[*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$]: Synthesis and Complexation Behaviour of a Novel, Cyclic, Bidentate Lewis Acid and Its Conversion into a Tin-Containing Fluorosilane with Intermolecular Si–F ··· Sn Bridges[+]

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Dedicated to Professor Herbert Schumann on the occasion of his 65th birthday

Abstract: Acid-catalysed hydrolysis of [$CH_2\{Sn(Ph_2)CH_2Si(O\textit{i}Pr)Me_2\}_2$] followed by subsequent reaction with mercuric chloride in acetone afforded the novel silicon- and tin-containing eight-membered ring [*cyclo*-$CH_2\{Sn(Cl_2)$-$CH_2Si(Me_2)\}_2O$] in good yield, the crystal structure of which is reported. ^{119}Sn NMR and X-ray studies indicate that [*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] acts as a bidentate Lewis acid towards chloride ions exclusively forming the 1:1 complex $[(Ph_3P)_2N]^+$[*cyclo*-CH_2-$\{Sn(Cl_2)CH_2Si(Me_2)\}_2OCl]^-$ upon addition of $[(Ph_3P)_2N]^+Cl^-$. Also reported are the synthesis and structure of [K(dibenzo[18]crown-6)]$^+$[*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2OF]^-$, the first completely characterised organostannate with a *C_2SnCl_2F*- substituent pattern. No ring-opening polymerisation could be achieved for [*cyclo*-CH_2-$\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] or for its perphenylated derivative [*cyclo*-CH_2-$\{Sn(Ph_2)CH_2Si(Me_2)\}_2O$]. The reaction of [*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] with $Me_3O^+BF_4^-$ gave the tin-containing fluorosilane [$CH_2\{Sn(Cl_2)CH_2Si(F)$-$Me_2\}_2$], in which the Si–F bond is activated by intermolecular Si–F ··· Sn interactions in the solid state.

Keywords: anion complexation · Lewis acids · ring-opening reactions · silicon · tin

Introduction

In recent years the selective complexation of anions and neutral donor molecules by molecular hosts has been a subject of growing interest.[1–7] This general concept includes the synthesis of multidentate Lewis acids in which the active sites are part of cyclic[8–16] or noncyclic[17–38] structures. Elements which serve as the Lewis acidic centres in these host molecules are for instance B,[39–42] Al,[38, 43, 44] In,[30–35] Si,[13, 45–47] Ge,[14] Sn[8–12, 16–29] and Hg.[15, 37, 38, 48–53] More recently, bidentate Lewis acids have attracted interest as activators for transition metal based olefin polymerisation catalysts.[38, 42, 54] Also, compounds showing selectivity towards different anions have been employed in liquid membranes for the design of ion sensitive electrodes (ISE).[55] Some time ago, we and others have shown that the methylene-bridged ditin compound $(PhCl_2Sn)_2CH_2$, when incorporated into a polyethylene membrane, exhibits a remarkable selectivity towards phosphate.[25, 26] One shortcoming of this type of electrode is its short lifetime. One possibility to overcome this disadvantage might be to make the $Cl_2SnCH_2SnCl_2$-fragment part of a polymer. In continuation of our studies on tin-based bidentate[16, 22–27, 29] and multidentate[28] Lewis acids we report here on the synthesis and structure of a novel cyclic eight-membered ditin compound containing a siloxane unit and on its complexation behaviour towards chloride[27] and fluoride[56] ions. Also presented are attempts at ring-opening reactions of this eight-membered ring and its perphenylated derivative leading, however, to a novel tin-containing fluorosilane.

Results and Discussion

Synthesis and properties of [*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] (2): The reaction of bis(diphenylfluorostannyl)methane[27] with two molar equivalents of $Me_2(\textit{i}PrO)SiCH_2MgCl$[57] afforded bis{[(dimethylisopropoxysilyl)methyl]diphenylstannyl}methane (**1**) as a colourless oil in almost quantitative yield (Scheme 1).

Treatment of [$CH_2\{Sn(Ph_2)CH_2Si(O\textit{i}Pr)Me_2\}_2$] (**1**) with diluted sulfuric acid in diethyl ether resulted in a crude reaction product, the ^{29}Si NMR spectrum ($CDCl_3$) of which showed two major signals at $\delta = 9.3$ (50%, $^2J(^{117/119}Sn,^{29}Si =$

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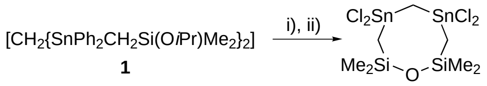
$$[CH_2(SnPh_2F)_2] \xrightarrow{i)} [CH_2\{SnPh_2CH_2Si(O\textit{i}Pr)Me_2\}_2]$$

1

Scheme 1. Synthesis of compound **1**. i) 2 Me(iPrO)SiCH$_2$MgCl (−2 MgClF).

39 Hz) and 17.5 (35 %, $^2J(^{117/119}Sn,^{29}Si = 29$ Hz), and two minor resonances at $\delta = 7.7$ and 17.2 (total integral approximately 15 % of the major signals). The ^{119}Sn NMR spectrum of the same sample displayed major signals at $\delta = -39.4$ (50 %) and −40.0 (30 %) and two minor resonances at $\delta = -40.4$ and −40.8 (total integral approximately 20 % of the major signals). The signals at $\delta = 9.3$ (^{29}Si) and −39.4 (^{119}Sn) belong to the eight-membered ring species $[CH_2\{Sn(Ph_2)CH_2Si(Me_2)\}O]$ (**5**). The signals at $\delta = 17.5$ (^{29}Si) and −40.0 (^{119}Sn) are assigned to the silanol $[CH_2\{Sn(Ph_2)CH_2Si(OH)Me_2\}_2]$, whereas the remaining resonances at $\delta = 7.7$ and 17.2 (^{29}Si) and −40.4 and −40.8 (^{119}Sn) are assigned with caution to the acyclic derivative $[\{Me_2(HO)SiCH_2Sn(Ph_2)CH_2Sn(Ph_2)CH_2Si(Me_2)\}_2O]$. None of these compounds were isolated from this reaction mixture, but the synthesis and isolation of compound **5** was achieved and is described below. Treatment of the crude product in acetone with two molar equivalents of mercuric chloride per tin provided, after working up, the eight-membered ring species $[CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}O]$ (**2**) in 72 % yield (Scheme 2). From this high yield it is apparent that both the cyclosiloxane derivative **5** and the open-chain compound $[CH_2\{Sn(Ph_2)CH_2Si(OH)Me_2\}_2]$ are transformed into the tin-functionalised cyclosiloxane derivative **2**. Compound **2** is a colorless crystalline solid that is soluble in dichloromethane, diethyl ether and benzene, but almost insoluble in hexane. Cyclic organotin compounds containing one tin atom and an Si-O-Si structural motif have been reported.[58, 59]



1 2

Scheme 2. Synthesis of the eight-membered ring **2**. i) 0.5 M H_2SO_4, Et_2O (−2 iPrOH); ii) 4 HgCl$_2$, acetone (−4 PhHgCl).

Abstract in German: *Aus $[CH_2\{Sn(Ph_2)CH_2Si(OiPr)Me_2\}_2]$ wurde durch säurekatalysierte Hydrolyse und Reaktion mit Quecksilberchlorid in Aceton der neuartige silicium- und zinnhaltige Achtring [cyclo-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] in guter Ausbeute erhalten und seine Struktur mittels Einkristall-röntgenstrukturanalyse bestimmt. ^{119}Sn-NMR-Studien und Untersuchungen durch Röntgenstrahlbeugung am Einkristall zeigen, dass $[CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O]$ sich gegenüber Chloridionen als bidentate Lewis-Säure verhält und mit $[(Ph_3P)_2N]^+Cl^-$ ausschliesslich unter Bildung des entsprechenden 1:1-Komplexes $[(Ph_3P)_2N]^+$[cyclo-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2OCl]^-$ reagiert. Ebenfalls berichtet wird über die Synthese und Struktur von $[K(dibenzo[18]Krone-6)]^+$[cyclo-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2OF]^-$, dem ersten vollständig charakterisierten Organostannat mit einem C_2SnCl_2F-Substitutionsmuster. Weder für [cyclo-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] noch für das perphenylierte Derivat [cyclo-$CH_2\{Sn(Ph_2)CH_2Si(Me_2)\}_2O$] gelang eine ringöffnende Polymerisation. Die Reaction von [cyclo-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] mit $Me_3O^+BF_4^-$ lieferte das zinnhaltige Organofluorsilan $[CH_2\{Sn(Cl_2)CH_2Si(F)Me_2\}_2]$. Dieses zeigt im Festkörper eine Aufweitung der Si-F-Bindung durch intermolekulare Si–F ⋯ Sn-Wechselwirkung.*

The molecular structure of **2** is shown in Figure 1. Unit cell data and refinement details are listed in Table 1. Compound **2** crystallises with two different conformers, which are connected by a weak intermolecular Cl(3) – Sn(1′) contact of 3.684(1) Å. The coordination geometry at Sn(1), Sn(2) and Sn(2′) can be best described as a monocapped tetrahedron ([4+1] coordination), with the position of the respective tin atoms along the path tetrahedron – trigonal bipyramid given by the difference of the sum of the equatorial and axial angles,[60–62] (i.e., $\Sigma\vartheta_{eq} - \Sigma\vartheta_{ax} = 17.83°$ for Sn(1), 26.29° for Sn(2) and 19.67° for Sn(2′). This configuration is realised by weak intramolecular Sn(1) ⋯ O(1), Sn(2) ⋯ O(1) and Sn(2′) ⋯ O(1′) contacts of 3.559(2), 3.074(2), and 3.184(2) Å, respectively; the approach occurs through the corresponding tetrahedral face. The intramolecular Sn ⋯ O distances are at the borderline or shorter than the sum of the van der Waals radii of tin (2.20 Å)[63] and oxygen (1.50 Å).[63] Intramolecular Sn ⋯ O contacts of 2.884(3) – 3.067(2) Å and 2.38(4) Å have been reported for compounds in which the tin and oxygen atoms are part of four-[64, 65] and five-membered[66, 67] rings, respectively. The Sn(2) – Cl(2′) distance amounts to 4.232(1) Å which is greater than the sum of the van der Waals radii of tin and chlorine (1.70 Å).[63] The Cl(2)-Sn(1)-O(1), Cl(3)-Sn(2)-O(1), and Cl(3′)-Sn(2′)-O(1′) angles amount to 139.26(4), 167.53(5), and 169.34(5)°, respectively, the deviations of these angles from the ideal value of 180° being the result of ring constraints. The Sn(1′) atom of the conformer shown on the right side in Figure 1 exhibits a [4+2] coordination geometry In other words, two Sn(1′) – C(1′/7′) bonds of 2.116(3) and 2.110(3) Å and two intramolecular Sn(1′) – Cl(1′/2′) bonds of 2.3470(9) and 2.341(1) Å are accompanied by one weak intramolecular Sn(1′) ⋯ O(1′) contact of 3.061(2) Å and one weak intermolecular Sn(1′) ⋯ Cl(3) contact of 3.684(1) Å with the last distance being shorter than the sum of the van der Waals radii of tin and chlorine.[63] The Cl(1′)-Sn(1′)-Cl(3) and Cl(2′)-Sn(1′)-O(1′) angles amount to 173.26(5) and 174.00(3)°, respectively, the deviations of the angles from the ideal value of 180° again being the result of ring constraints. In both conformers of **2**, the intramolecular Sn(1/2) ⋯ O(1) and Sn(1′/2′) ⋯ O(1′) contacts are associated with Si(1)-O(1)-Si(2) and Si(1′)-O(1′)-Si(2′) angles of 145.5(2) and 144.9(1)°, respectively, which are at the lower end of a range of corresponding angles in eight-membered *cyclo*-stannasiloxanes that have no such contacts.[68, 69] The Si(1/2) – O(1) and Si(1′/2′) – O(1′) bond lengths between 1.640(2) and 1.648(2) Å are close to standard Si–O bond lengths reported in the literature[70–72] and indicate the intramolecular Sn ⋯ O contact mentioned above to be mainly electrostatic. Nevertheless, compound **2** is an interesting model substance for a Si–O bond activation by an organotin Lewis acid.

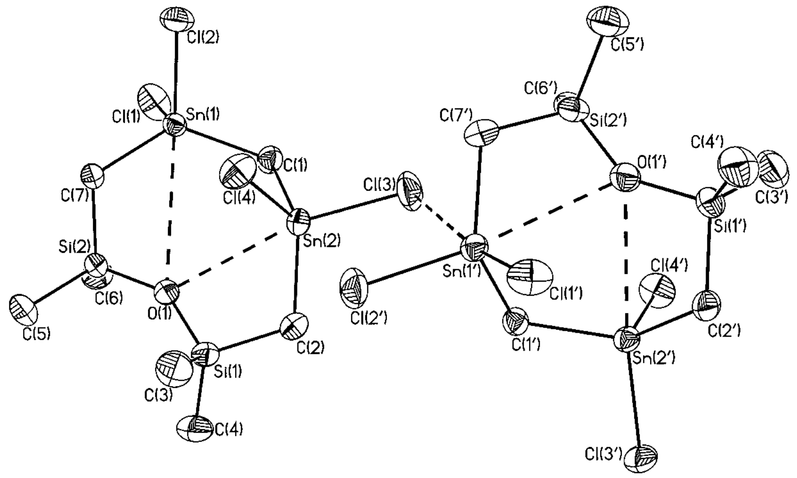


Figure 1. General view (SHELXTL) of the crystal structure of **2** showing 30% probability displacement ellipsoids and the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lenghts [Å] and angles [°]: Sn(1)–Cl(1) 2.3437(9), Sn(1)–Cl(2) 2.335(1), Sn(1)–O(1) 3.559(2), Sn(2)–Cl(3) 2.350(1), Sn(2)–Cl(4) 2.3471(9), Sn(2)–O(1) 3.074(2), Sn(1′)–Cl(1′) 2.3470(9), Sn(1′)–Cl(2′) 2.341(1), Sn(1′)–O(1′) 3.061(2), Sn(1′)–Cl(3) 3.684(1), Sn(2′)–Cl(3′) 2.339(1), Sn(2′)–Cl(4′) 2.3465(9), Sn(2′)–O(1′) 3.184(2), C(1)-Sn(1)-C(7) 125.0(1), C(1)-Sn(1)-Cl(1) 103.7(1), C(7)-Sn(1)-Cl(1) 107.33(9), C(1)-Sn(1)-Cl(2) 107.6(1), C(7)-Sn(1)-Cl(2) 109.25(9), Cl(1)-Sn(1)-Cl(2) 101.35(4), Cl(2)-Sn(1)-O(1) 139.26(4), C(1)-Sn(2)-C(2) 131.0(1), C(1)-Sn(2)-Cl(4) 99.44(9), C(2)-Sn(2)-Cl(4) 109.60(9), C(1)-Sn(2)-Cl(3) 104.0(1), C(2)-Sn(2)-Cl(3) 106.7(1), Cl(4)-Sn(2)-Cl(3) 103.05(4), Cl(3)-Sn(2)-O(1) 167.53(5), Si(1)-O(1)-Si(2) 145.5(2), C(1′)-Sn(1′)-C(7′) 126.4(1), Cl(1′)-Sn(1′)-Cl(2′) 101.19(4), Cl(1′)-Sn(1′)-Cl(3) 174.00(3), Cl(2′)-Sn(1′)-O(1′) 173.26(5), C(1′)-Sn(2′)-C(2′) 126.5(1), C(1′)-Sn(2′)-Cl(4′) 103.41(9), C(2′)-Sn(2′)-Cl(4′) 106.8(1), C(1′)-Sn(2′)-Cl(3′) 105.55(9), C(2′)-Sn(2′)-Cl(3′) 110.7(1), Cl(4′)-Sn(2′)-Cl(3′) 100.79(4), Cl(3′)-Sn(2′)-O(1′) 169.34(5), Si(1′)-O(1′)-Si(2′) 144.9(1).

The side views of the two conformers of **2** are shown in Figure 2. According to a classification scheme recently introduced[73] and applied for eight-membered rings,[68, 69] the left conformer is a F-type (000++00−) and the right conformer is a G-type (00++00++) structure.

From the solid-state structure of **2**, four ^{119}Sn cross-polarisation, magic-angle spinning (CP-MAS) resonances are to be expexted. Given the similarity of the configurations at Sn(1′) and Sn(2), and at Sn(1) and Sn(2′), only two resonances ($W\frac{1}{2} \approx 1500$ Hz) are observed at $\delta = 87$ and 114. In $CDCl_3$, however, the tin and the silicon atoms are equivalent on the respective NMR timescales, and single resonances are observed at δ (^{29}Si) = 14.2 ($^2J(^{117/119}Sn,^{29}Si) = 56/59$ Hz) and δ (^{119}Sn) = 109.0. The spectra remain virtually the same in CD_2Cl_2 at −85 °C. The eight-membered ring structure of **2** is retained in solution as was verified by molecular weight determination (calcd for **2**: $M = 554\ \mathrm{g\,mol^{-1}}$, found in CH_2Cl_2: $M = 547\ \mathrm{g\,mol^{-1}}$).

Table 1. Crystallographic data for **2**, **3**, **4a** and **6**.

	2	**3**	**4a**	**6**
formula	$C_7H_{18}Cl_4OSn_2Si_2$	$C_{44}H_{50}Cl_7OP_2NSn_2Si_2$	$C_{27}H_{43}Cl_4FO_{7.5}Sn_2Si_2K$	$C_7H_{18}Cl_4F_2Sn_2Si_2$
M_w	553.62	1212.60	990.14	575.62
crystal system	monoclinic	monoclinic	triclinic	orthorhombic
crystal size [mm]	0.15 × 0.10 × 0.10	0.20 × 0.12 × 0.10	0.40 × 0.08 × 0.08	0.12 × 0.10 × 0.10
space group	$P2_1/c$	$C2/c$	$P\bar{1}$	$Pbcn$
a [Å]	9.856(1)	43.532(1)	10.198(1)	19.726(1)
b [Å]	15.967(1)	9.522(1)	10.590(1)	8.917(1)
c [Å]	24.391(1)	33.304(1)	19.993(1)	10.994(1)
α [°]	90	90	83.163(1)	
β [°]	99.438(1)	128.904(1)	84.228(1)	
γ [°]	90	90	69.829(1)	
V [Å^3]	3786.5(5)	10743(1)	2008.2(3)	1933.8(3)
Z	8	8	2	4
ρ_{calcd} [Mg m^{-3}]	1.942	1.499	1.622	1.977
ρ_{measd} [Mg m^{-3}]	1.988(5)	1.514(8)	[a]	1.986(26)
μ [mm^{-1}]	3.312	1.415	1.716	3.257
$F(000)$	2112	4848	978	1096
θ range [°]	3.49–27.48	3.41–27.45	2.95–25.35	3.59–27.48
index ranges	$-12 \le h \le 12$	$-56 \le h \le 56$	$-12 \le h \le 12$	$-25 \le h \le 25$
	$-20 \le k \le 20$	$-9 \le k \le 9$	$-10 \le k \le 10$	$-11 \le k \le 11$
	$-25 \le l \le 25$	$-43 \le l \le 33$	$-23 \le l \le 24$	$-11 \le l \le 11$
reflns measured	47465	69399	22975	24918
completeness to θ_{max}	91.7	90.6	92.5	92.6
independent reflns/R_{int}	7968/0.040	11136/0.038	6812/0.038	2064/0.030
reflns observed [$I > 2\sigma(I)$]	5319	5002	3876	1432
parameters	298	576	412	81
GooF (F^2)	0.890	0.866	0.855	0.903
$R1$ (F) [$I > 2\sigma(I)$]	0.0252	0.0349	0.0317	0.0225
$wR2$ (F^2) (all Data)	0.0523	0.0705	0.0675	0.0532
$(\Delta/\sigma)_{max}$	0.001	0.001	0.001	0.001
largest diff. peak/hole [e Å^3]	0.372/−0.723	0.507/−0.533	0.522/−0.411	0.391/−0.566

[a] Not measured.

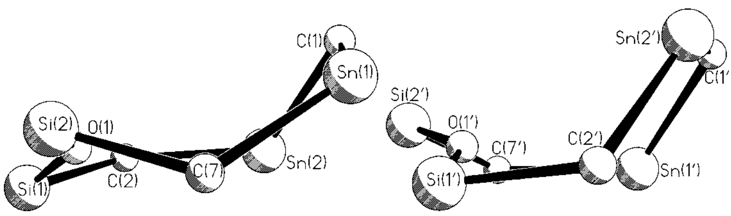


Figure 2. Side views of the two conformers of **2**.

Complexation behaviour of [*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] (2) towards chloride ions: The ^{119}Sn NMR chemical shifts of the eight-membered ring **2** to which various amounts of $[(Ph_3P)_2N]^+Cl^-$ have been added (Figure 3) indicate quantitative formation of the 1:1 complex with the chloride ion (**3**, Scheme 3). The pentachlorodistannate derivative **3** was isolated as a colorless crystalline solid. Interestingly, even though adduct formation appears to be almost quantitative, the observation of a single resonance during the course of the titration indicates a rapid intermolecular exchange of chloride ions between **2** and **3**.

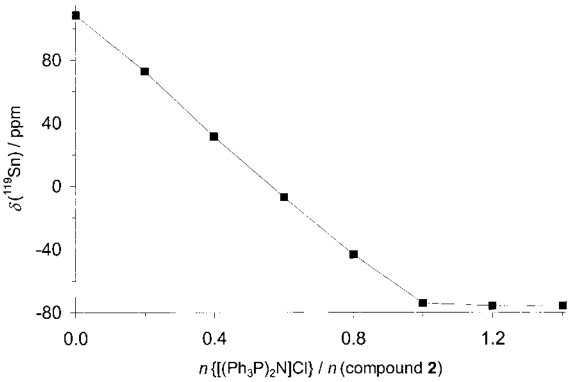
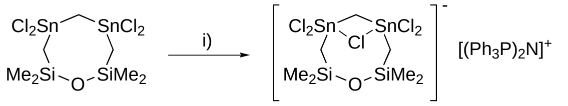


Figure 3. Plot of $^{119}Sn\{^1H\}$ NMR (111.92 MHz) chemical shift (ppm) versus molar ratio $[(Ph_3P)_2N]^+Cl^-$/compound **2** (0.11 M solution of **2** in CH_2Cl_2/D_2O_{ext}).



2 **3**

Scheme 3. Formation of the chloride complex **3**. i) $[(Ph_3P)_2N]_+Cl^-$.

In a solution of **3** in $CDCl_3$, both tin atoms are pentacoordinate as is evidenced i) by the ^{119}Sn NMR chemical shift of $\delta = -68.7$ being shifted to low-frequency with respect to compound **2**, which contains four-coordinate tin atoms ($\delta =$ 109.0), ii) by the observation of increased $^1J(^{117/119}Sn,^{13}C)$ and $^2J(^{117/119}Sn,^1H)$ couplings of 456/476, 134/140 Hz for $SiCH_2Sn$ and 559/585, 84/88 Hz for $SnCH_2Sn$ in comparison with the corresponding couplings measured for compound **2** (335/351, 115/121 Hz for $SiCH_2Sn$ and 370/387, 76/80 Hz for $SnCH_2Sn$) and iii) by the observation of an increased $^2J(^{117}Sn,^{119}Sn)$ coupling of 595 Hz for **3** as compared to 419 Hz for **2**. The chloride bridge in **3** is symmetric on the ^1H, ^{13}C, ^{29}Si, and ^{119}Sn NMR timescales (i.e., the methyl groups and methylene groups as well as the silicon and tin atoms are each equivalent). The equivalence at room temperature as well as at $-85\,°C$ of the methyl groups in the ^1H and ^{13}C NMR spectra indicate the chloride complex **3** to be kinetically labile. Thermodynamically, however, complex **3** appears to be rather stable; the ^{119}Sn NMR chemical shift (CD_2Cl_2) is almost temperature independent ($\delta = -72.6$ at 22 °C and -74.8 at -85 °C).

The molecular structure of **3** (anionic part) is illustrated in Figure 4. Unit cell data and refinement details are listed in Table 1. Compound **3** crystallises with one molar amount of dichloromethane in the unit cell. The lattice of **3** is composed of discrete [*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2OCl]^-$ anions and $[(Ph_3P)_2N]^+$ cations, with no significant interionic contacts. Both tin atoms in the anionic part of **3** exhibit a [5+1] coordination geometry with a distorted trigonal bipyramid ($\Sigma\vartheta_{eq} - \Sigma\vartheta_{ax} = 66.1°$ for Sn(1) and 72.4° for Sn(2)) with weak intramolecular Sn(1/2)$\cdots$O(1) contacts of 3.449(2) and 3.280(2) Å, respectively. The axial positions of the trigonal bipyramid at Sn(1) are occupied by Cl(2) and Cl(5) and at Sn(2) by Cl(4) and Cl(5). The Sn(1) and Sn(2) atoms are displaced from the equatorial planes, defined by C(1), C(7) and Cl(1) for Sn(1) and by C(1), C(2) and Cl(3) for Sn(2), in

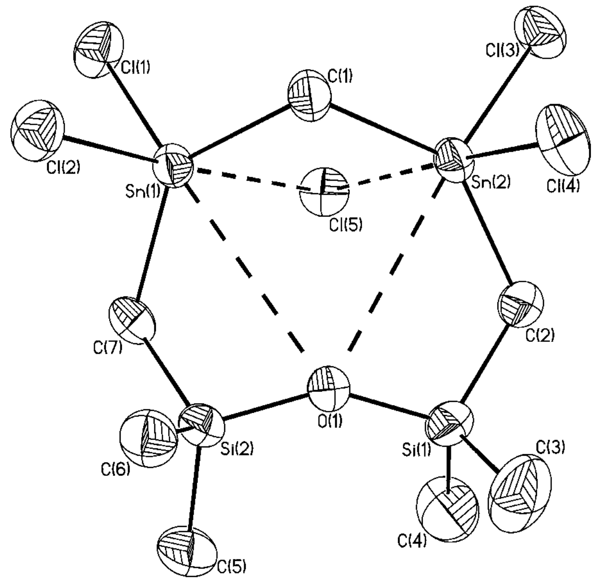
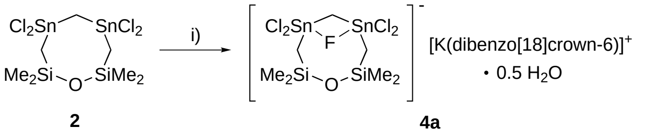


Figure 4. General view (SHELXTL) of the anionic part of **3** showing 30% probability displacement ellipsoids and the atom numbering scheme. The countercation $[(Ph_3P)_2N]^+$ and the hydrogen atoms are omitted for clarity. Selected bond lenghts [Å] and angles [°]: Sn(1)–Cl(1) 2.352(1), Sn(1)–Cl(2) 2.424(1), Sn(1)–Cl(5) 2.891(1), Sn(1)–O(1) 3.449(2), Sn(2)–Cl(3) 2.358(1), Sn(2)–Cl(4) 2.453(1), Sn(2)–Cl(5) 2.781(1), Sn(2)–O(1) 3.280(2), C(1)-Sn(1)-C(7) 132.6(2), C(1)-Sn(1)-Cl(1) 110.5(1), C(7)-Sn(1)-Cl(1) 112.7(1), C(1)-Sn(1)-Cl(2) 96.4(1), C(7)-Sn(1)-Cl(2) 98.6(1), Cl(1)-Sn(1)-Cl(2) 94.72(4), Cl(2)-Sn(1)-Cl(5) 174.18(3), Cl(1)-Sn(1)-O(1) 151.71(5), C(1)-Sn(2)-C(2) 140.4(1), C(1)-Sn(2)-Cl(4) 92.5(1), C(2)-Sn(2)-Cl(4) 95.0(1), C(1)-Sn(2)-Cl(3) 110.0(1), C(2)-Sn(2)-Cl(3) 107.4(1), Cl(4)-Sn(2)-Cl(3) 97.92(4), Cl(4)-Sn(2)-Cl(5) 169.99(3), Cl(3)-Sn(2)-O(1) 157.11(6), Si(1)-O(1)-Si(2) 147.2(2).

the direction of Cl(2) and Cl(4) by 0.255(2) and 0.181(2) Å, respectively. The bond lengths of tin to the equatorial chlorine atoms (Sn(1)–Cl(1) 2.352(1), Sn(2)–Cl(3) 2.358(1) Å) are shorter than those to the axial chlorine atoms (Sn(1)–Cl(2) 2.424(1), Sn(2)–Cl(4) 2.453(1) Å). The Sn(1)-Cl(5)-Sn(2) bridge is strongly asymmetric with Sn(1)–Cl(5) 2.891(1) Å and Sn(2)–Cl(5) 2.781(1) Å. A similar asymmetry was reported for the Sn-Cl-Sn bridge in the chloride complex of 1,1,5,5,9,9-hexachloro-1,5,9-tristannacyclododecane.[11] The Si(1)-O(1)-Si(2) angle of 147.2(2)° is similar to that observed for compound **2**.

Complexation behaviour of [*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] (2) towards fluoride ions: The reaction of the eight-membered ring **2** with one molar equivalent of potassium fluoride and dibenzo[18]crown-6 in the presence of air moisture gave a crude reaction product, the ^{29}Si NMR spectrum ($CDCl_3$) of which showed three signals at $\delta = 6.2$, 8.9 and 31.9 ($^1J(^{19}F,^{29}Si) = 276$ Hz) with an integral ratio of 15:75:10. The signals at $\delta = 6.2$ and 8.9 belong to the hydroxide complex **4b** and the fluoride complex **4a**, respectively. The signal at $\delta = 31.9$ reveals the presence of an acyclic fluorosilane, the identity of which has not been established yet, but it is different from compound **6** (see below). There are no signals visible in the ^{119}Sn NMR spectrum at room temperature. The fluoride complex **4a** was isolated in 56% yield by recrystallisation from CH_2Cl_2/hexane solution as an adduct with half a molar equivalent of water (Scheme 4).



Scheme 4. Formation of the fluoride complex **4a**. i) KF, dibenzo[18]-crown-6, CH_2Cl_2, H_2O.

The molecular structure of **4a** is illustrated in Figure 5. Unit cell data and refinement details are listed in Table 1. It is the first completely characterised fluoride complex of a diorganotin dichloride. The lattice of **4a** comprises [*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2OF]^-$ anions and [K(dibenzo[18]-crown-6)]$^+$ cations that are connected by K(1)···Cl(1)–, K(1)···Cl(3)– and K(1)···F(1) contacts of 3.157(1), 3.444(2), and 2.905(2) Å, respectively. These bond lengths are shorter than the sum of the van der Waals radii of potassium (2.80 Å)[63] and chlorine (1.70 Å) or potassium and fluorine (1.50 Å), respectively. The K(1) atom is coordinated by six oxygens of the crown ether with K(1)···O bond lengths of 2.768(3)–2.943(3) Å. In addition, there is a K(1)···O(8) contact of 2.96(2) Å of the potassium to the water molecule; this gives the K(1) a decacoordination (Figure 5). Both tin atoms exhibit a [5+1] coordination geometry with a distorted trigonal bipyramid similar to that of the related chloride complex **3** ($\Sigma\vartheta_{eq} - \Sigma\vartheta_{ax} = 70.0°$ for Sn(1) and 67.0° for Sn(2)) with weak intramolecular Sn(1/2)···O(1) contacts of 3.391(3) and 3.471(3) Å, respectively. The axial positions of the trigonal bipyramid at Sn(1) are occupied by Cl(2) and F(1) and at Sn(2) by Cl(4) and F(1). The Sn(1) and Sn(2) atoms are displaced from the equatorial planes, defined by C(1), C(7) and Cl(1) for Sn(1) and by C(1), C(2) and Cl(3) for Sn(2), in the direction of Cl(2) and Cl(4) by 0.222(2) and 0.248(2) Å, respectively. The bond lengths of tin to the equatorial chlorine atoms (Sn(1)–Cl(1) 2.348(1), Sn(2)–Cl(3) 2.349(1) Å) are shorter than those to the axial chlorine atoms (Sn(1)–Cl(2) 2.462(1), Sn(2)–Cl(4) 2.450(1) Å). The Sn(1)–F(1)–Sn(2) bridge is asymmetric with Sn(1)–F(1) 2.225(2) Å and Sn(2)–F(1) 2.271(2) Å. The Si(1)-O(1)-Si(2) angle amounts to 159.5(2)° and is significantly larger than the corresponding angles in compounds **2** and **3**.

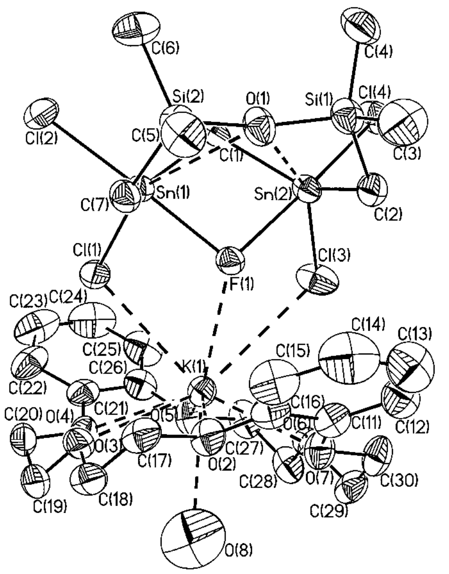
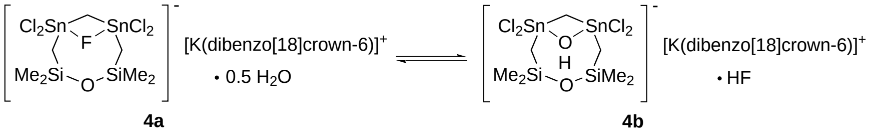


Figure 5. General view (SHELXTL) of a molecule of **4a** showing 30% probability displacement ellipsoids and the atom numbering scheme. Hydrogen atoms are omitted for clarity. Selected bond lenghts [Å] and angles [°]: Sn(1)–Cl(1) 2.348(1), Sn(1)–Cl(2) 2.462(1), Sn(1)–F(1) 2.225(2), Sn(1)–O(1) 3.391(3), Sn(2)–Cl(3) 2.349(1), Sn(2)–Cl(4) 2.450(1), Sn(2)–F(1) 2.271(2), Sn(2)–O(1) 3.471(3), K(1)–Cl(1) 3.157(1), K(1)–Cl(3) 3.444(2), K(1)–F(1) 2.905(2), K(1)–[O(2)–O(7)] 2.768(3) –2.943(3), K(1)–O(8) 2.96(2), C(1)-Sn(1)-C(7) 128.5(2), C(1)-Sn(1)-Cl(1) 111.0(1), C(7)-Sn(1)-Cl(1) 117.3(1), C(1)-Sn(1)-Cl(2) 98.5(1), C(7)-Sn(1)-Cl(2) 97.6(1), Cl(1)-Sn(1)-Cl(2) 90.67(4), Cl(2)-Sn(1)-F(1) 173.60(7), Cl(1)-Sn(1)-O(1) 151.82(6), Si(1)-O(1)-Si(2) 159.5(2).

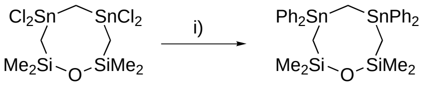
In CD_2Cl_2, the fluoride complex **4a** is in equilibrium with the hydroxide complex **4b**. (Scheme 5). The ratio of compounds **4a**:**4b** is approximately 3:1. Thus, the ^{29}Si and ^{119}Sn NMR spectra at −85 °C each display two resonances at $\delta =$ 10.4 and 9.3, and at $\delta = -80.3$ ($^1J(^{19}F,^{119}Sn) = 971$ Hz) and −74.7, respectively. In contrast to the chloride complex **2**, both the fluoride complex **4a** and the hydroxide complex **4b**



Scheme 5. Equilibrium of **4a** and **4b** in solution.

are kinetically inert on the ^{13}C NMR timescale at −90 °C. The ^{13}C NMR spectrum of the same solution as used for recording the ^{29}Si and ^{119}Sn NMR spectra shows two resonances for the methyl carbons of **4a** at $\delta = 1.62$ and 2.28 and two resonances for the methyl carbons of **4b** at $\delta = 1.62$ and 2.09. That the signal at $\delta = 1.62$ is a superposition of two resonances follows unambiguously from its higher intensity with respect to the signal at $\delta = 2.28$. The identity of the hydroxide complex **4b** was further confirmed by adding one molar equivalent of $Bu_4NOH \cdot 30\,H_2O$ to a solution of the eight-membered ring **2** in CD_2Cl_2. The ^{29}Si and ^{119}Sn NMR spectra at −90 °C of this solution exhibit the resonances assigned to the anion of **4b** as mentioned above.

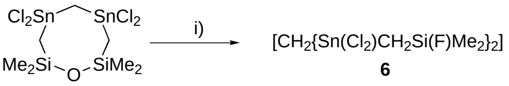
Studies on ring-opening reactions and synthesis of [CH$_2${Sn(Cl$_2$)CH$_2$Si(F)Me$_2$}$_2$]: Reaction of compound **2** with four molar equivalents of phenylmagnesium bromide provided exclusively 1,1,3,3-tetraphenyl-5,5,7,7-tetramethyl-1,3-distanna-5,7-disila-6-oxacyclooctane (**5**) as a colorless oil (Scheme 6). Attempts at cationic ring-opening polymerisation[74–77] of **2** using *para*-toluenesulfonic acid or concentrated sulfuric acid as catalyst, or at anionic ring-opening polymerisation of **5** by using KOSiMe$_3$ or KO*t*Bu were both unsuccessful. Reactions were carried out neat (for **2** and **5**) by heating the sample up to 180 °C as well as in acetone (for **2**) or in toluene (for **2** and **5**) under reflux conditions. The results reveal the high thermodynamic stability of these eight-membered ring compounds **2** and **5**.



2 **5**

Scheme 6. Synthesis of the cyclic compound **5**. i) 4 PhMgBr (−4 MgBrCl).

On the other hand, the reaction of the tetrachloro-substituted derivative **2** with $Me_3O^+BF_4^-$ gave under ring-opening and regioselective fluorination bis{dichloro[(dimethylfluorosilyl)methyl]stannyl}methane (**6**) in almost quantitative yield (Scheme 7). Compound **6** is a colorless solid which has good solubility in chlorinated solvents and diethyl ether; it is one of the very few examples of molecules with both halide functionalised tin and silicon sites.[78]



2 **6**

Scheme 7. Synthesis of the acyclic fluorosilane **6**. i) $Me_3O^+BF_4^-$ ($-Me_2O$, $-MeF$, $-\frac{1}{3}B_2O_3$, $-\frac{1}{3}BF_3$).

The crystal structure of **6** is illustrated in Figure 6. Unit cell data and refinement details are listed in Table 1. Both tin atoms in the molecular structure of **6** are equivalent and exhibit a [4+2] coordination geometry, that is, two Sn(1)−C(1/2) bonds of 2.122(2) and 2.108(3) Å, and two Sn(1)−Cl(1/2) bonds of 2.3428(9) and 2.3508(8) Å are accompanied by two intermolecular Sn(1) ⋯ F(1B/1C) contacts of 3.051(2) and 3.022(2) Å. The two last bond lengths are shorter than the sums of the van der Waals radii of tin (2.20 Å) and fluorine (1.50 Å). The deviation from an ideal octahedral configuration is especially manifested by the C(1)-Sn(1)-C(2) angle of 125.8(1)°, which is in between the ideal *cis* (90°) and *trans* (180°) angles. The Cl(1)-Sn(1)-F(1C) and Cl(2)-Sn(1)-F(1B) angles amount to 175.43(4) and 176.61(3)°, with only little deviation from the ideal value of 180°. As a result of the intermolecular Sn(1) ⋯ F(1B/1Cc) contacts, compound **6** has a one-dimensional polymeric structure in the solid state with alternating SnCSiFSnCSiF eight-membered rings and SnFSnFC-bicyclopentane fragments. The Si(1)−F(1) bond of 1.625(2) Å is not significantly affected by these intermolecular Sn ⋯ F contacts; this indicates its low polarisability. That the intermolecular Sn ⋯ F contacts are weak and have only little influence on the electronic situation at the tin atom is also reflected by the ^{119}Sn CP-MAS resonance at $\delta = 80$, which is only slightly shifted to low frequency with respect to the signal at $\delta = 106.7$ observed in solution.

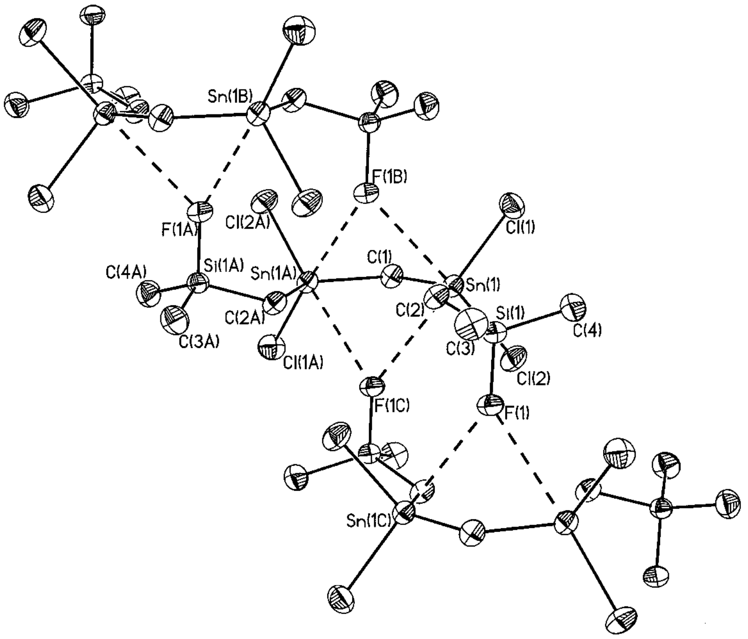


Figure 6. General view (SHELXTL) of a molecule of **6** and of its supramolecular structure showing 30% probability displacement ellipsoids and the atom numbering Scheme (Symmetry transformations used to generate equivalent atoms: A = $-x+1, y, -z+0.5$; B = $x, -y, z+0.5$; C = $-x+1, -y, -z$). Hydrogen are omitted for clarity. Selected bond lengths [Å] and angles [°]: Sn(1)−Cl(1) 2.3428(9), Sn(1)−Cl(2) 2.3508(8), Sn(1)−F(1B) 3.051(2), Sn(1)−F(1C) 3.022(2), Si(1)−F(1) 1.625(2), Cl(1)-Sn(1)-F(1C) 175.43(4), Cl(2)-Sn(1)-F(1B) 176.61(3), C(1)-Sn(1)-C(2) 125.8(1).

In solution, compound **6** is monomeric and the tin atoms are essentially tetracoordinated. This is verified by molecular weight determination and the ^{119}Sn NMR chemical shift mentioned above. The latter is close to the value of $\delta = 118$ observed for the related derivative $[CH_2\{Sn(Cl_2)CH_2SiMe_3\}_2]$[27] and typical for tetracoordinated diorganotin dichlorides.[79]

Conclusion

Linking together two organotin moities in a cyclic structure results in a new bidentate Lewis acid. This structural motif containing tin moieties and a disiloxane unit is easily accessible by a two-step hydrolysis/functionalisation reaction. Although no ring-opening polymerisation could be achieved with the particular compounds reported in this paper, the class of cyclic compounds that contains both tin and Si–O–Si units represents potential precursors for polymers serving as multidentate Lewis acidic hosts. We are currently extending our studies to di-, tri-, and polymethylene-bridged ditin compounds.

Experimental Section

General methods: All reactions were carried out under an atmosphere of dry argon. The solvents were purified by distillation from appropriate drying agents under argon. Mercuric chloride, bis(triphenylphosphoranylidene)ammonium chloride, dibenzo[18]crown-6, bromobenzene and trimethyloxonium tetrafluoroborate were commercial products. Bis(diphenylfluorostannyl)methane[27] and (chloromethyl)dimethylisopropoxysilane[80] were synthesised according to literature methods. The density of the crystals was measured by using a Micromeritics Accu Pyc 1330. Elemental analyses were performed on a LECO-CHNS-932 analyser, and mass spectrometry was performed using a Finnigan MAT 8200. Molecular weights were measured using a Knaur osmometer.

NMR spectroscopy: NMR spectra were recorded on Bruker DRX 400 and DPX 300 (in case of ^{19}F) FT NMR spectrometers with broad-band decoupling of ^{13}C at 100.63 MHz, ^{19}F at 282.40 MHz, ^{29}Si at 79.49 MHz and ^{119}Sn at 111.92 and 149.21 MHz by using internal deuterium lock. ^{1}H, ^{13}C, ^{19}F, ^{29}Si and ^{119}Sn NMR chemical shifts δ are given in ppm, and are referenced against external Me_4Si (^{1}H, ^{13}C, ^{29}Si), $CFCl_3$ (^{19}F) and Me_4Sn (^{119}Sn). The complexes for NMR investigations were generally prepared in situ.

Crystallography: Crystals of [*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] (**2**) were grown from a CH_2Cl_2/hexane/pentane solution at 5 °C, of $[(Ph_3P)_2N]^+$-[*cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2OCl]^-$ (**3**) and of [K(dibenzo[18]crown-6)]$^+$[*cyclo*-$CH_2[Sn(Cl_2)CH_2Si(Me_2)]_2OCl]^- \cdot 0.5\,H_2O$ (**4a**) from a CH_2Cl_2/hexane solution at 5 °C, and of $CH_2[Sn(Cl_2)CH_2Si(F)Me_2]_2$ (**6**) from a benzene solution at 5 °C. Intensity data for the colorless crystals were collected on a Nonius Kappa CCD diffractometer with graphite-monochromated $Mo_{K\alpha}$ radiation. The data collection covered almost the whole sphere of reciprocal space with 360 frames through ω rotation ($\Delta\omega = 1°$) at two times 10 s for **2**, two times 20 s for **3** and **4a** and two times 30 s for **6** per frame. The crystal-to-detector distance was 2.8 cm (**2**, **3**) and 3.0 cm (**4a**, **6**) with a detector-θ-offset of 5°. Crystal decay was monitored by repeating the initial frames at the end of data collection. Upon analysis the duplicate reflections there was no indication for any decay. The structures were solved by direct methods SHELXS 97[81] and successive difference Fourier syntheses. Refinement applied full-matrix least-squares methods SHELXL 97.[82] The H atoms were placed in geometrically calculated positions by using a riding model and refined with a common isotropic temperature factor for different C–H types (C–$H_{prim.}$ 0.96 Å, C–$H_{sec.}$ 0.97 Å, U_{iso} 0.099(2) Å^2 (**2**), U_{iso} 0.146(5) Å^2 (**3**), U_{iso} 0.106(3) Å^2 (**4a**), U_{iso} 0.090(4) Å^2 (**6**); C_{aryl}–H 0.93 Å (**3**), C_{aryl}–H 0.93 Å (**4a**), U_{iso} 0.113(3) Å^2 (**3**), U_{iso} 0.128(8) Å^2 (**4a**)). For compound **3** the occupany of the disordered phenyl rings were refined at 0.437(13) (C(55), C(56)), 0.563(13) (C(55′), C(56′)), 0.508(7) (C(65), C(66)) and 0.492(7) (C(65′), C(66′)). Atomic scattering factors for neutral atoms and real and imaginary dispersion terms were taken from the literature.[83] The figures were created by SHELXTL.[84] Crystallographic data are given in Table 1. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144295 (**2**), 144296 (**3**), 144297 (**4a**), and 144298 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Bis{[(dimethylisopropoxysilyl)methyl]diphenylstannyl}methane, [$CH_2\{Sn(Ph_2)CH_2Si(O\textit{i}Pr)Me_2\}_2$] (1): A solution of $Me_2(iPrO)SiCH_2MgCl$ (70 mL, 33.5 mmol) in THF, which was prepared from $Me_2(iPrO)SiCH_2Cl$ and magnesium turnings, was added dropwise to a suspension of bis(diphenylfluorostannyl)methane (10.00 g, 16.7 mmol) in THF (70 mL) at 0 °C. The reaction mixture was stirred at room temperature for 15 h before removing the solvent in vacuo. Hexane (100 mL) was added to the residue and after stirring thoroughly the mixture was filtered; the procedure was repeated three times. The solvent was removed in vacuo to give **1** (13.62 g, 16.6 mmol, 99 %) as a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta = 0.05$ (s, $^1J(^{13}C,^1H) = 121$ Hz, 12 H; $SiCH_3$), 0.22 (s, $^1J(^{13}C,^1H) = 117$ Hz, $^2J(^{117/119}Sn,^1H) = 74/77$ Hz, 4 H; $SiCH_2Sn$), 0.84 (s, $^1J(^{13}C,^1H) = 119$ Hz, $^2J(^{117/119}Sn,^1H) = 62$ Hz, 2 H; $SnCH_2Sn$), 1.15 (d, $^1J(^{13}C,^1H) = 125$ Hz, $^3J(^1H,^1H) = 6$ Hz, 12 H; CCH_3), 3.97 (sept, $^1J(^{13}C,^1H) = 138$ Hz, $^3J(^1H,^1H) = 6$ Hz, 2 H; OCH), 7.37 (m, 12 H; H_m/H_p), 7.52 (m, $^3J(^{117/119}Sn,^1H) = 47$ Hz, 8 H; H_o); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = -13.58$ (s, $^1J(^{117/119}Sn,^{13}C) = 274/287$ Hz; $SnCH_2Sn$), -3.17 (s, $^1J(^{117/119}Sn,^{13}C) = 246/257$ Hz, $^1J(^{29}Si,^{13}C) = 58$ Hz; $SiCH_2Sn$), 1.14 (s, $^1J(^{29}Si,^{13}C) = 58$ Hz, $^3J(^{117/119}Sn,^{13}C) = 10$ Hz; $SiCH_3$), 25.75 (s, $^3J(^{29}Si,^{13}C) = 17$ Hz; CCH_3), 64.58 (s; OCH), 127.97 (s, $^3J(^{117/119}Sn,^{13}C) = 49$ Hz; C_m), 128.33 (s, $^4J(^{117/119}Sn,^{13}C) = 11$ Hz; C_p), 136.60 (s, $^2J(^{117/119}Sn,^{13}C) = 38$ Hz; C_o), 141.35 (s, $^1J(^{117/119}Sn,^{13}C) = 467/488$ Hz, $^3J(^{117/119}Sn,^{13}C) = 12$ Hz; C_i); $^{29}Si\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.7$ (s, $^1J(^{13}CH_3/^{13}CH_2,^{29}Si) = 59$ Hz, $^2J(^{117/119}Sn,^{29}Si) = 19$ Hz); $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): $\delta = -38.3$ (s, $^1J(^{13}C_i,^{119}Sn) = 489$ Hz, $^1J(Sn^{13}CH_2,^{119}Sn) = 288$ Hz, $^2J(^{117}Sn,^{119}Sn) = 239$ Hz, $^2J(^{13}C_o,^{119}Sn) = 40$ Hz, $^3J(^{13}C_m,^{119}Sn) = 47$ Hz); elemental analysis calcd (%) for $C_{37}H_{52}O_2Sn_2Si_2$ (822.41): C 54.03, H 6.37; found: C 53.50, H 6.40.

1,1,3,3-Tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane, [*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2O$] (2): Diluted sulfuric acid (0.5 M) was added to a solution of **1** (13.30 g, 16.2 mmol) in diethyl ether (300 mL) and the resulting mixture was heated at reflux for 40 h. After phase separation, the organic phase was washed with water (100 mL) and the solvent removed in vacuo. A solution of mercuric chloride (17.56 g, 64.7 mmol) in acetone (80 mL) was added dropwise to a solution of the residue in acetone (80 mL) at 0 °C. The resulting suspension was stirred at room temperature for 14 h before removing the PhHgCl by filtration. After evaporating the filtrate in vacuo, the residue was suspended in hot hexane (100 mL). The suspension was filtered, the filtrate collected, and the procedure repeated with another 100 mL of hot hexane. The combined filtrates were allowed to stand overnight at 5 °C to give **2** (6.43 g, 11.6 mmol, 72 %) as a colorless solid. M.p. 107–109 °C; ^{1}H NMR ($CDCl_3$): $\delta = 0.31$ (s, $^1J(^{13}C,^1H) = 120$ Hz, 12 H; CH_3), 1.21 (s, $^1J(^{13}C,^1H) = 127$ Hz, $^2J(^{117/119}Sn,^1H) = 115/121$ Hz, 4 H; $SiCH_2Sn$), 1.70 (s, $^1J(^{13}C,^1H) = 137$ Hz, $^2J(^{117/119}Sn,^1H) = 76/80$ Hz, 2 H; $SnCH_2Sn$); $^{13}C\{^1H\}$ NMR ($CDCl_3$): $\delta = 2.67$ (s, $^1J(^{29}Si,^{13}C) = 61$ Hz, $^3J(^{117/119}Sn,^{13}C) = 22$ Hz; CH_3), 13.89 (s, $^1J(^{117/119}Sn,^{13}C) = 335/351$ Hz, $^1J(^{29}Si,^{13}C) = 55$ Hz; $SiCH_2Sn$), 16.91 (s, $^1J(^{117/119}Sn,^{13}C) = 370/387$ Hz; $SnCH_2Sn$); $^{29}Si\{^1H\}$ NMR ($CDCl_3$): $\delta = 14.2$ (s, $^2J(^{117/119}Sn,^{29}Si) = 56/59$ Hz); $^{119}Sn\{^1H\}$ NMR ($CDCl_3$): $\delta = 109.0$ (s, $^2J(^{117}Sn,^{119}Sn) = 419$ Hz); $^{119}Sn\{^1H\}$ CP-MAS NMR: $\delta = 87, 114$; elemental analysis calcd (%) for $C_7H_{18}Cl_4OSn_2Si_2$ (553.62): C 15.19, H 3.28; found: C 15.15, H 3.30; MS (70 eV, EI): *m/z* (%): 59 (11.83) $[CH_3OSi]^+$, 73 (11.29) $[C_2H_5OSi]^+$, 117 (11.59) $[C_3H_9OSi_2]^+$, 131 (52.65) $[C_4H_{11}OSi_2]^+$, 539 (100.00) $[M - CH_3]^+$; Mol. wt. (VPO, CH_2Cl_2): 547 (calcd: 554).

Bis(triphenylphosphoranylidene)ammonium (μ_2-chloro)-1,1,3,3-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane, $[(Ph_3P)_2N]^+$[*cyclo*-$CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2OCl]^-$ (3): Bis(triphenylphosphoranylidene)ammonium chloride (207 mg, 0.36 mmol) was added to a solution of **2** (200 mg, 0.36 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 10 min and the solvent removed in vacuo to give **3** (407 mg, 0.36 mmol, 100 %) as a colorless solid. M.p. 121–124 °C; ^{1}H NMR ($CDCl_3$): $\delta = 0.21$ (s, $^1J(^{13}C,^1H) = 119$ Hz, 12 H; CH_3), 1.12 (s,

$^{1}J(^{13}C,^{1}H) = 126$ Hz, $^{2}J(^{117/119}Sn,^{1}H) = 134/140$ Hz, 4H; $SiCH_2Sn$), 2.36 (s, $^{1}J(^{13}C,^{1}H) = 136$ Hz, $^{2}J(^{117/119}Sn,^{1}H) = 84/88$ Hz, 2H; $SnCH_2Sn$), 7.38–7.64 (m, 30H; PhP); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta = 2.75$ (s, $^{1}J(^{29}Si,^{13}C) = 60$ Hz, $^{3}J(^{117/119}Sn,^{13}C) = 31$ Hz; CH_3), 22.18 (s, $^{1}J(^{117/119}Sn,^{13}C) = 456/476$ Hz, $^{1}J(^{29}Si,^{13}C) = 56$ Hz; $SiCH_2Sn$), 37.83 (s, $^{1}J(^{117/119}Sn,^{13}C) = 559/585$ Hz; $SnCH_2Sn$), 126.54–133.58 (4 signals with ^{31}P couplings; PhP); $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): $\delta = 9.8$ (s, $^{1}J(^{13}CH_3-^{29}Si) = 60$ Hz, $^{2}J(^{117/119}Sn,^{29}Si) = 54$ Hz); $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$): $\delta = -68.7$ (s, $^{1}J(Sn^{13}CH_2,^{119}Sn) = 595$ Hz, $^{1}J(Si^{13}CH_2,^{119}Sn) = 474$ Hz, $^{2}J(^{117}Sn,^{119}Sn) = 633$ Hz); elemental analysis calcd (%) for $C_{44}H_{50}Cl_7OP_2NSn_2Si_2$ (1212.60, **3**$\cdot CH_2Cl_2$): C 43.58, H 4.16, N 1.16; found: C 43.50, H 4.40, N 1.10. Crystal structure determination shows one molar equivalent of CH_2Cl_2 which is supported by ^{1}H NMR spectroscopy ($\delta = 5.22$ (s, 2H; CH_2Cl_2)).

Potassium(dibenzo[18]crown-6) (μ_2-fluoro)-1,1,3,3-tetrachloro-5,5,7,7-tetramethyl-5,7-disila-1,3-distanna-6-oxacyclooctane, $[K(dibenzo[18]crown\text{-}6)]^{+}[cyclo\text{-}CH_2\{Sn(Cl_2)CH_2Si(Me_2)\}_2OF]^{-}$ (4): Dibenzo[18]crown-6 (139 mg, 0.39 mmol) and potassium fluoride (22 mg, 0.39 mmol) were added to a solution of **2** (213 mg, 0.39 mmol) in CH_2Cl_2 (10 mL). The mixture was stirred at room temperature for 14 h in order to dissolve the potassium fluoride. The solvent was then removed in vacuo, leaving a crude product which was recrystallised from CH_2Cl_2/hexane (1:1) in the presence of air moisture to give **4a**$\cdot 0.5\,H_2O$ (210 mg, 0.21 mmol, 56%) as a colorless solid of m.p. 189–190 °C. The ratio in solution of compounds **4a**:**4b** is approximately 3:1. ^{1}H NMR (CD_2Cl_2, 188 K): $\delta = 0.06$ (s, 6H; **4a**, CH_3), 0.11 (s, 6H; **4a**, CH_3), 0.27 (s, 12H; **4b**, CH_3), 1.55 (s, 4H; **4b**, $SiCH_2Sn$), 1.58 (d, $^{3}J(^{19}F,^{1}H) = 14$ Hz, 4H; **4a**, $SiCH_2Sn$), 2.04 (d, $^{3}J(^{19}F,^{1}H) = 12$ Hz, 2H; **4a**, $SnCH_2Sn$), 2.16 (s, 2H; **4b**, $SnCH_2Sn$), 4.00 (m, 16H; OCH_2), 6.88 (m; H_{Ar}), 6.92 (m; H_{Ar}); $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 188 K): $\delta = 1.62$ (s, $^{1}J(^{29}Si,^{13}C) = 63$ Hz; **4a/4b**, CH_3), 2.09 (s; **4b**, CH_3), 2.28 (s, $^{1}J(^{29}Si,^{13}C) = 63$ Hz; **4a**, CH_3), 16.05 (d, $^{1}J(^{117/119}Sn,^{13}C) = 465/484$ Hz, $^{2}J(^{19}F,^{13}C) = 11$ Hz; **4a**, $SiCH_2Sn$), 21.31 (s; **4b**, $SiCH_2Sn$), 26.18 (d, $^{2}J(^{19}F,^{13}C) = 49$ Hz; **4a**, $SnCH_2Sn$), 36.89 (s; **4b**, $SnCH_2Sn$), 65.70 (s; OCH_2), 68.80 (s; OCH_2), 110.45 (s; C_{Ar}), 120.80 (s; C_{Ar}), 145.75 (s; C_{Ar}); $^{29}Si\{^{1}H\}$ NMR (CD_2Cl_2, 188 K): $\delta = 9.3$ (s; **4b**), 10.4 (s; **4a**); $^{119}Sn\{^{1}H\}$ NMR (CD_2Cl_2, 188 K): $\delta = -80.3$ (d, $^{1}J(^{19}F,^{119}Sn) = 971$ Hz; **4a**), -74.7 (s; **4b**); IR (KBr): $\tilde{\nu} = 3428\ cm^{-1}$ (O–H); elemental analysis calcd (%) for $C_{27}H_{43}Cl_4FO_{7.5}Sn_2Si_2K$ (990.14, **4**$\cdot 0.5\,H_2O$): C 32.75, H 4.38; found: C 32.90, H 4.20. The crystal structure determination shows half a molar equivalent of H_2O.

5,5,7,7-Tetramethyl-1,1,3,3-tetraphenyl-5,7-disila-1,3-distanna-6-oxacyclooctane, $[cyclo\text{-}CH_2\{Sn(Ph_2)CH_2Si(Me_2)\}_2O]$ (5): A solution of phenylmagnesium bromide (0.470 M 15.4 mL, 7.24 mmol) in diethyl ether, which was prepared from bromobenzene (1.57 g, 10.0 mmol) and magnesium turnings (0.36 g, 15 mmol), was added dropwise to a solution of **2** (1.00 g, 1.81 mmol) in diethyl ether (50 mL) at 0 °C The reaction mixture was stirred at room temperature for 15 h before removing the solvent in vacuo. Hexane (50 mL) was added to the residue and after stirring thoroughly, the mixture was filtered; this procedure was repeated twice. The solvent was removed in vacuo to give **5** (1.29 g, 1.79 mmol, 99%) as a colorless oil. ^{1}H NMR ($CDCl_3$): $\delta = 0.12$ (s, $^{1}J(^{13}C,^{1}H) = 119$ Hz, 12H; CH_3), 0.28 (s, $^{1}J(^{13}C,^{1}H) = 119$ Hz, $^{2}J(^{117/119}Sn,^{1}H) = 73/76$ Hz, 4H; $SiCH_2Sn$), 0.74 (s, $^{1}J(^{13}C,^{1}H) = 126$ Hz, $^{2}J(^{117/119}Sn,^{1}H) = 60/63$ Hz, 2H; $SnCH_2Sn$), 7.31 (m, 12H; H_m/H_p), 7.47 (m, $^{3}J(^{117/119}Sn,^{1}H) = 46$ Hz, 8H; H_o); $^{13}C\{^{1}H\}$ NMR ($CDCl_3$): $\delta = -15.42$ (s, $^{1}J(^{117/119}Sn,^{13}C) = 289/302$ Hz; $SnCH_2Sn$), -2.66 (s, $^{1}J(^{117/119}Sn,^{13}C) = 251/263$ Hz, $^{1}J(^{29}Si,^{13}C) = 60$ Hz; $SiCH_2Sn$), 3.25 (s, $^{1}J(^{29}Si,^{13}C) = 59$ Hz, $^{3}J(^{117/119}Sn,^{13}C) = 14$ Hz; CH_3), 128.11 (s, $^{3}J(^{117/119}Sn,^{13}C) = 47$ Hz; C_m), 128.36 (s, $^{4}J(^{117/119}Sn,^{13}C) = 11$ Hz; C_p), 136.17 (s, $^{2}J(^{117/119}Sn,^{13}C) = 38$ Hz; C_o), 142.31 (s, $^{1}J(^{117/119}Sn,^{13}C) = 455/476$ Hz, $^{3}J(^{117/119}Sn,^{13}C) = 16$ Hz; C_i); $^{29}Si\{^{1}H\}$ NMR ($CDCl_3$): $\delta = 9.3$ (s, $^{1}J(^{13}CH_3/^{13}CH_2,^{29}Si) = 59$ Hz, $^{2}J(^{117/119}Sn,^{29}Si) = 39$ Hz); $^{119}Sn\{^{1}H\}$ NMR ($CDCl_3$): $\delta = -39.1$ (s, $^{1}J(^{13}C_i,^{119}Sn) = 477$ Hz, $^{1}J(Sn^{13}CH_2,^{119}Sn) = 301$ Hz, $^{1}J(Si^{13}CH_2,^{119}Sn) = 262$ Hz, $^{2}J(^{117}Sn,^{119}Sn) = 233$ Hz, $^{2}J(^{29}Si,^{119}Sn) = 39$ Hz); elemental analysis calcd (%) for $C_{31}H_{38}OSn_2Si_2$ (720.23): C 51.69, H 5.32; found: C 51.90, H 5.40; MS (70 eV, EI): *m/z* (%): 643 (100.00) $[M-Ph]^{+}$, 705 (2.66) $[M-CH_3]^{+}$.

Bis{dichloro[(dimethylfluorosilyl)methyl]stannyl}methane, $[CH_2\{Sn(Cl_2)\text{-}CH_2Si(F)Me_2\}_2]$ (6): Trimethyloxonium tetrafluoroborate (83 mg, 0.56 mmol) was added to a solution of **2** (310 mg, 0.56 mmol) in toluene (10 mL). The reaction mixture was stirred at room temperature for 3 d before removing the resulting B_2O_3 by filtration. The solvent was removed in vacuo to give **6** (319 mg, 0.56 mmol, 99%) as a colorless solid. M.p. 86 °C; ^{1}H NMR ($CDCl_3$): $\delta = 0.43$ (d, $^{1}J(^{13}C,^{1}H) = 120$ Hz, $^{3}J(^{19}F,^{1}H) = 7$ Hz, 12H; CH_3), 1.21 (d, $^{1}J(^{13}C,^{1}H) = 124$ Hz, $^{2}J(^{117/119}Sn,^{1}H) = 107/112$ Hz, $^{3}J(^{19}F,^{1}H) = 8$ Hz, 4H; $SiCH_2Sn$), 1.80 (s, $^{1}J(^{13}C,^{1}H) = 139$ Hz, $^{2}J(^{117/119}Sn,^{1}H) = 69/72$ Hz, 2H; $SnCH_2Sn$); $^{13}C\{^{1}H\}$ NMR (C_6D_6): $\delta = 1.04$ (d, $^{1}J(^{29}Si,^{13}C) = 63$ Hz, $^{2}J(^{19}F,^{13}C) = 15$ Hz, $^{3}J(^{117/119}Sn,^{13}C) = 19$ Hz; CH_3), 12.90 (d, $^{1}J(^{117/119}Sn,^{13}C) = 356/374$ Hz, $^{1}J(^{29}Si,^{13}C) = 53$ Hz, $^{2}J(^{19}F,^{13}C) = 18$ Hz; $SiCH_2Sn$), 18.55 (s, $^{1}J(^{117/119}Sn,^{13}C) = 388/407$ Hz; $SnCH_2Sn$); $^{19}F\{^{1}H\}$ NMR (CD_2Cl_2): $\delta = -141.5$ (s, $^{1}J(^{29}Si,^{19}F) = 277$ Hz, $^{3}J(^{117/119}Sn,^{19}F) = 94$ Hz); $^{29}Si\{^{1}H\}$ NMR (C_6D_6) $\delta = 31.4$ (d, $^{1}J(^{19}F,^{29}Si) = 277$ Hz, $^{1}J(^{13}CH_3,^{29}Si) = 63$ Hz, $^{1}J(^{13}CH_2,^{29}Si) = 51$ Hz, $^{2}J(^{117/119}Sn,^{29}Si) = 41$ Hz); $^{119}Sn\{^{1}H\}$ NMR (C_6D_6): $\delta = 106.7$ (d, $^{1}J(Sn^{13}CH_2,^{119}Sn) = 405$ Hz, $^{1}J(Si^{13}CH_2,^{119}Sn) = 369$ Hz, $^{3}J(^{19}F,^{119}Sn) = 93$ Hz); $^{119}Sn\{^{1}H\}$ CP-MAS NMR: $\delta = 80$; elemental analysis calcd (%) for $C_7H_{18}Cl_4F_2Sn_2Si_2$ (575.62): C 14.61, H 3.15; found: C 14.60, H 3.30; MS (70 eV, EI): *m/z* (%): 77 (18.11) $[C_2H_6FSi]^{+}$, 260 (23.99) $[C_3H_8Cl_2SnSi]^{+}$, 485 (100.00), $[M-CH_2(CH_3)_2\text{-}SiF]^{+}$, 561 (29.11) $[M-CH_3]^{+}$; Mol. wt. (VPO, CH_2Cl_2): 554 (calcd: 576).

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