1) distances of 2.9777(4) (**2**) and 2.9613(4) Å (**3**) are between the corresponding distances in compounds **A** and **B** of 2.888(0) and 3.0567(6) Å, respectively. The N(1)−Sn(1)−I(1) angles in **2** and **3** of 164.51(8)° and 169.76(9)°, respectively, are rather

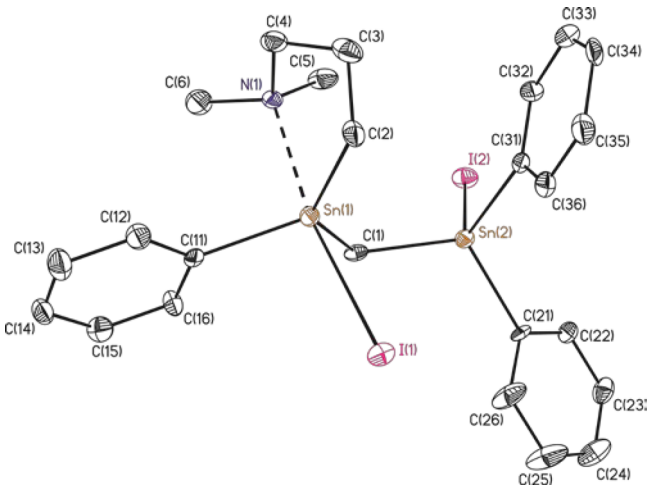


Figure 2. General view (SHELXTL) of a molecule of **3** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

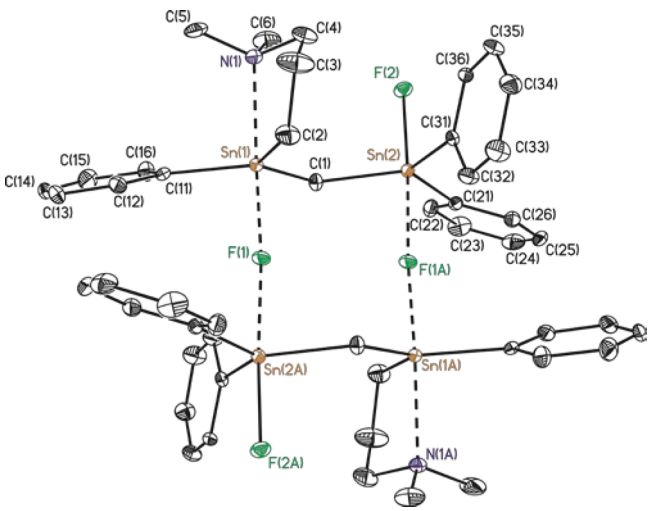


Figure 3. General view (SHELXTL) of a molecule of **4** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity.

close to the corresponding angles in **A** (167.9(1)°) and **B** (169.4(3)°).

The environments at Sn(2) in compounds **2** and **3** are distorted tetrahedral, with angles varying between 105.15(15)° (C(41)−Sn(2)−C(21)) and 114.07(16)° (C(21)−Sn(2)−C(31)) in **2** and between 103.77(9)° (C(31)−Sn(2)−I(2)) and 114.67(14)° (C(1)−Sn(2)−C(21)) in **3**. As expected, the Sn(2)−I(2) distance of 2.7050(5) Å in **3** is shorter than the Sn(1)−I(1) distances in **2** and **3**, as mentioned above.

Compound **4** forms a centrosymmetric head-to-tail dimer via unsymmetrical Sn(1)−F(1)−Sn(2A) bridges at distances of 2.1229(17) and 2.2291(17) Å. These distances are comparable with those reported for the organofluorido stannate complexes $NEt_4[CH_2(SnXPh_2)_2{\cdot}F]$ (X = F, Br, I) ranging between 2.204(2) and 2.274(5) Å.[6] Both tin atoms in **4** are pentacoordinated and exhibit distorted trigonal-bipyramidal geometries (geometric goodness $\Delta\Sigma(\theta)$ = 88.2° for Sn1 and 81.1° for Sn2) with the equatorial positions being occupied by three carbon atoms (C(1), C(2), and C(11) at Sn1, C(1), C(21), and C(31) at Sn2). The axial positions are occupied by

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Table 1. Selected Interatomic Distances (Å) and Angles (deg) in $\{Me_2N(CH_2)_3\}Ph(X1)SnCH_2SnPh_2(X2)$ (2–4)

	2, X1 = I(1), X2 = C(41)	3, X1 = I(1), X2 = I(2)	4, X1 = F(1), X2 = F(2)
Sn(1)–N(1)	2.486(4)	2.433(3)	2.400(3)
Sn(1)–X(1)	2.9777(4)	2.9613(4)	2.1229(17)
Sn(2)–X(1A)			2.2291(17)
Sn(2)–X(2)	2.161(2)	2.7050(5)	2.0300(18)
Sn(1)–C(1)–Sn(2)	119.7(2)	118.54(19)	118.32(15)
N(1)–Sn(1)–X(1)	164.51(8)	169.76(9)	168.99(9)
X(2)–Sn(2)–X(1A)			176.91(8)
Sn(1)–X(1)–Sn(2A)			172.05(10)
C(1)–Sn(1)–C(2)	132.60(17)	130.83(17)	121.87(15)
C(1)–Sn(1)–C(11)	109.20(17)	109.69(15)	116.38(13)
C(2)–Sn(1)–C(11)	117.89(17)	119.09(15)	121.71(15)
X(1)–Sn(1)–C(1)	88.56(13)	90.29(11)	91.09(11)
X(1)–Sn(1)–C(2)	89.76(13)	91.58(13)	89.43(11)
X(1)–Sn(1)–C(11)	98.26(12)	94.64(8)	91.28(10)
C(1)–Sn(2)–C(21)	111.77(15)	114.67(14)	114.54(13)
C(1)–Sn(2)–C(31)	110.96(16)	113.22(13)	124.24(12)
C(21)–Sn(2)–C(31)	114.07(16)	113.91(12)	120.55(13)
X(2)–Sn(2)–C(1)	109.13(15)	105.47(10)	91.60(11)
X(2)–Sn(2)–C(21)	105.15(15)	104.32(9)	94.13(10)
X(2)–Sn(2)–C(31)	105.29(16)	103.77(9)	92.51(10)

the N(1) and F(1) atoms at Sn1 and F(1A) and F(2) atoms at Sn2. The Sn(2)–F(2) distance of 2.0300(18) Å involving the terminal fluorine atom is close to the related distances in $NEt_4[CH_2(SnFPh_2)_2{\cdot}F]$ (2.004(2), 1.995(2) Å),[6] [2-$(Me_2NCH_2)C_6H_4]Me_2SnF$ (**C**, 2.0384(10) Å),[11] and [2-$(Me_2NCH_2)C_6H_4]Ph_2SnF$ (**D**, 2.0242(12) Å).[11] The Sn(1)–N(1) distance of 2.400(3) Å is considerably shorter than the sum of the van der Waals radii of Sn and N (3.75 Å)[12] and is shorter than the corresponding distances in compounds **C** (2.4899(14) Å)[11] and **D** (2.5294(18) Å).[11] The N(1)–Sn(1)–F(1) angle of 168.99(9)° is rather similar to the corresponding angles observed in compounds **C** and **D** of 167.37(5)°[11] and 166.82(6)°,[11] respectively. The angles F(1A)–Sn(2)–F(2) and Sn(1)–F(1)–Sn(2A) are 176.91(8)° and 172.05(10)°, respectively.

Structures of Compounds 1–4 in Solution. A ^{119}Sn NMR spectrum of compound **1** showed two equally intense resonances at δ −77 ppm (SnPh$_3$), being close to that reported for bis(triphenylstannyl)methane, $CH_2(SnPh_3)_2$, at δ −79 ppm,[13] and at δ −49 ppm ($Sn\{(CH_2)_3NMe_2\}Ph_2$), respectively. A ^{1}H NMR spectrum of compound **1** showed a singlet resonance with unresolved $^{117/119}$Sn satellites at δ 1.02 ppm ($^2J(^1H–^{117/119}Sn)$ = 60.7 Hz) assigned to the $SnCH_2Sn$ protons. This chemical shift is close to that reported for the corresponding protons in $CH_2(SnPh_3)_2$ at δ 0.96 ppm ($^2J(^1H–^{117/119}Sn)$ = 63.7 Hz).[13] In the ^{13}C NMR spectrum a chemical shift at δ −17.3 ppm ($^1J(^{13}C–^{117/119}Sn)$ = 252/262, 284/296 Hz) assigned to the $SnCH_2Sn$ carbon atom was observed. This chemical shift is close to that reported for the corresponding carbon atom in $CH_2(SnPh_3)_2$ at δ −16.2 ppm ($^1J(^{119}Sn–^{13}C)$ = 294 Hz).[13] The chemical shift of $SnCH_2CH_2$ in **1** at δ 9.0 ppm ($^1J(^{13}C–^{117/119}Sn)$ = 373/391 Hz) is close to that reported for the corresponding carbon atom in $Me_2N(CH_2)_3SnPh_3$ at δ 8.3 ppm ($^1J(^{13}C–^{117/119}Sn)$ = 399 Hz).[8] All these data are in agreement with the tin atoms in compound **1** being four-coordinated.

A ^{119}Sn NMR spectrum of **2** showed two equally intense resonances (total integral 90) at δ −86 ppm (SnPh$_3$) and δ −92 ppm ($Sn\{(CH_2)_3NMe_2\}PhI$). In addition to that, two equally intense resonances at δ −54 ppm and δ −102 ppm (integral 10) were observed. The two latter resonances are related to $SnIPh_2$ and $Sn\{(CH_2)_3NMe_2\}PhI$, respectively, in **3** (see Sn2 and Sn1 in Figure 2). The assignments are supported by comparison with the chemical shifts reported for $(Ph_3Sn)_2CH_2$ (δ −79 ppm) and $(IPh_2Sn)_2CH_2$ (δ −68 ppm), respectively.[13] Furthermore, the ^{13}C NMR chemical shifts of the $SnCH_2CH_2$ carbon atoms in the organotin iodides **2** and **3** at δ 19.1 and 18.7 ppm, respectively, are close to those reported for the corresponding carbon atoms in $Me_2N(CH_2)_3SnPh_2I$ (δ 18.5 ppm).[8] These data reveal the SnPh$_3$ and $SnIPh_2$ tin atoms in **2** and **3** to be four- and the $Sn\{(CH_2)_3NMe_2\}PhI$ tin atoms in both compounds to be five-coordinated. This view is further supported by comparison of the ^{119}Sn NMR chemical shifts of $Sn\{(CH_2)_3NMe_2\}PhI$ in the organotin iodides **2** (δ −92 ppm) and **3** (δ −102 ppm) with those for Me_2PhSnI (δ −18 ppm)[14] and {2-$(Me_2NCH_2)C_6H_4$}Me_2SnI (δ −73 ppm),[15] containing four- and five-coordinated tin atoms, respectively.

ESI mass spectra (positive mode) of the organotin iodides **2** and **3** showed mass clusters centered at m/z 646.1 and 696.0, respectively, which correspond to $[M - I]^+$.

A ^{119}Sn NMR spectrum of a solution of compound **4** in $CDCl_3$ at −35 °C reveals doublet of doublet resonances at δ −18 [$^1J(^{119}Sn–^{19}F)$ = 1168, $^3J(^{119}Sn–^{19}F)$ = 120 Hz, SnPhF] and δ −159 ppm [$^1J(^{119}Sn–^{19}F)$ = 2201, $J(^{119}Sn–^{19}F)$ = 560 Hz, SnPh$_2$F]. The chemical shift at −18 ppm is close to that reported for the pentacoordinated tin atom Sn^1 in $Ph_2FSnCH_2Sn^1FPh$-[19]-crown-6 at δ −17 ppm.[16] Noteworthy, the chemical shift of Sn^2 at −159 ppm and the coupling constants of 560 and 2201 Hz in **4** are close to the corresponding values of δ −159 ppm [$^1J(^{119}Sn–^{19}F^a)$ = 2216, $^1J(^{119}Sn–^{19}F^b)$ = 582, $^3J(^{119}Sn–^{19}F^b)$ = 116 Hz] reported for Sn^2 in the organofluorido stannate $NBu_4[(Ph_2F^aSn^2CH_2)_2$-$SnF^bPh{\cdot}F^b]$.[17] F^a and F^b are terminal and bridging fluorine atoms, respectively.

A ^{19}F NMR spectrum at ambient temperature of the same sample showed two equally intense resonances at δ −96 [$^1J(^{19}F–^{117/119}Sn)$ = 451, 1249 Hz, unresolved; satellite-to-satellite-to-signal-to-satellite-to-satellite ratio approximately 6:9:70:9:6] and −188 ppm [$^1J(^{19}F–^{117/119}Sn)$ = 2187 Hz, unresolved; satellite-to-signal-to-satellite ratio approximately 8:84:8]. These two chemical shifts are close to those reported for $NBu_4[(Ph_2F^aSnCH_2)_2SnF^bPh{\cdot}F^b]$ at δ −101 [$^1J(^{19}F–^{117/119}Sn)$ = 1174/1224, $^1J(^{19}F–^{117/119}Sn)$ = 573 Hz] and −182 ppm [$^1J(^{19}F–^{117/119}Sn)$ = 2163 Hz]. From a ^{1}H DOSY experiment a hydrodynamic radius of 5.4–5.7 Å was calculated, which in turn indicates compound **4** being monomeric in solution. Notably, an ESI mass spectrum (positive mode) revealed, in addition to the major mass cluster centered at m/z 588.1 that is assigned to $[M - F]^+$, a rather low-intense mass cluster centered at m/z 1191.0, which fits to $[2M - 3F + 2OH]^+$. At least, this supports the idea that the formation of dimers in solution might be possible.

From variable-temperature ^{1}H NMR spectroscopy showing for both compounds **3** and **4** two equally intense resonances for the NCH_3 protons at T = −80 °C (**3**: 1.84, 2.34 ppm; **4**: 1.88, 2.24 ppm) but only one resonance at room temperature (**3**: 2.08 ppm; **4**: 1.96 ppm) it is concluded that the intramolecular N→Sn coordination is kinetically labile on the NMR time scale at room temperature but inert at T = −80 °C.

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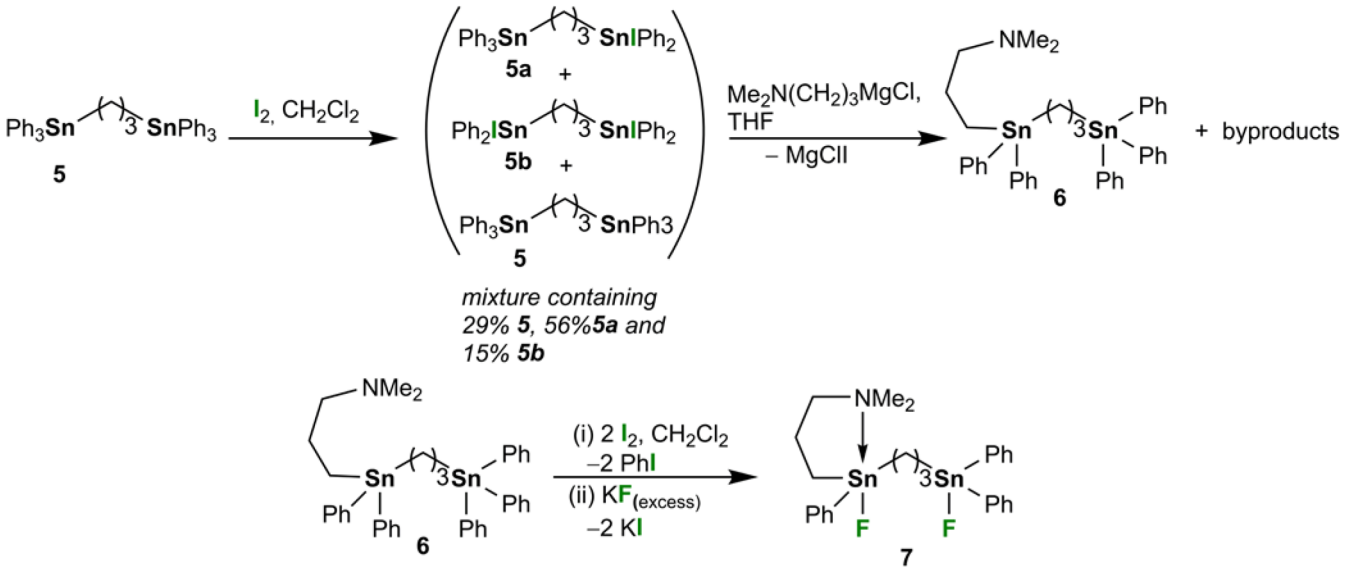
Scheme 2. Syntheses of the Trimethylene-Bridged Ditin Compounds 6 and 7



Synthesis of the Trimethylene-Bridged Ditin Compounds $\{Me_2N(CH_2)_3\}Ph(X)Sn(CH_2)_3Sn(X)Ph_2$ (X = Ph, F). In order to evaluate the effect of spacing between the tin centers on the molecular structure, the trimethylene-bridged ditin compounds $\{Me_2N(CH_2)_3\}Ph(X)Sn(CH_2)_3Sn(X)Ph_2$ (X = Ph, F) were synthesized according to Scheme 2.

The reaction of 1,3-bis(triphenylstannyl)propane, $(Ph_3SnCH_2)_2CH_2$ (**5**),[18] with 0.85 molar equiv of elemental iodine gave a crude reaction mixture, the ^{119}Sn NMR spectrum of which indicated this mixture to contain 29% **5** (δ −103.8 ppm), 56% $Ph_2ISn(CH_2)_3SnPh_3$ (**5a**, δ −59.6, −104.0 ppm), and 15% $(IPh_2SnCH_2)_2CH_2$ (**5b**, δ −60.9 ppm).

As attempts failed at isolating compound **5a** by both column chromatography and crystallization, the crude reaction mixture as mentioned above was used for subsequent reaction with an excess of $Me_2N(CH_2)_3MgCl$, providing, after purification by column chromatography, the corresponding $Me_2N(CH_2)_3$-substituted organotin compound $\{Me_2N(CH_2)_3\}Ph_2Sn(CH_2)_3SnPh_3$, **6**, as a light yellowish oil in moderate yield (Scheme 2). It shows good solubility in common organic solvents such as CH_2Cl_2, $CHCl_3$, THF, and diethyl ether. Its identity was, in addition to elemental analyses, ^{1}H and ^{13}C NMR spectroscopy, and ESI mass spectrometry (see Experimental Section), established by ^{119}Sn NMR spectroscopy, showing two equally intense resonances at δ −75 ($^4J(^{119}Sn-^{117}Sn)$ = 48 Hz, $SnPh_2(CH_2)_3NMe_2$) and δ −104 ppm ($^4J(^{119}Sn-^{117}Sn)$ = 48 Hz, $SnPh_3$), respectively. These chemical shifts indicate both tin atoms to be tetracoordinate, as the one for $SnPh_3$ is close to the chemical shift reported for $(Ph_3SnCH_2)_2CH_2$ (δ −103 ppm).[18] On the other hand, replacing one phenyl group with the 3-(dimethylamino)propyl substituent in compound **6** causes a lower field shift of about 28 ppm.

An ESI-MS spectrum (positive mode) of the tetraorganotin compound **6** showed two mass clusters centered at m/z 674.1 and 752.2, which correspond to $[M - Ph]^+$ and $[M + H]^+$, respectively.

The reaction of compound **6** with 2 molar equiv of elemental iodine provided a crude reaction mixture, a ^{119}Sn NMR spectrum of which showed two resonances of equal integral at δ −91 ppm ($\nu_{1/2}$ 41 Hz) and δ −54 ppm ($\nu_{1/2}$ 96 Hz), respectively, that are assigned to the tin atoms Sn^1 and Sn^2 in the corresponding iodine-substituted compound $\{Me_2N(CH_2)_3\}Ph(I)Sn^1(CH_2)_3Sn^2(I)Ph_2$. The Sn^1 atom is five-coordinate by intramolecular N→Sn coordination, as its ^{119}Sn chemical shift is close to the δ −102 ppm measured for the pentacoordinated tin atom Sn^1 in compound **3**. The Sn^2 atom is four-coordinate, as its ^{119}Sn chemical shift is close to that reported for $(Ph_2ISnCH_2)_2$ (δ −54 ppm).[19] The compound $\{Me_2N(CH_2)_3\}Ph(I)Sn(CH_2)_3Sn(I)Ph_2$ was not isolated, but reacted with an excess of potassium fluoride, KF, in CH_2Cl_2/water, providing the triorganotin fluoride derivative $\{Me_2N(CH_2)_3\}Ph(F)Sn(CH_2)_3Sn(F)Ph_2$, **7**, as a white solid material in moderate yield (Scheme 2). It shows good solubility in $CHCl_3$ and CH_2Cl_2 and moderate solubility in ethyl acetate. Single crystals of **7** suitable for X-ray diffraction analysis were obtained by recrystallization from its solution in ethyl acetate at 4 °C.

Molecular Structure in the Solid State of Compound 7. The molecular structure of **7** is presented in Figure 4, and selected interatomic distances and angles are listed in the figure caption.

Compound **7** is a monomer in the solid state with F1→Sn2 intramolecular coordination giving a six-membered ring of half-chair conformation (Figure 5).[20]

Both Sn(1) and Sn(2) tin atoms are pentacoordinated and exhibit distorted trigonal bipyramidal geometries (geometric goodness $\Delta\Sigma(\theta)$ = 85.1° for Sn1 and 79.4° for Sn2) with the equatorial positions being occupied by three carbon atoms [C(3), C(4), C(11) at Sn(1) and C(1), C(21), and C(31) at Sn(2)]. The axial positions are occupied by the N(1) and F(1) atoms (at Sn(1)) and by the F(1) and F(2) atoms (at Sn(2)).

The Sn(1)−N(1) distance of 2.407(3) Å is similar to 2.400(3) Å found for the corresponding distance in the methylene-bridged ditin compound **4**. It is longer than the sum of the covalent radii of Sn and N (2.15 Å),[21] but is considerably shorter than the sum of the van der Waals radii (3.75 Å).[12] The Sn(1)−F(1), Sn(2)−F(1), and Sn(2)−F(2) distances of 2.1266(19), 2.240(2), and 2.027(2) Å, respectively, are close to 2.1229(17), 2.2291(17), and 2.0300(18) Å found for the corresponding distances in **4**. Also rather similar to compound **4** (see Table 1) are the interatomic angles N(1)−Sn(1)−(F1) (169.46(11)°) and F(1)−Sn(2)−F(2) (177.27(9)°).

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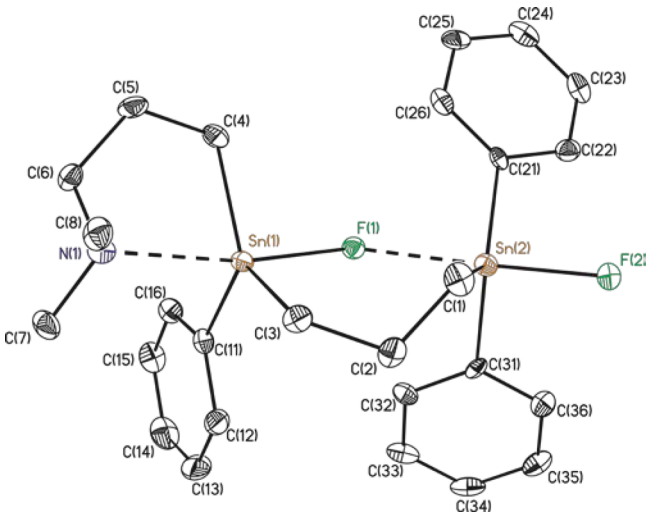


Figure 4. General view (SHELXTL) of a molecule of **7** showing 30% probability displacement ellipsoids and the crystallographic numbering scheme. Hydrogen atoms are omitted for clarity. Selected interatomic distances (Å): Sn(1)−N(1) 2.407(3), Sn(1)−F(1) 2.1266(19), Sn(2)−F(1) 2.240(2), Sn(2)−F(2) 2.027(2). Selected interatomic angles (deg): Sn(1)−F(1)−Sn(2) 137.68(10), F(1)−Sn(1)−N(1) 169.46(11), F(1)−Sn(2)−F(2) 177.27(9), C(3)−Sn(1)−C(4) 128.24(16), C(3)−Sn(1)−C(11) 115.94(15), C(4)−Sn(1)−C(11) 115.58(15), C(3)−Sn(1)−F(1) 94.26(12), C(4)−Sn(1)−F(1) 89.91(12), C(11)−Sn(1)−F(1) 90.52(9), C(1)−Sn(2)−C(21) 127.11(14), C(1)−Sn(2)−C(31) 116.14(14), C(21)−Sn(2)−C(31) 115.81(9), C(1)−Sn(2)−F(2) 294.24(13), C(21)−Sn(2)−F(2) 91.90(10), C(31)−Sn(2)−F(2) 93.52(11).

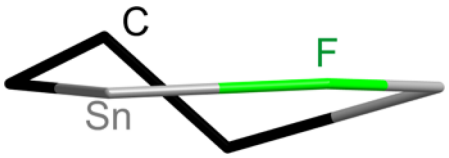


Figure 5. Conformation of the six-membered SnC_3SnF ring in compound **7**. All atoms bound to the six-membered ring are omitted for clarity.

Structure of the Compound 7 in Solution. A ^{119}Sn NMR spectrum at room temperature in $CDCl_3$ of compound **7** reveals a doublet resonance at δ −48 [$^1J(^{119}\text{Sn}-^{19}\text{F})$ = 1680 Hz, *Sn*PhF] and a doublet of doublet resonance at δ −191 ppm [$^1J(^{119}\text{Sn}-^{19}\text{F})$ = 2030, 960 Hz, *Sn*Ph_2F]. In addition to these resonances with a total integral of 98, one signal at δ −71 ppm (integral 2) was observed, which, however, was not assigned.

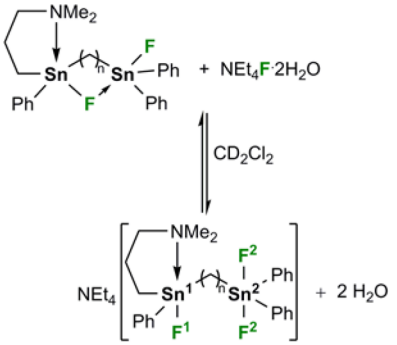
A ^{19}F NMR spectrum of the same sample at room temperature showed two broad resonances of 1:1 integral ratio at δ −145 [$\nu_{1/2}$ 183 Hz, $^1J(^{19}\text{F}-^{117/119}\text{Sn})$ = 1688, 927 Hz, F^1] and δ −177 ppm [$\nu_{1/2}$ 387 Hz, $^1J(^{19}\text{F}-^{117/119}\text{Sn})$ = 2097 Hz, F^2], respectively, with the satellites being unresolved. These two chemical shifts are close to δ −140 [$^1J(^{119}\text{Sn}-^{19}\text{F})$ = 1250 Hz] and δ −169 ppm [$^1J(^{119}\text{Sn}-^{19}\text{F})$ = 2042 Hz] reported for $\{Ph_2(Cl)Sn(CH_2)_3Sn(F)Ph_2{\cdot}F\}^-$ [6] and to δ −139 [$^1J(^{119}\text{Sn}-^{19}\text{F}^b)$ = 1264 Hz] and −165 ppm [$^1J(^{119}\text{Sn}-^{19}\text{F})$ = 2030 Hz] reported for $\{Ph_2(F)Sn(CH_2)_3Sn(F)Ph_2{\cdot}F\}^-$.[6]

An ESI mass spectrum (positive mode) of the organotin fluoride **7** showed a mass cluster at *m*/*z* 632.2 that is assigned to $[M - 2F + 2OH + H]^+$. There is no mass cluster containing four tin atoms, which supports that compound **7** is monomeric in solution.

Complexation Behavior of 4 and 7 toward Fluoride Anion. The reaction of compounds **4** and **7** with fluoride anion (as $NEt_4F{\cdot}2H_2O$) in CD_2Cl_2 solution was investigated.

A ^{119}Sn NMR spectrum at −65 °C of a solution of compound **4** to which had been added 1 molar equiv of $NEt_4F{\cdot}2H_2O$ showed a doublet resonance at δ −60 ppm [$^1J(^{119}\text{Sn}-^{19}\text{F})$ = 1899 Hz] and a triplet resonance at δ −252 ppm [$^1J(^{119}\text{Sn}-^{19}\text{F})$ = 1907 Hz], which are assigned to Sn^1 and Sn^2, respectively (Scheme 3). The latter signal is close to the triplet resonance at δ −244 ppm [$^1J(^{119}\text{Sn}-^{19}\text{F})$ = 1840 Hz] measured at −100 °C for the anion $[(F_2Ph_2Sn)_2CH_2]^{2-}$.[6]

Scheme 3. Reaction of $\{Me_2N(CH_2)_3\}Ph(F)Sn(CH_2)_nSn(F)Ph_2$ with $NEt_4F{\cdot}2H_2O$



NEt_4[**4**·F], n = 1; NEt_4[**7**·F], n = 3

A ^{19}F NMR spectrum of the same sample at −60 °C showed two resonances with a 2:1 ratio (total integral 45) at δ −140 ppm [$^1J(^{19}\text{F}-^{117/119}\text{Sn}^2)$ = 1833/1895 Hz, F^2] and δ −141 ppm [$^1J(^{19}\text{F}-^{117/119}\text{Sn}^1)$ = 1854 Hz, F^1], respectively. These chemical shifts are close to δ −142 ppm [$^1J(^{19}\text{F}-^{119}\text{Sn}^1)$ = 1840 Hz] reported for $[(F_2Ph_2Sn)_2CH_2]^{2-}$ at −100 °C.[6] In addition to these two resonances, four broad signals were observed at δ −93 (integral 12), δ −163 (integral 16), δ −167 (integral 19), and δ −181 ppm (integral 8). These signals were not assigned. With caution, these signals might originate from products formed by hydrolysis reactions. The latter are facilitated by the presence in compound **4** of the dimethylaminopropyl moiety acting as a base. This view gets support from an ESI-mass spectrum (negative mode) revealing a major mass cluster centered at *m*/*z* 719.1 that fits with [**4** + OH + MeCN + $3H_2O$]$^-$.

A ^{119}Sn NMR spectrum at −80 °C of a solution of compound **7** to which had been added 1 molar equiv of $NEt_4F{\cdot}2H_2O$ showed a doublet resonance at δ −47 (d, $^1J(^{119}\text{Sn}-^{19}\text{F})$ = 1566 Hz, integral 30, *Sn*PhF, **7**) and a doublet of doublet resonance at δ −203 ppm ($^1J(^{119}\text{Sn}-^{19}\text{F})$ = 2067, 941 Hz, integral 32, *Sn*FPh_2, **7**). In addition there are minor intense resonances at δ −86 (d, $^1J(^{119}\text{Sn}-^{19}\text{F})$ = 1957 Hz, integral 12, Sn^1, NEt_4[**7**·F]), δ −88 (d, $^1J(^{119}\text{Sn}-^{19}\text{F})$ = 1973 Hz), integral 13, not assigned), δ −222 (3%), δ −226 (integral 4, not assigned), δ −235 (integral 2, not assigned), and δ −270 ppm (Sn^2, NEt_4[**7**·F]). A ^{19}F NMR spectrum at −80 °C of the same sample showed two doublet resonances at δ −143 ($^1J(^{19}\text{F}-^{117/119}\text{Sn})$ = 1124, 1498/1564 Hz), $^2J(^{19}\text{F}-^{19}\text{F})$ = 83 Hz, integral 31, Sn*F*Ph, **7**) and δ −174 ppm ($^1J(^{19}\text{F}-^{117/119}\text{Sn})$ = 1976/2070 Hz), $^2J(^{19}\text{F}-^{19}\text{F})$ = 83 Hz, integral 29, Sn*F*Ph_2, **7**). In addition there are minor intense resonances at δ −154 (integral 14, F^2, NEt_4[**7**·F]), δ −158 (integral 7, F^1, NEt_4[**7**·F]), δ −159 (integral 8, not

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assigned), δ −162 (integral 2, not assigned), and δ −169 ppm (integral 9, not assigned).

A ^{119}Sn NMR spectrum at −80 °C of a solution of compound **7** to which had been added 2 molar equiv of $NEt_4F\cdot 2H_2O$ showed a doublet resonance at δ −86 ($^1J(^{119}Sn-^{19}F)$ = 1957 Hz, integral 40, Sn^1, NEt_4[**7**·F]) and a triplet at δ −271 ppm ($^1J(^{119}Sn-^{19}F)$ = 1888 Hz, integral 40, Sn^2, NEt_4[**7**·F]). In addition there are minor intense resonances at δ −47 (d, $^1J(^{119}Sn-^{19}F)$ = 1563 Hz, integral 5, *Sn*PhF, **7**), δ −88 (d, $^1J(^{119}Sn-^{19}F)$ = 1973 Hz, integral 7, not assigned), and δ −203 ppm (dd, $^1J(^{119}Sn-^{19}F)$ = 2067, 941 Hz, integral 7, *Sn*FPh_2, **7**).

A ^{19}F NMR spectrum at −80 °C of the same sample showed two resonances with a 2:1 ratio (total integral 69) at δ −154 (integral 46, F^2, NEt_4[**7**·F]) and δ −158 ppm (integral 23, F^1, [NEt_4][**7**·F]). In addition there are minor intense resonances at δ −143 (d, integral 5, Sn*F*Ph, **7**), δ −151 (integral 5, not assigned), δ −156 (integral 6, not assigned), δ −160 (integral 6, not assigned), δ −169 (integral 5, not assigned), and δ −174 ppm (d, integral 5, Sn*F*Ph_2, **7**). No resonances were observed in the ^{119}Sn NMR spectra at ambient temperature.

The ^{119}Sn and ^{19}F NMR data are consistent with the equilibrium shown in Scheme 3. It is fast on the ^{19}F and ^{119}Sn NMR time scales at room temperature but slow at low temperature. For the methylene-bridged compound **4** (n = 1) this equilibrium is on the side of the organostannate complex NEt_4[**4**·F] by addition of 1 molar equiv of fluoride anion only, while 2 molar equiv of fluoride anion is needed to cause formation of NEt_4[**7**·F]. The results indicate the six-membered ring involving the intramolecular Sn−F→Sn coordination in **7** to be more stable against fluoride anion attack than the four-membered ring in **4**.

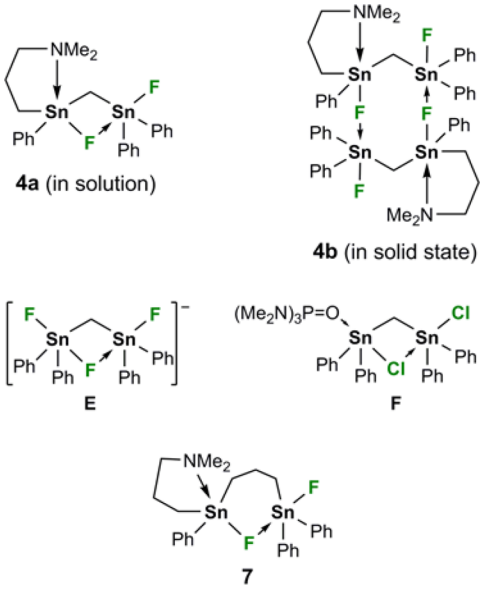
CONCLUSION

A series of unsymmetrically substituted methylene- and trimethylene-bridged organoditin compounds containing the [3-(dimethylamino)propyl] moiety was synthesized and characterized. They show N→Sn *intramolecular* interactions both in solution and in the solid state. For the organotin fluorides **4** and **7**, this interaction results in a much better solubility in common organic solvents with respect to the corresponding compounds $Ph_2FSn(CH_2)_nSnPh_2F$ (n = 1, 3), lacking an *intramolecularly* coordinating substituent. Notably, the latter compounds do not get solubilized by addition of triethyl amine, NEt_3, or even HMPA, $(Me_2N)_3PO$.[6] Compound **4** is monomeric in solution and shows an intramolecular F→Sn coordination that is kinetically inert at low temperature on the ^{19}F and ^{119}Sn NMR time scales (see **4a** in Chart 2). Upon crystallization, it dimerizes as a result of *intermolecular* F→Sn coordination (see **4b** in Chart 2). The organostannate anion **E**, however, in which the *intramolecularly* coordinating dimethylaminopropyl moiety in **4** is formally replaced by a phenyl substituent and a fluoride anion, does not dimerize in the solid state and shows an *intramolecular* Sn−F−Sn bridge.[6a]

In the chlorine-substituted compound **F** even the neutral Lewis base $(Me_2N)_3PO$ causes an *intramolecular* Sn−Cl−Sn bridge, but no dimerization.[6b]

Upon addition to compound **4** of fluoride anion, as $NEt_4F\cdot 2H_2O$, in CD_2Cl_2 solution, the salt NEt_4[**4**·F] containing an organostannate anion is formed. The same holds for compound **7**, giving the salt NEt_4[**7**·F]. On the basis of NMR data, the intramolecular N→Sn coordination is retained and the incoming fluoride anion does not bridge the two tin centers but is bound to the diphenyl-substituted tin atom only. In contrast to compound **4**, the trimethylene-bridged ditin compound **7** is monomeric both in solution and in the solid state stabilized by intramolecular N→Sn and F→Sn coordination. The structural difference between **4** and **7** is likely the higher ring strain in a four-membered compared to a six-membered ring.

Chart 2. Methylene- and Trimethylene-Bridged Ditin Compounds Showing Either *Inter*- or *Intra*molecular Sn−X−Sn Bridges (X = Cl, F) in the Solid State and in Solution



EXPERIMENTAL SECTION

General Considerations. All solvents were dried and purified according to standard procedures and freshly distilled prior to use. $Me_2N(CH_2)_3Cl$,[8] $\{Me_2N(CH_2)_3\}(Ph_2)SnI$,[8] Ph_3SnCH_2Br,[9] $(Ph_3Sn)_2CH_2$,[13] and $(Ph_3SnCH_2)_2CH_2$[18] were synthesized according to literature methods. $\{Me_2N(CH_2)_3Cl\}\cdot HCl$ and tetraethylammonium fluoride were commercially available, and they were used without further purification. Bruker DPX-300, DRX-400, and AVIII-500 spectrometers were used to obtain ^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR spectra. Solution ^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR chemical shifts are given in ppm and were referenced to Me_4Si (^{1}H, ^{13}C), $CFCl_3$ (^{19}F), and Me_4Sn (^{119}Sn). Elemental analyses were performed on a LECO-CHNS-932 analyzer. The electrospray mass spectra were recorded with a Thermoquest−Finnigan instrument, using CH_3CN, MeOH, or CH_2Cl_2 as the mobile phase.

The DOSY (diffusion-ordered spectroscopy) measurement was performed with a pulse sequence using double stimulated echo for convection compensation and LED and bipolar gradient pulses for diffusion (A. Jerschow and N. Mueller, *J. Magn. Reson. A* **1996**, *123*, 222−225; A. Jerschow and N. Mueller, *J. Magn. Reson. A* **1997**, *125*, 372−375). The measurements were executed with an AVANCE-III HD 600 MHz NMR spectrometer equipped with a 5 mm helium-cooled BBFO probe from Bruker BioSpin GmbH (Rheinstetten, Germany). Thirty-two different gradient strengths varying between 3% and 95% of the maximum strength of 53 G/cm were used. Thirty-two scans per gradient strength were acquired with 16 kB data points of the FID (acquisition time of 0.97 s) and a relaxation delay of 1.5 s. According to the DOSY figure, the expansion indicates two components with diffusion coefficients of 7.09 × 10^{-10} and 7.45 × 10^{-10} m^2/s. With the Stokes−Einstein equation, a hydrodynamic radius of about 0.57−0.54 nm can be calculated.

Crystallography. Intensity data for all crystals were collected on an XcaliburS CCD diffractometer (Oxford Diffraction) using Mo Kα

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radiation at 110 K. The structures were solved with direct methods using SHELXS-97, and refinements were carried out against F^2 by using SHELXL-2014.[22] The C−H hydrogen atoms were positioned with idealized geometry and refined using a riding model. All non-hydrogen atoms were refined using anisotropic displacement parameters. Parts of compound **2** are affected by substitutional disorder: the same site is occupied by the phenyl group C(41)−C(46) in 90% of unit cells and by iodide I(2) in 10% of unit cells. This disorder was refined by a split model over two positions; their occupancies were allowed to refine freely to yield 0.89527:0.10473 and then restrained to integer values 0.9:0.1.

CCDC-1484757 (**2**), CCDC-1484758 (**3**), CCDC-1484759 (**4**), and CCDC-1484760 (**7**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of $\{Me_2N(CH_2)_3\}Ph_2SnCH_2SnPh_3$ (1). A solution of Ph_3SnCH_2MgBr, prepared from Ph_3SnCH_2Br (2.000 g, 4.51 mmol) and magnesium (0.110 g, 4.51 mmol) in THF (50 mL), was added dropwise to a stirred solution of $Me_2N(CH_2)_3Ph_2SnI$ (1.970 g, 4.05 mmol) in THF (60 mL) for a period of 1 h. After the addition had been completed, the reaction mixture was heated at reflux overnight and then cooled to room temperature. THF was distilled off under reduced pressure; then cold water (60 mL) was added, and the mixture was extracted three times with 50 mL of dichloromethane. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated under vacuum to give the crude product. It was purified by column chromatography (SiO_2, *n*-hexane/ethyl acetate, 5:1, ethanol) to give 1.240 g (38%) of **1** as a yellow oil.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.02 (s, $^2J(^1H-^{117/119}Sn)$ = 60.7 Hz, 2H, $SnCH_2Sn$), 1.24 (t, 2H, $Sn-CH_2$), 1.84 (m, 2H, $SnCH_2CH_2$), 2.26 (s, 6H, $N(CH_3)_2$), 2.30 (t, 2H, CH_2N), 7.39−7.69 (25H, Ph). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ −17.3 ($^1J(^{13}C-^{117/119}Sn)$ = 252/262, 284/296 Hz, $SnCH_2Sn$), 9.0 ($^1J(^{13}C-^{117/119}Sn)$ = 373/391 Hz, $SnCH_2$), 24.1 ($^2J(^{13}C-^{117/119}Sn)$ = 19 Hz, $SnCH_2CH_2$), 45.2 $N(CH_3)_2$, 63.0 ($^3J(^{13}C-^{117/119}Sn)$ = 70 Hz, CH_2N), 128.1 ($^3J(^{13}C-^{117/119}Sn)$ = 47 Hz, $SnPh_2$, C_m), 128.2 ($^3J(^{13}C-^{117/119}Sn)$ = 50 Hz, $SnPh_3$, C_m), 128.4 ($SnPh_2$, C_p), 128.7 ($^4J(^{13}C-^{117/119}Sn)$ = 12 Hz, $SnPh_3$, C_p), 136.4 ($^2J(^{13}C-^{117/119}Sn)$ = 36 Hz, $SnPh_2$, C_o), 136.7 ($^2J(^{13}C-^{117/119}Sn)$ = 38 Hz, $SnPh_3$, C_o), 139.3 ($^1J(^{13}C-^{117/119}Sn)$ = 488/510 Hz, $^3J(^{13}C-^{117/119}Sn)$ = 9 Hz, $SnPh_3$, C_i), 140.4 ($^1J(^{13}C-^{117/119}Sn)$ = 448/468 Hz, $^3J(^{13}C-^{117/119}Sn)$ = 13 Hz, $SnPh_2$, C_i). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −49 ($^2J(^{119}Sn-^{117/119}Sn)$ = 236 Hz, *Sn*Ph_2), −77 ($^2J(^{119}Sn-^{117/119}Sn)$ = 232 Hz, *Sn*Ph_3). Anal. Calcd (%) for $C_{36}H_{39}NSn_2$ (723.09): C 59.79, H 5.44, N 1.94. Found: C 60.0, H 5.6, N 1.6.

Synthesis of $\{Me_2N(CH_2)_3\}PhISnCH_2SnPh_3$ (2). Elemental iodine (0.035 g, 0.41 mmol) was added in small portions and under ice cooling to a stirred solution of **1** (0.100 g, 0.41 mmol) in CH_2Cl_2 (20 mL). Stirring was continued while warming to room temperature overnight. The solvent and the iodobenzene were removed in vacuo to afford 0.086 g (80%) of **2** as a slightly yellow solid. Single crystals of **2** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in CH_2Cl_2/*n*-hexane.

^{1}H NMR (499.79 MHz, $CDCl_3$): δ 0.59 (s, 2H, $SnCH_2Sn$), 1.27−1.65 (complex pattern, 4H, $SnCH_2$ + $SnCH_2CH_2$), 1.92 (s, 6H, $N(CH_3)_2$), 2.16 (t, 2H, CH_2N), 7.34−7.88 (20H, Ph). $^{13}C\{^1H\}$ NMR (125.68 MHz, $CDCl_3$): δ −5.2 ($^1J(^{13}C-^{117/119}Sn)$ = 281/295 Hz, $SnCH_2Sn$), 19.1 ($SnCH_2$), 21.9 ($^2J(^{13}C-^{117/119}Sn)$ = 35 Hz, $SnCH_2CH_2$), 46.3 ($N(CH_3)_2$), 61.1 ($^3J(^{13}C-^{117/119}Sn)$ = 61 Hz, CH_2N), 128.4 ($^3J(^{13}C-^{117/119}Sn)$ = 51 Hz, SnIPh + $SnPh_3$, C_m), 128.8 (SnIPh, C_p), 128.9 (^4J ($^{13}C-^{117/119}Sn$) = 11 Hz, $SnPh_3$, C_p), 134.1($^2J(^{13}C-^{117/119}Sn)$ = 45 Hz, SnIPh, C_o), 137.1 ($^2J(^{13}C-^{117/119}Sn)$ = 38 Hz, $SnPh_3$, C_o), 139.1 ($^1J(^{13}C-^{117/119}Sn)$ = 497/520, $SnPh_3$, C_i), 144.5 (SnIPh, C_i). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −54 (5%), −86 (*Sn*Ph_3), −92 (*Sn*IPh), −102 (5%). Electrospray MS: *m*/*z* (%) positive mode, 646.1 (100, $[M - I]^+$), 614.1 (40, $[M - I - 2Ph + 2OH + MeOH + 3H_2O]^+$), (1, $[M + H]^+$); negative mode, 127.0 (100, I^-), 380.8 (17, I_3^-).

Synthesis of $[\{Me_2N(CH_2)_3\}PhISnCH_2SnIPh_2]$ (3). Iodine (0.912 g, 3.60 mmol) was added in small portions and under ice cooling to a stirred solution of **1** (1.300 g, 1.80 mmol) in CH_2Cl_2 (70 mL). Stirring was continued while warming to room temperature overnight. The solvent and the iodobenzene were removed in vacuo to afford 1.410 g (95%) of **3** as a slightly yellow solid (mp 163−165). Single crystals of **3** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in CH_2Cl_2/*n*-hexane.

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.30−1.73 (m, 4H, $SnCH_2Sn$ + $SnCH_2$), 2.09 (8H, $N(CH_3)_2$ + $SnCH_2CH_2$), 2.36 (t, 2H, CH_2N), 7.36−7.99 (15H, Ph). $^{13}C\{^1H\}$ NMR (100.63 MHz, $CDCl_3$): δ 7.1 ($SnCH_2Sn$), 18.7 ($SnCH_2$), 21.7 ($^2J(^{13}C-^{117/119}Sn)$ = 33 Hz, $SnCH_2CH_2$), 46.3 ($N(CH_3)_2$), 61.1 (CH_2-N), 128.5 ($^3J(^{13}C-^{117/119}Sn)$ = 65 Hz, $SnIPh_2$, C_m), 128.6 ($^3J(^{13}C-^{117/119}Sn)$ = 60 Hz, SnIPh, C_m), 129.3 (SnIPh, C_p), 129.8 ($^4J(^{13}C-^{117/119}Sn)$ = 14 Hz, $SnIPh_2$, C_p), 134.3 (SnIPh, C_o), 136.6 ($^2J(^{13}C-^{117/119}Sn)$ = 51 Hz, $SnIPh_2$, C_o), 137.2 (SnIPh, C_i), 138.2 ($SnIPh_2$, C_i). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −54 (*Sn*IPh_2), −102 (*Sn*IPh). Anal. Calcd (%) for $C_{24}H_{29}I_2NSn_2$ (822.72): C 35.04, H 3.55, N 1.70. Found: C 35.2, H 3.6, N 1.5. Electrospray MS: *m*/*z* (%) positive mode, 696.0 (20, $[M - I]^+$); negative mode, 380.7 (100, I_3^-), 126.9 (64, I^-).

Synthesis of $[\{Me_2N(CH_2)_3\}PhFSnCH_2SnFPh_2]$ (4). A solution of **3** (1.000 g, 1.22 mmol) in CH_2Cl_2 (30 mL) was mixed with a solution of KF (71 mg, 12.15 mmol) in water (30 mL). The biphasic mixture was stirred at room temperature for 8 days. The organic phase was then separated and dried over $MgSO_4$. Removing the solvent in vacuo afforded a yellow solid. This solid was dissolved in acetone, and the solution was cooled at −5 °C for several days to give 400 mg (53%) of pure **4** as a white solid (mp 168−170 °C). Single crystals of **4** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in acetone at −5 °C.

^{1}H NMR (499.79 MHz, $CDCl_3$): δ 0.86−2.23 (complex pattern, 14H), 6.80−7.86 (15H, Ph). $^{13}C\{^1H\}$ NMR (125.68 MHz, $CDCl_3$): δ 2.9 ($SnCH_2Sn$), 9.9 ($SnCH_2$), 21.5 ($SnCH_2CH_2$), 46.2 ($N(CH_3)_2$), 61.7 (CH_2N), 128.0 ($^3J(^{13}C-^{117/119}Sn)$ = 66 Hz, $SnFPh_2$, C_m), 128.7 (SnFPh, C_m), 128.9 ($SnFPh_2$, C_p), 129.7 (SnFPh, C_p), 135.1 (SnFPh, C_o), 136.2 ($SnFPh_2$, C_o), 140.2 (SnFPh, C_i), 142.7 ($SnFPh_2$, C_i). $^{19}F\{^1H\}$ NMR (282.36 MHz, $CDCl_3$): δ −95 ($^1J(^{19}F-^{119}Sn)$ = 1120 Hz, Sn*F*Ph), −185 ($^1J(^{19}F-^{119}Sn)$ = 2221 Hz, Sn*F*Ph_2). $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$, −35 °C): δ −18 (dd, $^1J(^{119}Sn-^{19}F)$ = 1168 Hz, $^3J(^{119}Sn-^{19}F)$ = 120 Hz, *Sn*FPh), −159 (dd, $^1J(^{119}Sn-^{19}F)$ = 2201 Hz, 560 Hz Sn*F*Ph_2). Anal. Calcd (%) for $C_{24}H_{29}F_2NSn_2$ (606.91): C 47.50, H 4.82, N 2.31. Found: C 47.2, H 5.0, N 2.0. Electrospray MS: *m*/*z* (%) positive mode, 588.1 (100, $[M - F]^+$), 1191.0 (4, $[2M - 3F + 2OH]^+$), negative mode 624.1 (2, $[M + OH]^-$).

Reaction of $\{Me_2N(CH_2)_3\}Ph(F)SnCH_2Sn(F)Ph_2$ (4) with $NEt_4F\cdot 2H_2O$. Compound **4** (0.070 g, 0.12 mmol) and tetraethylammonium-fluoride dihydrate (0.021 g, 0.12 mmol) were mixed in CD_2Cl_2 and stirred for 5 min. From the resulting solution, NMR spectra were recorded.

$^{19}F\{^1H\}$ NMR (282.36 MHz, CD_2Cl_2, −60 °C): δ −93(12%), −140 (30%, $^1J(^{19}F-^{117/119}Sn)$ = 1833/1895 Hz, 2F, SnF_2Ph), −141 (15%, $^1J(^{19}F-^{117/119}Sn)$ = 1854 Hz, SnFPh), −163(16%), −167(19%), −181(8%). $^{119}Sn\{^1H\}$ NMR (111.89 MHz, CD_2Cl_2, −65 °C): δ −60 (d, $^1J(^{119}Sn-^{19}F)$ = 1899 Hz, SnFPh), −252 (t, $^1J(^{119}Sn-^{19}F)$ = 1907 Hz, SnF_2Ph). Electrospray MS: *m*/*z* (%) positive mode, 130.2 (100, NEt_4^+); negative mode, 719.1 (100, M − Et_4N − F + OH + $3H_2O$ + MeCN).

Synthesis of $\{Me_2N(CH_2)_3\}Ph_2Sn(CH_2)_3SnPh_3$ (6). Elemental iodine (2.910 g, 11.45 mmol) was added in small portions under ice-cooling to a stirred solution of $Ph_3Sn(CH_2)_3SnPh_3$ (10.000 g, 13.47 mmol) in CH_2Cl_2 (200 mL). The reaction mixture was stirred overnight. The solvent and the iodobenzene were removed in vacuo. The residue thus obtained contained a mixture, hereafter referred to as mixture A, consisting of three compounds. $^{119}Sn\{^1H\}$ NMR (111.92 MHz, $CDCl_3$): δ −59.6 ($Ph_3Sn(CH_2)_3SnPh_2I$, 28%), −60.9 ($(IPh_2SnCH_2)_2CH_2$, 15%), −103.8 ($(Ph_3SnCH_2)_2CH_2$, 29%), −104.0 ($Ph_3Sn(CH_2)_3SnPh_2I$, 28%). To a solution of the mixture **A** in THF (150 mL) was added the Grignard reagent prepared from

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$Me_2N(CH_2)_3Cl$ (1.390 g, 11.43 mmol) and magnesium turnings (0.300 g, 12.3 mmol) in THF (40 mL). After the completion of the addition, the mixture was stirred overnight at room temperature. The mixture was then heated at reflux for 3 h before it was cooled to room temperature. THF was distilled off under reduced pressure; then cold water (100 mL) was added, and the mixture was extracted with dichloromethane. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated in vacuo to give the crude product. The latter was purified by column chromatography on silica gel using CH_2Cl_2 to separate the unreacted $Ph_3Sn(CH_2)_3SnPh_3$ compound, then using acetone to separate the target compound **6**. The latter was obtained as a yellow oil (2.410 g, 24% overall yield).

^{1}H NMR (400.13 MHz, $CDCl_3$): δ 1.20 (t, 2H, $SnCH_2$), 1.51 (t, 2H, $CH_2SnCH_2(CH_2)_2Sn$), 1.66 (t, 2H, $Sn(CH_2)_2CH_2Sn$), 2−2.15 (m, 4H, 2H $SnCH_2CH_2$ + 2H $SnCH_2CH_2CH_2Sn$), 2.59 (s, 6H, $N(CH_3)_2$), 2.95 (t, 2H, CH_2N), 7.34−7.63 (25H, Ph). ^{13}C{^{1}H} NMR (100.63 MHz, $CDCl_3$): δ 6.2 ($^1J(^{13}C-^{117/119}Sn)$ = 319/333 Hz, $Sn-CH_2(L)$), 15.5 ($^1J(^{13}C-^{117/119}Sn)$ = 352/368 Hz, $SnCH_2$), 15.9 ($^1J(^{13}C-^{117/119}Sn)$ = 382 Hz, $SnCH_2$), 21.1 ($^2J(^{13}C-^{117/119}Sn)$ = 15 Hz, $SnCH_2CH_2CH_2Sn$), 24.1 ($^2J(^{13}C-^{117/119}Sn)$ = 20 Hz, $SnCH_2CH_2$), 42.5 $N(CH_3)_2$, 60.3 ($^3J(^{13}C-^{117/119}Sn)$ = 67 Hz, CH_2N), 128.2 ($SnPh_3$, C_m), 128.4 ($SnPh_2$, C_m), 128.6 ($SnPh_3$, C_p), 128.7 ($SnPh_2$, C_p), 136.5 ($^2J(^{13}C-^{117/119}Sn)$ = 35 Hz, $SnPh_2$, C_o), 136.7 ($^2J(^{13}C-^{117/119}Sn)$ = 35 Hz, $SnPh_3$, C_o) 138.1 ($SnPh_2$, C_i), 138.5 ($SnPh_3$, C_i). ^{119}Sn{^{1}H} NMR (111.92 MHz, $CDCl_3$): δ −76 ($SnPh_2$), −104 ($SnPh_3$). Anal. Calcd (%) for $C_{38}H_{43}NSn_2$ (751.19): C 60.76, H 5.77, N 1.86. Found: C 60.0, H 5.9, N 1.8. Electrospray MS: m/z (%) positive mode, 674.1 (58, $[M - Ph]^+$), 752.2 (2, $[M + H]^+$).

Synthesis of $\{Me_2N(CH_2)_3\}PhFSn(CH_2)_3SnFPh_2$ (7). Elemental iodine (0.300 g, 1.20 mmol) was added in small portions and under ice cooling to a stirred solution of **6** (0.450 g, 0.60 mmol) in CH_2Cl_2 (30 mL). Stirring was continued while warming to room temperature overnight. The solvent and iodobenzene were removed in vacuo to afford $\{Me_2N(CH_2)_3\}Ph(I)Sn(CH_2)_3Sn(I)Ph_2$ as a yellow oil, which was used for the next reaction without further purification. ^{119}Sn{^{1}H} NMR ($CDCl_3$, 149.26 MHz): δ −54 ($SnIPh_2$), −91 ($\{Me_2N(CH_2)_3\}SnIPh$). A solution of $\{Me_2N(CH_2)_3\}Ph(I)Sn(CH_2)_3Sn(I)Ph_2$ (0.300 g, 0.35 mmol) in CH_2Cl_2 (10 mL) was mixed with a solution of KF (0.200 g, 3.53 mmol) in water (15 mL). The biphasic mixture was stirred at room temperature for 3 days. The organic phase was then separated and dried over $MgSO_4$. Removing the solvent in vacuo afforded a white solid. This solid was dissolved in ethyl acetate, and the solution was cooled at −5 °C for several days to give 0.100 g (45%) of **7** as a white solid (mp 142−144 °C). Single crystals of **7** suitable for X-ray diffraction analysis were obtained by slow evaporation of a solution of the compound in ethyl acetate at 4 °C.

^{1}H NMR (300.13 MHz, $CDCl_3$): δ 12.7 (complex pattern, 18H), 6.90−7.86 (15H, Ph). ^{13}C{^{1}H} NMR (75.48 MHz, $CDCl_3$): δ 10.2 ($Sn-CH_2$), 10.5 ($SnCH_2$), 18.5 ($SnCH_2$), 21.4 ($^2J(^{13}C-^{117/119}Sn)$ = 29 Hz, $SnCH_2CH_2$), 22.1 ($SnCH_2CH_2CH_2-Sn$), 45.8 $N(CH_3)_2$, 61.6 (CH_2N), 127.6 ($SnFPh_2$, C_m), 128.3 ($SnFPh$, C_m), 128.7 ($SnFPh_2$, C_p), 129.5 ($SnFPh$, C_p), 135.2 ($SnFPh$, C_o), 136.3 ($SnFPh_2$, C_o) 136.9 ($SnFPh$, C_i), 137.3 ($SnFPh_2$, C_i). ^{19}F{^{1}H} NMR (376.61 MHz, $CDCl_3$): δ −146 ($\nu_{1/2}$ 183 Hz, $^1J(^{19}F-^{117/119}Sn)$ = 1688, 927 Hz, $SnFPh$), −177 ($\nu_{1/2}$ 387 Hz, $^1J(^{19}F-^{117/119}Sn)$ = 2097 Hz, $SnFPh_2$). ^{119}Sn{^{1}H} NMR (149.26 MHz, $CDCl_3$): δ −47 (d, $^1J(^{119}Sn-^{19}F)$ = 1698 Hz, $SnFPh$), −190 (dd, $^1J(^{119}Sn-^{19}F)$ = 2062, 950 Hz, $SnFPh_2$). Anal. Calcd (%) for $C_{26}H_{33}F_2NSn_2\cdot CH_2Cl_2$ (719.90): C 45.05, H 4.90, N 1.95. Found: C 45.5, H 5.2, N 2.0. Electrospray MS: m/z (%) positive mode, 632.2 (5, $[M - 2F + 2OH + H]^+$).

Reaction of $\{Me_2N(CH_2)_3\}Ph(F)Sn(CH_2)_3Sn(F)Ph_2$ (7) with 1 molar equiv of $NEt_4F\cdot 2H_2O$. Compound **7** (0.040 g, 0.06 mmol) and tetraethylammonium fluoride dihydrate (0.012 g, 0.06 mmol) were mixed in CD_2Cl_2 and stirred for 5 min.

^{19}F{^{1}H} NMR (376.6 MHz, CD_2Cl_2, −80 °C): δ −143 (31%, d, $^1J(^{19}F-^{117/119}Sn)$ = 1124, 1498/1564 Hz), $^2J(^{19}F-^{19}F)$ = 83 Hz, $SnFPh$, **7**), −154 (14%, SnF_2Ph_2, $[NEt_4][7\cdot F]$), −158 (7%, $SnFPh$, $[NEt_4][7\cdot F]$), −159 (8%), − 162 (2%), −169 (9%), −174 (29%, d, $^1J(^{19}F-^{117/119}Sn)$ = 1976/2070 Hz), $^2J(^{19}F-^{19}F)$ = 83 Hz, $SnFPh_2$, **7**). ^{119}Sn{^{1}H} NMR (149.26 MHz, CD_2Cl_2, −80 °C): δ −47 (30%, d, $^1J(^{119}Sn-^{19}F)$ = 1566 Hz, $SnFPh$, **7**), −86 (12%, d, $^1J(^{119}Sn-^{19}F)$ = 1957 Hz, $SnFPh$, $[NEt_4][7\cdot F]$), −88 (13%, d, $^1J(^{119}Sn-^{19}F)$ = 1973 Hz), −203 (32%, dd, $^1J(^{119}Sn-^{19}F)$ = 2067, 941 Hz, $SnFPh_2$, **7**), −222 (3%), −226 (4%), −235 (2%), −270 (SnF_2Ph_2, $[NEt_4][7\cdot F]$).

Reaction of $\{Me_2N(CH_2)_3\}Ph(F)Sn(CH_2)_3Sn(F)Ph_2$ (7) with 2 molar equiv of $NEt_4F\cdot 2H_2O$. Compound **7** (0.035 g, 0.06 mmol) and tetraethylammonium fluoride dihydrate (0.020 g, 0.11 mmol) were mixed in CD_2Cl_2 and stirred for 5 min.

^{19}F{^{1}H} NMR (376.6 MHz, CD_2Cl_2, −80 °C): δ −143 (5%, d, $SnFPh$, **7**), −151 (5%), −154 (46%, SnF_2Ph_2, $[NEt_4][7\cdot F]$), −156 (6%), −158 (23%, $SnFPh$, $[NEt_4][7\cdot F]$), −160 (6%), −169 (5%), −174 (5%, d, $SnFPh_2$, **7**). ^{119}Sn{^{1}H} NMR (149.26 MHz, CD_2Cl_2, −80 °C): δ −47 (5%, d, $^1J(^{119}Sn-^{19}F)$ = 1563 Hz, $SnFPh$, **7**), −86 (40%, d, $^1J(^{119}Sn-^{19}F)$ = 1957 Hz, $SnFPh$, $[NEt_4][7\cdot F]$), −88 (8%, d, $^1J(^{119}Sn-^{19}F)$ = 1973 Hz), −203 (7%, dd, $^1J(^{119}Sn-^{19}F)$ = 2067, 941 Hz, $SnFPh_2$, **7**), −271 (40%, t, $^1J(^{119}Sn-^{19}F)$ = 1888 Hz, SnF_2Ph_2, $[NEt_4][7\cdot F]$).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00500.

NMR spectra, ESI mass spectra, and crystallographic data (PDF)

Crystallographic data for **2**−**4** and **7** (CIF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: klaus.jurkschat@tu-dortmund.de.

Notes

The authors declare no competing financial interest.

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