o-Bis(haloorganostannyl)benzenes As Powerful Bidentate Lewis Acids toward Halide Ions†

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The synthesis of the *o*-phenylene-bridged ditin species *o*-$C_6H_4(SnXMe_2)_2$ (**2,** X = Cl; **4**, X = F) and *o*-$C_6H_4(SnCl_2Me)_2$ (**3**) is reported and the crystal structures of [*o*-$C_6H_4(SnClMe_2)_2\cdot Cl]^-[(Ph_3N)_2P]^+$ (**5**) and [*o*-$C_6H_4(SnClMe_2)_2\cdot F]^-[K\cdot C_{20}H_{24}O_6]^+$ (**7**) are described. Variable-temperature ^{119}Sn and ^{19}F NMR studies indicate that **2** and **4** act as bidentate Lewis acids toward chloride and fluoride ions exclusively forming the stable anionic 1:1 complexes **5**, **7**, and [*o*-$C_6H_4(SnFMe_2)_2\cdot F]^-[Et_4N]^+$ (**8**). No formation of dianionic 1:2 adducts was observed even with excess of halide ions. The affinity of **2** toward fluoride is greater than toward chloride. Reaction of **2** with HMPA gives the neutral complex *o*-$C_6H_4(SnClMe_2)_2\cdot(Me_2N)_3PO$ (**10**), the crystal structure of which is also described.

Introduction

In recent years the selective complexation of anions and neutral donor molecules by tailor-made molecular hosts has been a subject of growing interest.[1] Part of this general concept is the synthesis of multidentate Lewis acids in which the latter are incorporated in open chain[2−4] or cyclic structures.[5−9] Elements which function as Lewis acids in these host molecules include for instance B,[10] Al,[11] In,[4] Si,[6c,7] Ge,[8] Sn,[2,3,5,6] and Hg.[12]

One observation from the investigations reported so far is that high guest selectivity and high stability of the host−guest complexes are achieved in cases where the host shows a high degree of preorganization and rigidity. This holds especially for the *o*-phenylene-bridged dimercury[12] and disilicon[13] species of type **A**. The power of 1,8-bis(alkylstannyl)naphthalene in alkylation reactions has been demonstrated recently.[14a] Diels−Alder reactions were also shown to be catalyzed by bidentate tin-containing Lewis acids.[14b]

In continuation of our studies on tin-based bidentate Lewis acids,[3a−f] we report here on the synthesis of the

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† This paper includes part of the intended Ph.D. thesis of R. Altmann.

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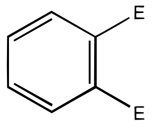
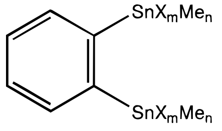


(**A**)

E = HgCl, SiPhF$_2$, SiPh$_2$F



(**B**)

2, X = Cl, m = 1, n = 2
3, X = Cl, m = 2, n = 1
4, X = F, m = 1, n = 2

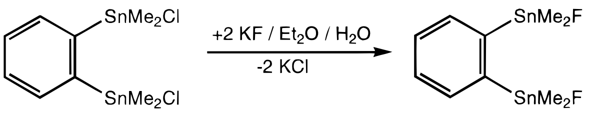
corresponding *o*-phenylene-bridged derivatives of type **B** and on their complexation behavior toward chloride ions, fluoride ions, and HMPA.

Results and Discussion

Synthetic Aspects. The synthesis of *o*-bis(trimethylstannyl)benzene (**1**) has been reported but yield[15a–c] and purity[15a] were not satisfying. Modification of the reported procedure[15a] provided compound **1** in 70% yield.

Treatment of **1** with 2 molar equiv of Me$_2$SnCl$_2$ or 2 molar equiv of SnCl$_4$ afforded *o*-bis(dimethylchlorostannyl)benzene (**2**) and *o*-bis(methyldichlorostannyl)benzene (**3**), respectively, in high yield (Scheme 1).

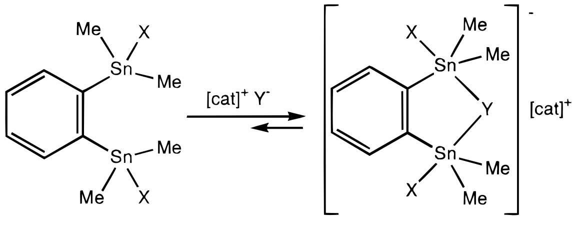
Reaction of **2** with potassium fluoride gave almost quantitatively *o*-bis(dimethylfluorostannyl)benzene (**4**) (eq 1).



2 **4** (1)

Attempts failed to prepare 1,8-bis(dimethylchlorostannyl)naphthalene $C_{10}H_6$-1,8-$(SnClMe_2)_2$ by reaction of 1,8-bis(trimethylstannyl)naphthalene[16] $C_{10}H_6$-1,8-$(SnMe_3)_2$ with dimethyldichlorostannane. The reaction gave 7,7,14,14-tetramethyldinaphtho[1,8-*bc*:1′,8′-*fg*][1,5]distannocine[17] as the major product (Scheme 2).

The treatment of **2** with 1 molar equiv $[(Ph_3P)_2N]^+Cl^-$ afforded the corresponding chloride complex $[o\text{-}C_6H_4(SnClMe_2)_2\bullet Cl]^-[(Ph_3P)_2N]^+$ (**5**) as crystalline solid (eq 2).

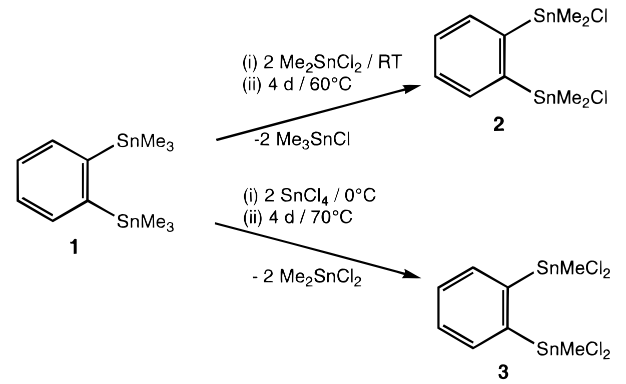


(2)

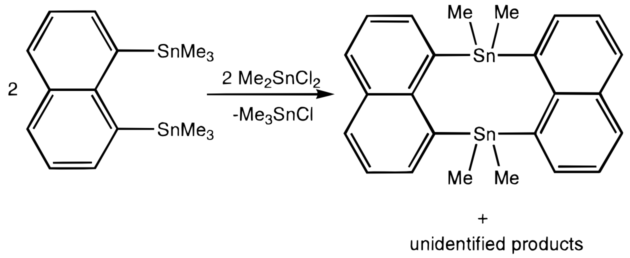
2, X =Cl
4, X = F

5, X = Y = Cl, cat$^+$ = $(Ph_3P)_2N^+$
6, X = Cl, Y = F, cat$^+$ = Et_4N^+
7, X = Cl, Y = F, cat$^+$ = $(K\cdot C_{20}H_{24}O_6)^+$
8, X = Y = F, cat$^+$ = Et_4N^+
9, X = Y = F, cat$^+$ = $(K\cdot C_{12}H_{24}O_6)^+$

Scheme 1



Scheme 2

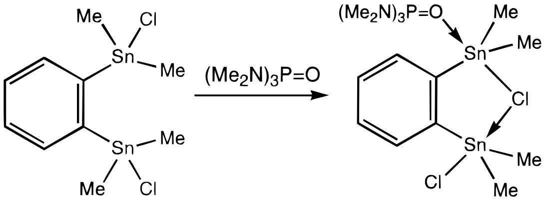


Reaction of **2** with Et$_4$NF·2H$_2$O gave the anionic fluoride adduct $[o\text{-}C_6H_4(SnClMe_2)_2\cdot F]^-$ as crystalline $[Et_4N]^+$ salt **6** (eq 2), which was of insufficient quality for X-ray analysis. Better quality crystals of anionic $[o\text{-}C_6H_4(SnClMe_2)_2\cdot F]^-$ were obtained as the potassium salt $[o\text{-}C_6H_4(SnClMe_2)_2\cdot F]^-$ [K·dibenzo-18-crown-6]$^+$ (**7**), from reaction of *o*-bis(dimethylchlorostannyl)benzene (**2**) and equimolar quantities of potassium fluoride and dibenzo-18-crown-6 (eq 2).

Reaction of *o*-bis(dimethylfluorostannyl)benzene (**4**) with Et$_4$NF·2H$_2$O afforded the fluoride complex $[o\text{-}C_6H_4(SnFMe_2)_2\cdot F]^-$ $[Et_4N]^+$ (**8**), and reaction of **4** with potassium fluoride and 18-crown-6 gave the potassium salt $[o\text{-}C_6H_4(SnFMe_2)_2\cdot F]^-$ [K·18-crown-6]$^+$ (**9**) (eq 2).

Compounds **2**–**9** are colorless solids. The chloro-substituted derivatives **2** and **3** as well as the chloride and fluoride complexes **5**–**9** are soluble in common organic solvents such as CH$_2$Cl$_2$, CHCl$_3$, toluene, and THF. The fluoro-substituted derivative **4** is almost insoluble in common organic solvents.

Treatment of *o*-bis(dimethylchlorostannyl)benzene (**2**) with HMPA afforded the neutral 1:1 complex $o\text{-}C_6H_4(SnClMe_2)_2\cdot(Me_2N)_3PO$ (**10**) as a crystalline colorless solid (eq 3).



2 **10** (3)

Complexation Behavior in Solution of Compounds 2 and 3 toward Chloride Ions. Information on the complexation behavior of compounds **2** and **3** toward anions is provided by NMR spectroscopy and electrospray mass spectrometry.

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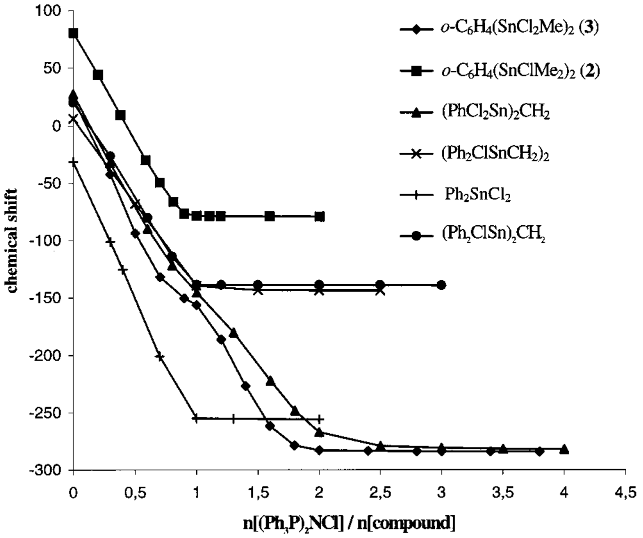

Figure 1. Plot of ^{119}Sn NMR chemical shift (ppm) versus molar ratio $[(Ph_3P)N]^+ Cl^-$/compound.

The ^{119}Sn NMR chemical shifts of the chloro-substituted derivatives **2** and **3** to which various amounts of $[(Ph_3P)_2N]^+Cl^-$ have been added are shown in Figure 1. The corresponding slopes for Ph_2SnCl_2 and the methylene- and dimethylene-bridged ditin compounds $(Ph_2ClSn)_2CH_2$, $(PhCl_2Sn)_2CH_2$, and $(Ph_2ClSnCH_2)_2$ are given for comparison.[3c,18] For the dichloro derivative **2** the measurements clearly indicate the formation of a one-to-one complex with chloride ion, as was confirmed by isolation of the chloride complex **5** and as was to be expected from comparison with the behavior of the aliphatic analogue $(Ph_2ClSnCH_2)_2$.[3c] The structure in solution of chloride complex **5** is very likely to be similiar to its solid-state structure (see below) with the two tin atoms being bridged by chloride resulting in trigonal bipyramidal configurations. This is supported by observation of increased $^2J(^1H-^{119/117}Sn)$ and $^1J(^{13}C-^{119/117}Sn)$ couplings of 72/69 and 530/506 Hz, respectively, in compound **5** in comparison with the corresponding couplings measured for compound **2** (61/59, 408/389 Hz). The chloride bridge in **5** is symmetric on the ^{1}H, ^{13}C, and ^{119}Sn NMR time scales, i.e., the methyl groups as well as the tin atoms are equivalent.

The tetrachloro derivative **3** forms both a one-to-one and a one-to-two complex as is indicated by observation of a inflection point at about δ $^{119}Sn = -150$ ppm (Figure 1). None of these complexes were isolated. A similar complexation behavior is observed for $(PhCl_2Sn)_2CH_2$, whereas Ph_2SnCl_2 forms a one-to-one complex with chloride (see Figure 1).

Formation constants K_a of one-to-one Lewis-acid/Lewis-base complexes can be estimated by application of the Benesi−Hildebrandt treatment.[19] However, the absolute K_a values calculated from the NMR experiments have to be taken with great caution as we have obtained different values from several independent measurements on the same complex. For instance, the K_a values for compound **2**, which have been obtained under standard conditions (20 °C, $c = 0.1$ mol/L), lie between 4200 and 11 000 M^{-1}. It is more reliable to directly compare the complexation behavior of the hosts **2** and **3** toward chloride (eq 4; Table 1) as was recently shown by Tamao et al. for related silicon species.[13a]

$$\mathbf{A} + \mathbf{B} + \mathbf{C} + Cl^- \rightleftharpoons m[\mathbf{A}\cdot Cl]^- + n[\mathbf{B}\cdot C]^- + o[\mathbf{C}\cdot Cl]^- \qquad (4)$$

Equimolar amounts of $[Ph_3P{=}N{=}PPh_3]^+Cl^-$ and the corresponding organotin compounds **A**−**C** (Table 1, eq 4) were dissolved in 2 mL of dichloromethane ($c = 0.2-0.25$ mol/L), and the resulting solutions were investigated by ^{119}Sn NMR spectroscopy. From the chemical shifts observed and the calibration curves shown in Figure 1, the molar fractions m, n, and o can be estimated.

From these experiments the following qualitative sequence results of the affinity of organotin chlorides toward chloride ions: $Ph_3SnCl \ll Ph_2SnCl_2 \ll (Ph_2ClSnCH_2)_2 \approx (Ph_2ClSn)_2CH_2 \approx C_6H_4(SnClMe_2)_2$ (**2**) $\ll (PhCl_2Sn)_2CH_2 \approx C_6H_4(SnCl_2Me)_2$ (**3**).

The sequence shows (i) the bidentate ditin species to be more efficient than the monotin derivatives, (ii) the methylene-, dimethylene-, and *o*-phenylene-bridged bis(diorganochlorostannyl) derivatives to be in the same order of magnitude, (iii) the bidentate tetrachlorides to be more efficient than the bidentate dichlorides, and (iv) the methylene- and *o*-phenylene-bridged bis(organodichlorostannyl) species to be in the same order of magnitude.

The negative-ion electrospray mass spectrum of a solution of o-$C_6H_4(SnClMe_2)_2$ (**2**) in acetonitrile shows an isotopic cluster pattern centered at $m/z = 481$ which is consistent with self-ionization to give the monoanion $[\mathbf{2} + Cl]^-$. The positive-mode electrospray mass spectrum of the same solution gives spectra consistent with $[\mathbf{2} - 2Cl + OH]^+$ as major species ($m/z = 391$) and small amounts of $[\mathbf{2} - Cl]^+$ ($m/z = 409$) and $[\mathbf{2} - 2Cl + OH + MeCN]^+$ ($m/z = 432$). Interestingly, also present are small quantities of dimeric species $[2\cdot\mathbf{2} - 4Cl + O + OH]^+$ ($m/z = 781$), $[2\cdot\mathbf{2} - 3Cl + O]^+$ ($m/z = 799$), and $[2\cdot\mathbf{2} - 3Cl + 2OH]^+$ ($m/z = 817$).

The negative-ion electrospray mass spectrum of the complex $[o\text{-}C_6H_4(SnClMe_2)_2\cdot Cl]^-[(Ph_3P)_2N]^+$ (**5**) in acetonitrile shows an isotopic cluster pattern of $[\mathbf{2} + Cl]^-$ at $m/z = 481$ and a less intense signal consistent with $[\mathbf{2} - Cl + O]^-$ ($m/z = 425$). The positive-mode electrospray mass spectrum shows in addition to the cluster of $[(Ph_3P)_2N]^+$ at $m/z = 538$ a minor ion-paired species $[\mathbf{2} + Cl + 2\cdot(Ph_3P)_2N]^+$ ($m/z = 1557$). After addition of 1 molar equiv of chloride ion (as its tetrabutylammonium salt), the spectra in both modes do not change and there is no evidence for dianionic species.

The negative-ion electrospray mass spectrum of a solution of *o*-bis(methyldichlorostannyl)benzene (**3**) in acetonitrile shows an isotopic cluster pattern centered at $m/z = 521$ which is consistent with self-ionization to give the monoanion $[\mathbf{3} + Cl]^-$. There are also weaker cluster patterns (approximately 5−10% relative abundance) consistent with the presence of $[\mathbf{3} - Cl + O]^-$ ($m/z = 467$), $[\mathbf{3} + OH]^-$ ($m/z = 503$), and $[2\cdot\mathbf{3} - 7Cl + 4O]^-$ ($m/z = 787$). The positive-ion electrospray mass spectrum carries very little ion current and contains weak signals consistent with the presence of $[\mathbf{3} - 2Cl + OH]^+$ ($m/z = 431$), $[\mathbf{3} - 2Cl + OH + MeCN]^+$ ($m/z =$

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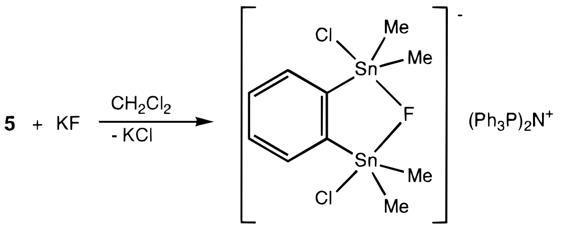
Table 1. Comparison of the Complexation Behavior toward Chloride Ions of Selected Tin Containing Bidentate Lewis Acids

compounds				^{119}Sn NMR chemical shift δ/ppm		
A	**B**	**C**		m [**A**·Cl]$^-$	n [**B**·Cl]$^-$	o [**C**·Cl]$^-$
2	**3**		$n \gg m$	35.2	−150.6	
2	$(Ph_2ClSn)_2CH_2$		$m \approx n$	−17.7	−91.6	
2	$(Ph_2ClSnCH_2)_2$		$m \approx n$	−26.7	−68.9	
2	$(Ph_2ClSn)_2CH_2$	$(PhCl_2Sn)_2CH_2$	$o \gg m \approx n$	51.6	−3.9	−135.3
2	$(PhCl_2Sn)_2CH_2$		$n \gg m$	43.0	−140.4	
2	Ph_2SnCl_2	Ph_3SnCl	$m \gg n \approx o$	−48.1	−129.8	−54.2
	Ph_2SnCl_2	Ph_3SnCl	$n \gg o$		−223.5	−69.4
3	$(PhCl_2Sn)_2CH_2$		$m \approx n$	−89.5	−82.9	

472), and the dimeric species [2·**3** − 5Cl + 2O]$^+$ (m/z = 825), [2·**3** − 4Cl + O + OH]$^+$ (m/z = 863), and [2·**3** − 3Cl + O]$^+$ (m/z = 881).

Complexation Behavior in Solution of Compounds 2−5 toward Fluoride Ions. The ^{119}Sn NMR spectrum at room temperature of the fluoride complex **6** shows a doublet at $\delta = -100.8$ ppm ($^1J(^{119}Sn - ^{19}F)$ = 1107 Hz) and the ^{19}F NMR spectrum displays a single resonance at $\delta = -137.1$ ppm ($^1J(^{19}F - ^{119}Sn)$ = 1108 Hz). These results are consistent with a bridging fluoride and demonstrate the high kinetic stability of **6** in comparison with the related complexes $[(Ph_2ClSn)_2(CH_2)_n{\cdot}F]^-$ (n = 1, 3) for which no ^{119}Sn NMR spectra could be obtained at room temperature.[3f] The high kinetic stability of **6** on the ^{119}Sn NMR time scale is further illustrated by the absence of any coalescence phenomena in its ^{119}Sn NMR spectrum in pyridine at 100 °C. However, the ^{119}Sn NMR spectrum in CH_2Cl_2 of **6** to which has been added 1 molar equiv of **2** shows no signal at room temperature and a very broad signal at −44 ppm ($W_{1/2} \approx 1600$ Hz) at −80 °C, indicating fast exchange.

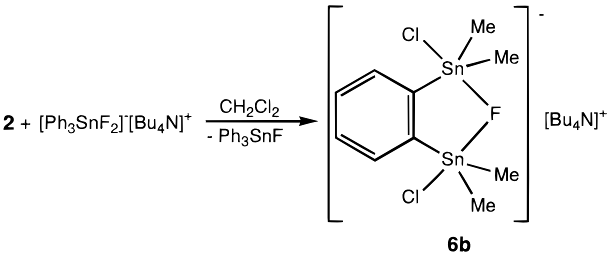
Treatment of the chloride complex **5** with an equimolar amount of potassium fluoride in dichloromethane gave quantitative *in situ* formation of the fluoride complex **6a** (eq 5).



(5)

6a

The fluoride complex **6b** was formed quantitatively *in situ* by reaction of o-bis(dimethylchlorostannyl)benzene (**2**) with $[Ph_3SnF_2]^-[Bu_4N]^+$ (eq 6). Both reactions illustrate the high affinity of the bidentate Lewis acid **2** toward fluoride.



(6)

6b

The ^{119}Sn NMR spectrum in CD_2Cl_2 at room temperature of the fluoride complex **8** displays a doublet of doublets resonance at $\delta = -138.3$ ppm ($^1J(^{119}Sn - ^{19}F)$ = 1954/1187 Hz). The ^{19}F NMR spectrum of the same but diluted solution exhibits one triplet resonance at $\delta = -126.8$ ppm ($^1J(^{19}F - ^{119}Sn)$ = 1172 Hz, $^2J(^{19}F - ^{19}F)$ = 84 Hz) and a doublet resonance at $\delta = -155.4$ ppm ($^1J(^{19}F - ^{119}Sn)$ = 1912 Hz, $^2J(^{19}F - ^{19}F)$ = 83 Hz) with an integral ratio of 1:2. The spectra are consistent with a structure containing one bridging and two terminal fluorine atoms as shown in eq 2. Addition of 1 molar equiv of fluoride ion gives no evidence for formation of a dianionic fluoride complex.

The negative-ion electrospray mass spectrum of the complex [K·dibenzo-18-crown-6]$^+$[o-$C_6H_4(SnClMe_2)_2{\cdot}F$]$^-$ (**7**) in acetonitrile shows an isotopic cluster of [**2** + F]$^-$ at m/z = 463 and weak signals of [**2** + Cl]$^-$ (m/z = 481) and [**2** + 2F − Cl]$^-$ (m/z = 447). The positive-mode electrospray mass spectrum of **7** contains the expected clusters of potassium and sodium dibenzo-18-crown-6 salts. Addition of 1 molar equiv of fluoride ion (as its tetrabutylammonium salt) provides no evidence for dianionic species.

After addition of 1 molar equiv of fluoride ion (as its tetrabutylammonium salt) to an acetonitrile solution of o-$C_6H_4(SnCl_2Me)_2$ (**3**) the negative-ion electrospray mass spectrum shows the isotopic cluster pattern of [**3** + Cl]$^-$ at m/z = 521 (100% relative abundance) and [**3** + F]$^-$ at m/z = 505 (80% relative abundance). There is again a weaker cluster pattern for [**3** − Cl +O]$^-$ at m/z = 467. The positive mode shows a weak signal consistent with [**3** − 2Cl + OH]$^+$ at m/z = 431.

The negative-ion electrospray mass spectrum of o-$C_6H_4(SnFMe_2)_2$ (**4**) in acetonitrile solution contains an isotopic cluster pattern for [**4** − F + 2Cl]$^-$ (m/z = 463), [**4** + Cl]$^-$ (m/z = 446), and [**4** + F]$^-$ (m/z = 431). There are also weaker signals (approximately 2% relative abundance) centered at m/z = 843 and m/z = 859 consistent with the dimeric species [2·**4** + F]$^-$ and [2·**4** + Cl]$^-$. The positive-ion electrospray mass spectrum carries very little ion current and contains weak signals consistent with the presence of [**4** − 2F + OH]$^+$ (m/z = 391), [**4**+H]$^+$ (m/z = 413), [**4** + Na]$^+$ (m/z = 435), [**4** + K]$^+$ (m/z = 451), [**4** + Na + MeCN]$^+$ (m/z = 476), and the dimeric compound [2·**4** − 3F + 2OH]$^+$ (m/z = 801).

The negative-ion electrospray mass spectrum of the complex [K·18-crown-6]$^+$[o-$C_6H_4(SnFMe_2)_2{\cdot}F$]$^-$ (**9**) in acetonitrile shows an isotopic cluster pattern for [**4** + F]$^-$ at m/z = 431 and a less intense signal consistent with [**4** + Cl]$^-$ (m/z = 447). The presence of dimeric species is again confirmed by weak isotopic clusters (approximately 3% relative abundance) at m/z = 843 and $m/z = 903$ assigned to $[2{\cdot}\mathbf{4} + F]^-$ and $[2{\cdot}\mathbf{4} + Br]$. Related dimeric mercury complexes $[(o\text{-}C_6H_4(HgCl)_2)_2{\cdot}Cl]^-[Ph_4P]^+$ and $[(o\text{-}C_6H_4(HgCl)_2)_2{\cdot}Cl]^-[Bu_4N]^+$ were isolated and fully characterized.[12a−d] The positive-mode electrospray mass spectrum contains in addition to the cluster of $[K{\cdot}18\text{-crown-}6]^+$ at $m/z = 303$ a very weak signal assigned to a species with two countercations $[\mathbf{4} + F + 2{\cdot}(K{\cdot}18\text{-crown-}6)]^+$ ($m/z = 1037$).

Addition of 1 molar equiv of Bu_4NF shows again the cluster pattern of $[\mathbf{4} + F]^-$ as the most intense signal and weak isotopic clusters (approximately 2% relative abundance) for the dimeric species $[2{\cdot}\mathbf{4} + F]^-$ at $m/z = 843$ and $[2{\cdot}\mathbf{4} + 2F + K]^-$ at $m/z = 901$. There is no evidence for dianionic species. The positive mode shows weak signals for $[\mathbf{4} + F + (K{\cdot}18\text{-crown-}6) + Bu_4N]^+$ at $m/z = 976$ and $[\mathbf{4} + F + 2{\cdot}(K{\cdot}18\text{-crown-}6)]^+$ at $m/z = 1037$.

The complexation behavior toward fluoride of *o*-bis(methyldichlorostannyl)benzene (**3**) and of related $[(Me_3Si)_2CH(Cl_2)Sn]_2CMe_2$ is more complex and will be a subject of a forthcoming paper.

Reaction of *o*-bis(dimethylchlorostannyl)benzene (2) with HMPA. The complexes of bis(halodiphenylstannyl)methane, 1,2-bis(halodiphenylstannyl)ethane, and bis((diphenylchlorostannyl)methyl)phenylchlorostannane with the nonbridging donor HMPA have previously been described.[3a,c,g]

The ^{119}Sn NMR spectrum at room temperature of an equimolar solution of **2** and HMPA in CD_2Cl_2 shows a broad signal at $\delta = -71$ ppm ($W_{1/2} = 650$ Hz). The ^{31}P NMR spectrum at room temperature displays a signal at 24.6 ppm without $^{119/117}Sn$ NMR satellites. Both spectra indicate a fast exchange process. At −80 °C the ^{119}Sn NMR spectrum splits into two sharp resonances, a singlet at −52.9 ppm and a doublet at −98.9 ppm ($^2J(^{119}Sn{-}^{31}P) = 140$ Hz) with integral ratio of 1:1. In addition, there are three signals of lower intensity (20% of the major resonances) at −79.1, −82.2, and −136.7 ppm for which no assignment is made. The ^{31}P NMR spectrum at −80 °C shows the signal at −24.5 ppm with an unresolved $^2J(^{31}P{-}^{119/117}Sn)$ coupling of 135 Hz. Both ^{119}Sn and ^{31}P NMR are consistent with formation of the neutral complex $o\text{-}C_6H_4(SnClMe_2)_2{\cdot}HMPA$ (**10**) and are similar to those for the related complex $(Ph_2ClSnCH_2)_2{\cdot}HMPA$.[3c]

After addition of a second molar equivalent of HMPA, the ^{119}Sn NMR spectrum differs only in the intensity of the signal at −79.1 ppm (reaching half of the intensity of the major resonances) for which no assignment could be made. There was no evidence for the formation of a 1:2 complex $o\text{-}C_6H_4(SnClMe_2)_2{\cdot}2HMPA$.

Molecular Structures of 5, 7, and 10. The molecular structures of **5**, **7**, and **10** are illustrated in Figures 2−4, respectively, showing the crystallographic numbering scheme and confirming the stoichiometries of the compounds. Unit cell data, refinement details, and selected interatomic parameters are listed in Tables 2 and 3 and provide detailed information on the molecular geometries.

The lattice of **5** and **7** comprises discrete $[o\text{-}C_6H_4(SnMe_2Cl)_2{\cdot}Cl]^-$ and $[o\text{-}C_6H_4(SnMe_2Cl)_2{\cdot}F]^-$ anions, respectively, and countercations (**5**, $[(Ph_3P)_2N]^+$; **7**, $[K{\cdot}dibenzo\text{-}18\text{-crown-}6]^+$). For **5** there is no significant interionic contact. Compound **7** crystallizes with a 0.5 molar equiv of dichloromethane. There is an interaction between the K^+ ion in the crown ether and Cl(1) confirmed by a Cl(1)−K(1) distance of 3.133(3) Å, which is comparable to the K−Cl distance in potassium chloride (3.14 Å).[20]

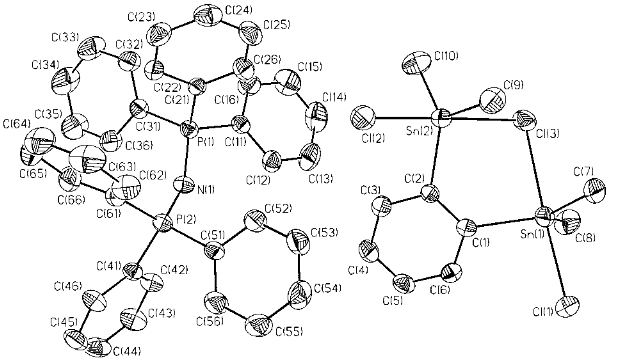


Figure 2. General view (SHELXTL-PLUS) of a molecule of **5** showing 30% probability displacement ellipsoids and the atom numbering.

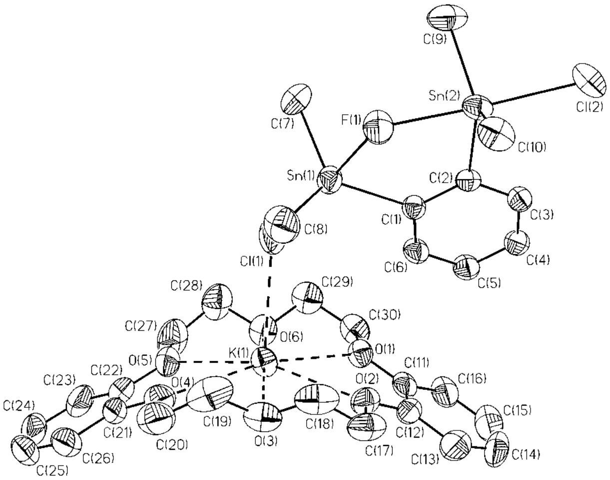


Figure 3. General view (SHELXTL-PLUS) of a molecule of **7** showing 30% probability displacement ellipsoids and the atom numbering.

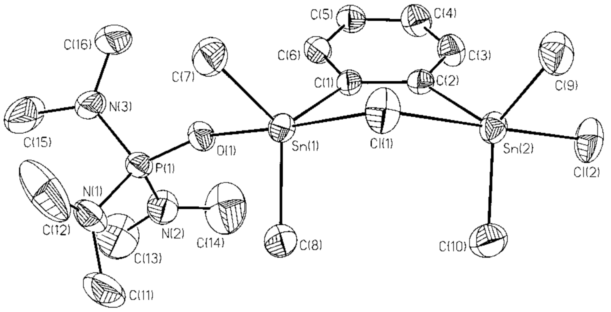


Figure 4. General view (SHELXTL-PLUS) of a molecule of **10** showing 30% probability displacement ellipsoids and the atom numbering.

The tin atoms in the anions of **5** and **7** exhibit a trigonal bipyramidal configuration with the axial positions being occupied by Cl(1), X for Sn(1) and Cl(2), X for Sn(2) (**5**, X = Cl(3); **7**, X = F). The carbon atoms C(1), C(7), C(8) (for Sn(1)) and C(2), C(9), C(10) (for Sn(2)) define the equatorial planes. The tin atoms in **5** are displaced by 0.148(2) Å (Sn(1)) and 0.099(2) Å (Sn(2))

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[20] Huheey, J. E. *Anorganische Chemie, Prinzipien von Struktur und Reaktivität*; Walter de Gruyter: Berlin, 1988.

Table 2. Crystallographic Data of 5, 7, and 10

	5	**7**	**10**
formula	$C_{46}H_{46}Cl_3NP_2Sn_2$	$C_{30}H_{40}Cl_2FKO_6Sn_2\cdot .5\ CH_2Cl_2$	$C_{16}H_{34}Cl_2N_3OPSn_2$
fw, g/mol	1018.51	905.46	623.71
cryst syst	monoclinic	monoclinic	orthorhombic
cryst size, mm	0.30 × 0.20 × 0.18	0.40 × 0.20 × 0.10	0.20 × 0.15 × 0.15
space group	$P2_1/n$	$C2/c$	$P2_12_12_1$
a, Å	13.380(1)	30.513(4)	9.968(1)
b, Å	24.361(1)	9.858(1)	15.070(1)
c, Å	14.360(1)	25.093(4)	17.178(1)
β, deg	95.314(1)	90.37(1)	
V, Å^3	4595.9(5)	7547.7(17)	2580.4(3)
Z	4	8	4
ρ_{calcd}, mg/m^3	1.472	1.594	1.605
ρ_{meas}, mg/m^3	1.466(1)	1.637(12)	1.676(2)
μ, mm^{-1}	1.362	1.688	2.214
F(000)	2040	3608	1232
θ range, deg	4.53 to 25.58	2.09 to 24.98	3.41 to 25.99
index ranges	$-15 \le h \le 15$ $-29 \le k \le 29$ $-17 \le l \le 17$	$-1 \le h \le 36$ $-1 \le k \le 11$ $-29 \le l \le 29$	$-12 \le h \le 12$ $-16 \le k \le 16$ $-21 \le l \le 21$
no. of reflns collcd	61416	7946	36231
completeness to θ_{max}	97.1	100.0	94.9
no. of indep reflns/R_{int}	8316/0.053	6635/0.018	4871/0.066
no. of reflns obsd with ($I > 2\sigma(I)$)	4698	4106	3769
abs corrn	nm[a]	ψ-scan	nm[a]
T_{max}/T_{min}		1.00/0.825	
no. of refined params	493	399	238
GOF (F^2)	0.855	1.020	0.942
$R1$ (F) ($I > 2\sigma(I)$)	0.0612	0.1000	0.0502
$wR2$ (F^2) (all data)	0.0321	0.0388	0.0265
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001
largest diff. peak/hole, e/Å^3	0.372/−0.343	0.536/−0.398	0.372/−0.594

[a] nm = not measured.

Table 3. Selected Interatomic Bond Distances (Å) and Angles (deg) for 5, 7, and 10

	compound		
	5 X = Cl(3); Y(1) = Cl(1); Y(2) = Cl(2)	**7** X = F(1); Y(1) = Cl(1); Y(2) = Cl(2)	**10** X = Cl(1); Y(1) = O(1); Y(2) = Cl(2)
Bond Distances			
Sn(1)−X	2.7414(11)	2.139(3)	2.6108(13)
Sn(2)−X	2.8027(10)	2.213(3)	2.7831(13)
Sn(1)−Y(1)	2.5267(11)	2.608(2)	2.236(3)
Sn(2)−Y(2)	2.4762(11)	2.532(2)	2.4831(13)
Sn(1)−C(1)	2.139(4)	2.152(5)	2.150(4)
Sn(1)−C(7)	2.127(3)	2.129(6)	2.115(5)
Sn(1)−C(8)	2.128(3)	2.119(7)	2.109(4)
Sn(2)−C(2)	2.153(3)	2.171(4)	2.163(4)
Sn(2)−C(9)	2.116(3)	2.127(6)	2.113(5)
Sn(2)−C(10)	2.109(4)	2.113(5)	2.115(5)
Bond Angles			
X−Sn(1)−Y(1)	177.44(3)	177.82(9)	176.87(8)
C(1)−Sn(1)−C(7)	126.20(14)	117.1(2)	117.73(18)
C(1)−Sn(1)−C(8)	110.5(2)	123.5(2)	119.56(17)
C(7)−Sn(1)−C(8)	122.7(2)	118.8(3)	122.7(2)
C(1)−Sn(1)−Y(1)	94.64(10)	95.17(12)	90.52(13)
C(7)−Sn(1)−Y(1)	90.64(11)	90.0(2)	87.71(18)
C(8)−Sn(1)−Y(1)	92.96(12)	92.0(2)	89.90(16)
C(1)−Sn(1)−X	87.32(10)	86.95(14)	90.32(11)
C(7)−Sn(1)−X	86.87(11)	88.7(2)	89.22(16)
C(8)−Sn(1)−X	87.88(12)	87.3(2)	92.31(14)
C(2)−C(1)−Sn(1)	127.3(2)	122.0(3)	126.2(3)
C(6)−C(1)−Sn(1)	114.8(3)	120.2(3)	115.8(3)
X−Sn(2)−Y(2)	178.84(4)	177.68(9)	175.54(5)
C(2)−Sn(2)−C(9)	121.00(14)	119.6(2)	116.59(18)
C(2)−Sn(2)−C(10)	116.2(2)	116.6(2)	119.88(18)
C(9)−Sn(2)−C(10)	121.3(2)	121.8(2)	121.9(2)
C(2)−Sn(2)−Y(2)	93.81(9)	96.81(14)	97.00(11)
C(9)−Sn(2)−Y(2)	93.00(12)	92.2(2)	92.66(16)
C(10)−Sn(2)−Y(2)	95.21(13)	95.2(2)	93.14(17)
C(2)−Sn(2)−X	85.29(9)	85.0(2)	86.84(11)
C(9)−Sn(2)−X	86.85(12)	85.7(2)	83.58(16)
C(10)−Sn(2)−X	85.85(13)	85.3(2)	86.85(17)
C(1)−C(2)−Sn(2)	126.3(3)	123.6(3)	126.7(3)
C(3)−C(2)−Sn(2)	115.0(3)	117.0(3)	114.5(3)
Sn(1)−X−Sn(2)	91.66(3)	119.56(13)	94.83(4)

and in **7** by 0.089(4) Å (Sn(1)) and 0.174(4) Å (Sn(2)) in direction of the terminal chlorine atoms Cl(1) and Cl(2), respectively.

In **5** the Sn(1)−Cl(3)-Sn(2) bridge is slightly asymmetric with Sn(1)−Cl(3) 2.7414(11) Å and Sn(2)−Cl(3) 2.8027(10) Å. Consequently, the Sn(1)−Cl(1) distance of 2.5267(11) Å is greater than the Sn(2)−Cl(2) distance of 2.4762(11) Å. A similar asymmetry of a Sn−Cl−Sn bridge was previously reported for $[(Ph_2ClSnCH_2)_2{\cdot}Cl]^-[(Ph_3P)N]^+$.[3c] In contrast to the latter compound, the C(1), C(2), Sn(1), and Sn(2) atoms in **5** lie within a plane from which the bridging Cl(3) is displaced by 1.512(2) Å.

With bond distances of Sn(1)−F(1) 2.139(3) Å and Sn(2)−F(1) 2.213 Å for the Sn(1)−F(1)-Sn(2) bridge, **7** shows a greater asymmetry than **5** and the related compound $[(Ph_2ClSnCH_2)_2{\cdot}F]^-[Et_4N]^+$.[3f] This can be explained by the interaction between K(1) and Cl(1) causing Cl(1)−Sn(1) (2.608(2) Å) to be greater than Sn(2)−Cl(2) (2.532(2) Å). In contrast to the related complex $[(Ph_2ClSnCH_2)_2{\cdot}F]^-[Et_4N]^+$ the C(1), C(2), Sn(1), and Sn(2) atoms in **7** lie within a plane from which the bridging F(1) is displaced by only 0.3776(4) Å.

The crystal structure of the neutral complex **10** confirms the conclusion drawn from the low-temperature ^{119}Sn NMR measurement. The HMPA molecule acts as a monodentate donor toward the Sn(1) atom whereas the Cl(1) atom bridges the two tin centers unsymmetrically (Sn(1)−C(1) 2.6108(13) Å; Sn(2)−Cl(1) 2.7831(13) Å). Nevertheless, the asymmetry is smaller than that for related complexes $(Ph_2ClSnCH_2)_2{\cdot}(Me_2N)_3PO$ and $(Ph_2ClSn)_2CH_2{\cdot}(Me_2N)_3PO$ and is caused by the rigid *o*-benzene spacer.[3a,c] Both tin atoms are inequivalent and display distorted trigonal bipyramidal geometries with the axial positions being occupied by O(1), Cl(1) for Sn(1) and Cl(1), Cl(2) for Sn(2). The carbon atoms C(1), C(7), C(8) (for Sn(1)) and C(2), C(9), C(10) (for Sn(2)) define the equatorial planes. The tin atoms in **10** are displaced from these planes by 0.023(3) Å (for Sn(1) in direction of Cl(1)) and 0.157(3) Å (for Sn(2) in direction of Cl(2)), respectively. In analogy to **5**, the atoms C(1), C(2), Sn(1), and Sn(2) lie within a plane from which the bridging Cl(1) is displaced by 1.188(3) Å. The Sn(1)−O(1) distance of 2.236(3) Å is comparable with the Sn−O distance found in $(Ph_2ClSnCH_2)_2{\cdot}(Me_2N)_3PO$.[3c]

Conclusion. Linking together organotin compounds results in new and potent Lewis acids. Ditin compounds separated by two carbon atoms readily form 1:1 adducts with a variety of Lewis bases including chloride and fluoride. The stability of these adducts is apparently affected not only by the Lewis acidity of the two tin centers but is also assisted by formation of particularly stable five-membered chelate rings. These results form a basis for development of new organotin polydentate Lewis acids capable of greater selectivity toward Lewis acids such as halides.

Experimental Section

General Methods. All reactions were carried out under an atmosphere of dry nitrogen. The solvents were purified by distillation from appropriate drying agents under nitrogen. The tetraalkylammonium fluorides, 18-crown-6, dibenzo-18-crown-6, $(Ph_3P)_2NCl$, HMPA, and tin tetrachloride were commercial products.

The density of the crystals was measured using a Micromeritics Accu Pyc 1330. Elemental analyses were performed on a LECO-CHNS-932 analyzer.

NMR Spectroscopy. NMR spectra were recorded on Bruker DRX400 and Bruker DPX300 FT NMR spectrometers with broad band decoupling of ^{119}Sn at 149.21 and 111.92 MHz, respectively, ^{19}F at 282.41 and 376.50 MHz, and ^{13}C at 100.61 MHz, using external and internal deuterium locks. ^{1}H, ^{13}C, ^{19}F, and ^{119}Sn NMR chemical shifts δ are given in ppm and referenced to external Me_4Sn (^{119}Sn), $CFCl_3$ (^{19}F), and Me_4Si (^{13}C, ^{1}H), respectively. Temperatures were maintained using a Bruker control system. The complexes for NMR investigations were generally prepared *in situ*, and the concentrations of the organotin halides were typically about 0.1−0.2 M.

Electrospray Mass Spectrometry. Electrospray mass spectra were obtained with a Platform II single quadrupole mass spectrometer (Micromass, Altrincham, UK) 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 $\mu L\ min^{-1}$. 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}. Typically, 10 signal-averaged spectra were collected.

Synthesis of 1,2-Bis(trimethylstannyl)benzene, *o*-$C_6H_4(SnMe_3)_2$ (1). 1,2-Dichlorobenzene (22.6 g, 154 mmol) was added dropwise at −78 °C to a magnetically stirred solution of trimethylstannylsodium prepared from hexamethyldistannane (50.4 g, 160 mmol), sodium (7.36 g, 320 mmol), and a catalytical amount of naphthalene (2.5 g, 20 mmol) in 300 mL of THF. The mixture was stirred for 2 h at −78 °C, 16 h at room temperature, and 24 h under reflux. Two-thirds of the THF was distilled off, and 120 mL of diethyl ether was added. After hydrolysis and filtration of the reaction mixture, the organic layer was separated, dried over Na_2SO_4, and filtered. The solvent was evaporated and naphthalene was removed by sublimation *in vacuo* (5×10^{-3} Torr, 100 °C). Distillation of the residue *in vacuo* afforded 42 g (67%) of *o*-$C_6H_4(SnMe_3)_2$ (**1**) as colorless liquid, bp 120 °C (5×10^{-3} Torr). ^{119}Sn{^{1}H} NMR (CH_2Cl_2): δ −33.2 ($^{3}J(^{119}Sn-^{117}Sn) = 220$ Hz, $^{1}J(^{119}Sn-^{13}C_{Me}) = 340$ Hz). ^{1}H NMR ($CDCl_3$): δ 0.29 (s, $^{2}J(^{1}H-^{119/117}Sn) = 53/51$ Hz, 18H, CH_3), 7.2−7.3 (m, 2H, Ph), 7.4−7.6 (m, 2H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ −7.0 ($^{1}J(^{13}C-^{119}Sn) = 340$ Hz, CH_3), 127.6 ($^{3}J(^{13}C-^{119}Sn) = 47$ Hz, C_{aryl}), 138.8 ($^{2}J(^{13}C-^{119}Sn) = 63$ Hz, $^{3}J(^{13}C-^{119}Sn) = 48$ Hz, C_{aryl}), 151.7 ($^{1}J(^{13}C-^{119/117}Sn) = 515/494$ Hz, $^{2}J(^{13}C-^{119}Sn) = 72$ Hz, C_{aryl}).

Synthesis of 1,2-Bis(dimethylchlorostannyl)benzene, *o*-$C_6H_4(SnClMe_2)_2$ (2). Dimethyltin dichloride (16.46 g, 74.91 mmol) was added at room temperature to 1,2-bis(trimethylstannyl)benzene (**1**) (15.12 g, 37.45 mmol). The mixture was magnetically stirred at 60 °C for 4 days, and trimethyltin chloride formed was removed by sublimation *in vacuo* (5×10^{-3} Torr, 100 °C). The residue was dissolved in 50 mL of dichloromethane and filtered. The solvent was removed *in vacuo*, and the residue was refluxed in 500 mL of hexane. After filtration of the hot mixture, the filtrate was stored at −30 °C for 1 day. A precipitate formed which was filtered and washed twice with cold hexane to give 10.4 g (62%) of *o*-$C_6H_4(SnClMe_2)_2$ (**2**) as colorless amorphous solid, mp 87−90 °C. ^{119}Sn{^{1}H} NMR (CH_2Cl_2): δ 81.4 ($^{3}J(^{119}Sn-^{117}Sn) = 307$ Hz). ^{1}H NMR ($CDCl_3$): δ 0.91 (s, $^{2}J(^{1}H-^{119/117}Sn) = 61/59$ Hz, 12H, CH_3), 7.3−7.5 (m, 2H, Ph), 7.7−7.9 (m, 2H, Ph). ^{13}C{^{1}H} NMR ($CDCl_3$): δ 1.89 ($^{1}J(^{13}C-^{119/117}Sn) = 408/389$ Hz, CH_3), 129.4 ($^{3}J(^{13}C-^{119}Sn) = 58$ Hz, $^{4}J(^{13}C\text{-}^{119}Sn) = 15$ Hz, C_{aryl}), 136.9 ($^{2}J(^{13}C-^{119}Sn) = 73$ Hz, $^{3}J(^{13}C-^{119}Sn) = 63$ Hz, C_{aryl}), 150.0 ($^{1}J(^{13}C-^{119/117}Sn) = 591/564$ Hz, $^{2}J(^{13}C-^{119}Sn) = 76$ Hz, C_{aryl}). Anal. Calcd for $C_{10}H_{16}Cl_2Sn_2$ (444.52): C, 27.0; H, 3.6. Found: C, 27.9; H, 3.8.

Synthesis of 1,2-Bis(methyldichlorostannyl)benzene, *o*-$C_6H_4(SnCl_2Me)_2$ (3). Tin tetrachloride (13.60 g, 52.22 mmol) was added dropwise at 0 °C to 1,2-bis(trimethylstannyl)benzene (**1**) (10.54 g, 26.11 mmol). The mixture was magnetically stirred at 70 °C for 4 days, and the dimethyltin dichloride formed was removed by sublimation *in vacuo* (5×10^{-3} Torr, 100 °C). The residue was dissolved in 50 mL of dichloromethane, and a dark brown solid was filtered off. The solvent was removed *in vacuo*, and the light brown residue was refluxed in 500 mL of hexane. After filtration of the hot reaction mixture, the solvent was removed and 50 mL of hexane were added to the residue. This mixture was treated at 50 °C for 6 h in an ultrasonic bath. The resulting suspension was stored at −30 °C for 1 day. The precipitate was filtered, washed twice with cold hexane, and dried *in vacuo* to yield 5.0 g (40%) of *o*-$(MeCl_2Sn)_2C_6H_4$ (**3**) as colorless amorphous solid, mp 110−112 °C. $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2): δ 24.0 ($^3J(^{119}Sn-^{117}Sn) = 595$ Hz). ^1H NMR ($CDCl_3$): δ 1.60 (s, $^2J(^1H-^{119/117}Sn) = 79/76$ Hz, 6H, CH_3), 7.5−7.7 (m, 2H, Ph), 7.8−8.1 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 14.1 ($^1J(^{13}C-^{119/117}Sn) = 612/630$ Hz, CH_3), 130.5 ($^3J(^{13}C-^{119}Sn) = 78$ Hz, $^4J(^{13}C-^{119}Sn) = 19$ Hz, C_{aryl}), 136.7 ($^2J(^{13}C-^{119}Sn) = 98$ Hz, $^3J(^{13}C-^{119}Sn) = 66$ Hz, C_{aryl}), 150.7 ($^1J(^{13}C-^{119/117}Sn) = 886/847$ Hz, $^2J(^{13}C-^{119}Sn) = 94$ Hz, C_{aryl}). Anal. Calcd for $C_8H_{10}Cl_4Sn_2$ (485.36): C, 19.8; H, 2.1. Found: C, 20.0; H, 2.2.

Synthesis of 1,2-Bis(dimethylfluorostannyl)benzene, *o*-$C_6H_4(SnFMe_2)_2$ (4). A solution of 1,2-bis(dimethylchlorostannyl)benzene (**2**) (1.00 g, 2.25 mmol) in 20 mL of ether was added dropwise to a magnetically stirred solution of KF (523 mg, 9.00 mmol) in 10 mL of water, and the stirring was continued overnight. The colorless precipitate was filtered and washed twice with water, ethanol, and ether to give 0.65 g (70%) of *o*-$C_6H_4(SnFMe_2)_2$ (**4**) as a colorless amorphous solid, mp > 300 °C. Anal. Calcd for $C_{10}H_{16}F_2Sn_2$ (411.61): C, 29.2; H, 3.9. Found: C, 29.4; H, 4.0.

Synthesis of Bis(triphenylphosporanylidene)ammonium-1,2-bis(dimethylchlorostannyl)benzene Chloride, $[o\text{-}C_6H_4(SnClMe_2)_2\cdot Cl]^-$ $[(Ph_3N)_2P]^+$ (5). 1,2-Bis(dimethylchlorostannyl)benzene (**2**) (306 mg, 0.69 mmol) was dissolved in 10 mL of dichloromethane, and $(Ph_3P)_2NCl$ (395 mg, 0.69 mmol) was added under magnetic stirring. The solution was stirred for 1 h and filtered. Hexane was added to the filtrate, and slow evaporation of the dichloromethane afforded 605 mg (86%) of $[o\text{-}C_6H_4(SnClMe_2)_2\cdot Cl]^-[(Ph_3N)_2P]^+$ (**5**) as colorless crystals, mp 197−200 °C. $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2): δ −78.3. ^1H NMR ($CDCl_3$): δ 0.93 (s, $^2J(^1H-^{119/117}Sn) = 72/69$ Hz, 12H, CH_3), 7.1−7.2 (m, 2H, PhSn), 7.3−7.7 (m, 30H, PhN), 8.2−8.3 (m, 2H, PhSn). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 7.7 ($^1J(^{13}C-^{119/117}Sn) = 530/506$ Hz, CH_3), 125.0−132.0 (4 signals with ^{31}P coupling, PhN), 133.4 (C_{aryl}), 137.6 ($^2J(^{13}C-^{119}Sn) = 80$ Hz, $^3J(^{13}C-^{119}Sn) = 57$ Hz, C_{aryl}), 154.5 ($^2J(^{13}C\text{-}^{119}Sn) = 85$ Hz, C_{aryl}). $\rho_{exptl} = 1.466$ g/cm^3. Anal. Calcd for $C_{46}H_{46}Cl_3NP_2Sn_2$ (1018.51): C, 54.2; H, 4.6; N, 1.4. Found: C, 54.6; H, 4.6; N, 1.4.

Synthesis of Tetraethylammonium-1,2-bis(dimethylchlorostannyl)benzene Fluoride, $[o\text{-}C_6H_4(SnClMe_2)_2\cdot F]^-$ $[Et_4N]^+$ (6). 1,2-Bis(dimethylchlorostannyl)benzene (**2**) (331 mg, 0.74 mmol) was dissolved in 10 mL of dichloromethane and $Et_4NF\cdot 2H_2O$ (138 mg, 0.74 mmol) added under magnetic stirring. The solution was stirred for 2 h and filtered. Hexane was added to the filtrate, and slow evaporation of the dichloromethane afforded 370 mg (84%) of $[o\text{-}C_6H_4(SnClMe_2)_2\cdot F]^-$ $[Et_4N]^+$ (**6**) as an amorphous solid, mp 127−130 °C. $^{119}Sn\{^1H\}$ NMR (CH_2Cl_2): δ −100.7 (d, $^1J(^{119}Sn-^{19}F) = 1107$ Hz). $^{19}F\{^1H\}$ NMR (CH_2Cl_2): δ −137.08 ($^1J(^{19}F-^{119}Sn) = 1100$ Hz). ^1H NMR ($CDCl_3$): δ 0.69 (s, $^2J(^1H-^{119}Sn) = 71$ Hz, 12H, CH_3), 1.18 (t, 12H, NCH_2CH_3), 3.00 (q, 8H, NCH_2), 7.2−7.4 (m, 2H, Ph), 8.4−8.6 (m, 2H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 4.3 (CH_3), 7.3 (NCH_2CH_3), 52.2 (NCH_2), 127.7 ($^3J(^{13}C-^{119}Sn) = 62$ Hz, C_{aryl}), 137.3 ($^2J(^{13}C-^{119}Sn) = 81$ Hz, $^3J(^{13}C-^{119}Sn) = 62$ Hz, C_{aryl}), 152.5 (C_{aryl}). Anal. Calcd for $C_{18}H_{36}NFCl_2Sn_2$ (593.77): C, 36.4; H, 6.1; N, 2.4. Found: C, 36.8; H, 6.2; N, 2.3.

Synthesis of Potassium Dibenzo-18-crown-6−1,2-bis(dimethylchlorostannyl)benzene Fluoride, $[o\text{-}C_6H_4(SnClMe_2)_2\cdot F]^-[K\cdot C_{20}H_{24}O_6]^+$ (7). A suspension of 1,2-bis(dimethylchlorostannyl)benzene (**2**) (220 mg, 0.495 mmol), potassium fluoride (29 mg, 0.495 mmol), and dibenzo-18-crown-6 (178 mg, 0.495 mmol) in 10 mL of dichloromethane was magnetically stirred overnight. The clear solution was filtered, and hexane was added to the filtrate. Slow evaporation of the dichloromethane afforded 305 mg (72%) of $[o\text{-}C_6H_4(SnClMe_2)_2\cdot F]^-$ $[K\cdot C_{20}H_{24}O_6]^+$ (**7**) as colorless crystals, mp 136−140 °C. ^1H NMR ($CDCl_3$): δ 0.68 ($^2J(^1H-^{119}Sn) = 72$ Hz, 12H, CH_3), 3.96 (8H, OCH_2), 4.11 (8H, OCH_2), 6.8−6.9 (4H, $Ph_{18-crown-6}$), 6.9−7.0 (4H, $Ph_{18-crown-6}$), 7.05−7.15 (2H, Ph), 8.3−8.5 (2H, Ph). $\rho_{exptl} = 1.637$ g/cm^3. Anal. Calcd for $C_{30}H_{40}O_6FKCl_2Sn_2$ (863.02): C, 41.8; H, 4.7. Found: C, 40.4; H, 4.6. Crystal structure determination shows 0.5 molar equiv of dichloromethane in the elemental cell and ^1H NMR ($\delta = 5.28$ ppm (s, 1H, CH_2Cl_2) supporting this. Anal. Calcd for $C_{30}H_{40}O_6FKCl_2Sn_2\cdot 0.5CH_2Cl_2$ (905.49): C, 40.5; H, 4.6.

Synthesis of Tetraethylammonium-1,2-bis(dimethylfluorostannyl)benzene Fluoride, $[o\text{-}C_6H_4(SnFMe_2)_2\cdot F]^-$ $[Et_4N]^+$ (8). A suspension of 1,2-bis(dimethylfluorostannyl)benzene (**4**) (161 mg, 0.391 mmol) and $Et_4NF\cdot 2H_2O$ (72 mg, 0.391 mmol) in 2 mL of dichloromethane was magnetically stirred for 3 h. The clear solution was filtered, and evaporation of the solvent afforded 156 mg (71%) of $[o\text{-}C_6H_4(SnFMe_2)_2\cdot F]^-$ $[Et_4N]^+$ (**8**) as a colorless amorphous solid, mp 181−183 °C. $^{119}Sn\{^1H\}$ NMR (CD_2Cl_2): δ −138.3 (dd, $^1J(^{119}Sn-^{19}F_I) = 1954$ Hz, $^1J(^{119}Sn-^{19}F_{II}) = 1187$ Hz). $^{19}F\{^1H\}$ NMR (CD_2Cl_2): δ −126.8 (t, $^1J(^{19}F_{II}-^{119}Sn) = 1172$ Hz, $^2J(^{19}F_{II}-^{19}F_I) = 84$ Hz, 1F, F_{II}), −155.4 (d, $^1J(^{19}F_I-^{119}Sn) = 1912$ Hz, $^2J(^{19}F_I-^{19}F_{II}) = 83$ Hz, 2F, F_I). ^1H NMR ($CDCl_3$): δ 0.42 (s, $^2J(^1H-^{119}Sn) = 73$ Hz, 12H, CH_3), 1.02 (t, 12H, NCH_2CH_3), 2.86 (q, 8H, NCH_2), 7.1−7.2 (2H, Ph), 7.9−8.1 (2H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −0.22 (t, $^1J(^{13}C-^{119}Sn) = 581$ Hz, $^2J(^{13}C-^{19}F) = 19$ Hz, CH_3), 7.0 (NCH_2CH_3), 51.9 (NCH_2), 126.1 (C_{aryl}), 135.6 (C_{aryl}), 152.0 (C_{aryl}). Anal. Calcd for $C_{18}H_{36}NF_3Sn_2$ (560.96): C, 38.5; H, 6.5; N, 2.5. Found: C, 38.8; H, 6.6; N, 2.4.

Synthesis of Potassium 18-Crown-6-1,2-bis(dimethylfluorostannyl)benzene Fluoride, $[o\text{-}C_6H_4(SnFMe_2)_2\cdot F]^-$-$[K\cdot C_{12}H_{24}O_6]^+$ (9). A suspension of 1,2-bis(dimethylfluorostannyl)benzene (**4**) (150 mg, 0.364 mmol), potassium fluoride (21 mg, 0.364 mmol) and 18-crown-6 (96 mg, 0.364 mmol) in 10 mL of dichloromethane was magnetically stirred for 3 h. The clear solution was filtered, and hexane was added to the filtrate. Slow evaporation of the dichloromethane afforded 180 mg (67%) of $[o\text{-}C_6H_4(SnFMe_2)_2\cdot F]^-[K\cdot C_{12}H_{24}O_6]^+$ (**9**) as a colorless amorphous solid, mp 206−209 °C. $^{119}Sn\{^1H\}$ NMR (pyridine-*d*$_5$): δ −146.6 (dd, $^1J(^{119}Sn-^{19}F_I) = 1980$ Hz, $^1J(^{119}Sn-^{19}F_{II}) = 1218$ Hz). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −129.8 (t, $^1J(^{19}F_{II}-^{119}Sn) = 1232$ Hz, $^2J(^{19}F_{II}-^{19}F_I) = 84$ Hz, 1F, F_{II}), −160.3 (d, $^1J(^{19}F_I-^{119}Sn) = 1892$ Hz, $^2J(^{19}F_I-^{19}F_{II}) = 81$ Hz, 2F, F_I). ^1H NMR ($CDCl_3$): δ 0.43 (s, $^2J(^1H-^{119}Sn) = 74$ Hz, 12H, CH_3), 3.58 (t, 24H, OCH_2), 7.2.-7.3 (2H, Ph), 8.0−8.2 (2H, Ph). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ −0.04 (t, $^1J(^{13}C-^{119}Sn) = 587$ Hz, $^2J(^{13}C-^{19}F) = 20$ Hz, CH_3), 69.7 (OCH_2), 127.2 (C_{aryl}), 136.5 (C_{aryl}), 154.3 (C_{aryl}). Anal. Calcd for $C_{22}H_{40}O_6F_3KSn_2$ (736.05): C, 36.0; H, 5.5. Found: C, 36.3; H, 5.5.

Synthesis of the HMPA Complex of 1,2-Bis(dimethylchlorostannyl)benzene, *o*-$C_6H_4(SnClMe_2)_2\cdot(Me_2N)_3PO$ (10). To a solution of HMPA (157 mg, 0.877 mmol) in 3 mL of CH_2Cl_2 was added a solution of 1,2-bis(dimethylchlorostannyl)benzene (**2**) (390 mg, 0.877 mmol) in 3 mL of CH_2Cl_2. After 2 h of stirring, the solvent was removed *in vacuo*, and the oily residue was dissolved in 25 mL of diethyl ether. Slow evaporation of the solvent afforded 440 mg (81%) of *o*-$C_6H_4(SnClMe_2)_2\cdot(Me_2N)_3PO$ (**10**) as a crystalline solid, mp 143−147 °C. $^{119}Sn\{^1H\}$ NMR (−80 °C, CD_2Cl_2): δ −52.9 (s, 1Sn), −98.9 (d, $^2J(^{119}Sn-^{31}P) = 140$ Hz, 1Sn). ^{31}P NMR $\{^1H\}$ (−80 °C, CD_2Cl_2): δ 25.5 (s, $^2J(^{31}P-^{119}Sn) = 135$ Hz). ^1H NMR (RT, $CDCl_3$) δ 0.90 (s, $^2J(^1H-^{119/117}Sn) = 69/66$ Hz, 12H, CH_3), 2.56 (d,

$^3J(^1\mathrm{H}-^{31}\mathrm{P}) = 10$ Hz, 18H, NCH$_3$), 7.2−7.4 (2H, Ph), 7.8−8.1 (2H, Ph). ^{13}C{^{1}H} NMR (RT, CDCl$_3$) δ 5.8 ($^1J(^{13}\mathrm{C}-^{119/117}\mathrm{Sn}) = 523/500$ Hz, CH$_3$), 36.7 (NCH$_3$), 127.7 ($^3J(^{13}\mathrm{C}-^{119}\mathrm{Sn}) = 61$ Hz, $^4J(^{13}\mathrm{C}-^{119}\mathrm{Sn}) = 16$ Hz, C$_{\mathrm{aryl}}$), 137.0 ($^2J(^{13}\mathrm{C}-^{119}\mathrm{Sn}) = 83$ Hz, $^3J(^{13}\mathrm{C}-^{119}\mathrm{Sn}) = 56$ Hz, C$_{\mathrm{aryl}}$), 153.4 ($^2J(^{13}\mathrm{C}-^{119}\mathrm{Sn}) = 84$ Hz, C$_{\mathrm{aryl}}$). IR (KBr) $\nu_{\mathrm{P=O}} = 1130$. IR (5% CHCl$_3$) $\nu_{\mathrm{P=O}} = 1144$ cm^{-1}. $\rho_{\mathrm{exptl}} = 1.677$ g/cm^3. Anal. Calcd for $C_{16}H_{34}Cl_2N_3OPSn_2$ (623.71): C, 30.8; H, 5.5; N, 6.7. Found: C, 30.9; H, 5.6; N, 6.8.

Reaction of 1,8-Bis(trimethylstannyl)naphthalene, $C_{10}H_6$-1,8-(SnMe$_3$)$_2$, with Dimethyldichlorostannane, Me$_2$SnCl$_2$. Dimethyltin dichloride (4.12 g, 18.73 mmol) was added at room temperature to 1,8-bis(trimethylstannyl)naphthalene (4.25 g, 9.37 mmol). The mixture was magnetically stirred at 60 °C for 1 day. A mixture of dimethyltin dichloride and trimethyltin chloride (4.22 g; ratio 1:2) was removed by sublimation *in vacuo* (5×10^{-3} Torr, 100 °C). The resulting black residue was recrystallized from THF to give 1.20 g (48%) of 7,7,14,14-tetramethyldinaphtho[1,8-*bc*:1′,8′-*fg*][1,5]distannocine[17] as the major product, mp 276−280 °C (lit.[17] 272−274 °C). ^{119}Sn{^{1}H} NMR (CH$_2$Cl$_2$): δ −62.3. ^{1}H NMR (CDCl$_3$): δ 0.50 (s, $^2J(^1\mathrm{H}-^{119/117}\mathrm{Sn}) = 53/51$ Hz, 12H, CH$_3$), 7.41 (dd, 4H, H-3), 7.75 (d, 4H, H-4), 7.80 (d, 4H, H-2). ^{13}C{^{1}H} NMR (CDCl$_3$): δ −2.8 ($^1J(^{13}\mathrm{C}-^{119/117}\mathrm{Sn}) = 369/352$ Hz, CH$_3$), 124.8 ($^3J(^{13}\mathrm{C}-^{119}\mathrm{Sn}) = 55$ Hz, C$_3$), 130.1 (C$_4$), 136.9 ($^2J(^{13}\mathrm{C}-^{119}\mathrm{Sn}) = 33$ Hz, C$_2$), 146.6 (C$_1$).

Crystallography. Crystals of $[o\text{-}C_6H_4(SnClMe_2)_2\cdot Cl]^-[(Ph_3P)_3N]^+$ (**5**) and $[o\text{-}C_6H_4(SnClMe_2)_2\cdot F]^-[K\cdot C_{20}H_{24}O_6]^+$ (**7**) were grown from a CH$_2$Cl$_2$/hexane solution and of o-C$_6$H$_4$-(SnClMe$_2$)$_2\cdot$(Me$_3$N)$_3$PO (**10**) from a CDCl$_3$ solution by slow evaporation. Intensity data for the colorless crystals were collected on a Nonius MACH3 (**5**) and KappaCCD (**7** and **10**) diffractometer with graphite-monochromated Mo Kα radiation at 291 K. Three standard reflections were recorded every 60 min (**5**), and an anisotropic intensity loss up to 1.9% (**5**) was detected during X-ray exposure. The data collections for (**5** and **10**) covered almost the whole sphere of reciprocal space with 360 frames via ω-rotation ($\Delta/\omega = 1°$) at two times 5s (**5**) and 10s (**10**) per frame. The crystal-to-detector distance was 2.6 cm (**5**) and 2.6 cm (**10**). Crystal decay was monitored by repeating the initial frames at the end of data collection. Analyzing the duplicate reflections there was no indication for any decay (**5** and **10**). The structures were solved by direct methods SHELXS86[21a] and successive difference Fourier syntheses. Refinement-applied full-matrix least-squares methods SHELXL93[21b] and SHELXL97.[21c]

The absolute configuration for **10** could not be determined by refinement of the Flack[21d] parameter 0.36(2). The correctness of the absolute configuration was deduced from the X-ray data by comparison of the *R*-values of this and the inverted structure.

The H atoms were placed in geometrically calculated positions using riding model and refined with common isotropic temperature factors for different C−H types (C$_{\mathrm{primary}}$−H 0.96 Å, C$_{\mathrm{sec}}$ −H 0.97 Å U_{iso} 0.139(5) (**5**), 0.136(5) (**7**), 0.162(6) (**10**) Å^2; C$_{\mathrm{aryl}}$−H 0.93 Å, U_{iso} 0.075(2) (**5**), 0.113(7) (**7**), 0.142(8) (**10**) Å^2).

Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from ref 21e. Figures were created by SHELXTL-Plus.[21f] Crystallographic data are given in Table 2. Selected bond lengths [Å] and angles [°] are listed in Table 3.

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Supporting Information Available: Tables of all coordinates, anisotropic displacement parameters, and geometric data for compounds **5**, **7**, and **10** (21 pages). Ordering information is given on any current masthead page.

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