

Sulphur(IV) compounds as ligands

XX *. Adduct formation and ring opening of thiirane-1-oxide with organotin halides. Crystal structure of $[(4\text{-FC}_6\text{H}_4)_2\text{SnCl}_2(\text{C}_2\text{H}_4\text{SO})_2]$

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Abstract

The organotin halides $\text{R}_n\text{SnX}_{4-n}$ ($\text{R} = \text{Ph}, 4\text{-MeC}_6\text{H}_4, 4\text{-FC}_6\text{H}_4$; $\text{X} = \text{Cl}, \text{Br}$; $n = 0, 1, 2, 3$) and Me_2SnCl_2 form adducts with thiirane-1-oxide. In general, for $n = 0, 1, 2$ these have a 1:2 stoichiometry and are octahedral, as shown by a single-crystal structural study of $[(4\text{-FC}_6\text{H}_4)_2\text{SnCl}_2(\text{C}_2\text{H}_4\text{SO})_2]$ (**4c**). In **4c** the aryl groups are *trans* to each other and the chloride and sulphoxide ligands mutually *cis*. The S–O bond is 0.04 Å longer than that in uncoordinated thiirane-1-oxide, whereas the bonds within the three-membered ring are shortened by a similar amount. Depending on the reaction conditions, 1:1 adducts $[\text{R}_2\text{SnX}_2(\text{C}_2\text{H}_4\text{SO})]$ ($\text{R} = 4\text{-MeC}_6\text{H}_4, \text{X} = \text{Cl}, \text{Br}$; $\text{R} = \text{Me}, \text{tBu}, \text{X} = \text{Cl}$) can also be isolated, while triorganotin halides form only 1:1 complexes. Analogous dimethylsulphoxide (DMSO) adducts have been synthesized for comparison. On the basis of vibrational spectroscopic data it can be concluded that thiirane-1-oxide is a weaker base than DMSO. This is supported by an NMR study of the formation of the 1:1 adduct between Me_2SnCl_2 and thiirane-1-oxide (**9**), which gave the following thermodynamic data: $K_{\text{eq}} = 8.6 \text{ M}^{-1}$, $\Delta H^{\text{R}} = -20.4 \text{ kJ mol}^{-1}$, $\Delta S^{\text{R}} = -50 \text{ J mol}^{-1} \text{ K}^{-1}$. Decomposition of the thiirane-1-oxide adducts at room temperature gives the thiosulphinic acid esters $\text{XC}_2\text{H}_4\text{S(O)SC}_2\text{H}_4\text{X}$ ($\text{X} = \text{Cl}$: **18a**, Br : **18b**) in high yields.

Key words: Tin; Sulfur; Sulfoxide

1. Introduction

The most notable difference between organotin compounds of the type $\text{R}_n\text{SnX}_{4-n}$ ($\text{R} = \text{alkyl}, \text{aryl}$; $\text{X} = \text{halide}, \text{or other electronegative group}$; $n = 0\text{--}3$) and their silicon or germanium analogues is the pronounced tendency of the central tin atom to expand its coordination number to five, six or even seven [2]. In terms of the HSAB concept these Lewis acids are borderline cases, and as such form adducts with a wide variety of both hard and soft bases. In fact, the investigation of systems of this type has contributed much to the understanding of acid–base chemistry in non-aqueous solutions [3]. Triorganotin halides generally form trigonal bipyramidal 1:1 adducts, whereas treatment of the more acidic di-, tri- and tetra-halides with bases

usually results in isolation of six-coordinate 1:2 adducts [2]. However, there is now a large body of evidence suggesting that, even in these cases 1:1 adducts are the dominant species in solution, the greater ease of isolation of the 1:2 adducts being the result of their generally lower solubility [2a,4].

Sulphoxides are ambidentate ligands which may coordinate to Lewis acids through either sulphur or oxygen [5]. Only O-coordination has been observed towards Main Group compounds, and for organotin complexes, in particular, this has been confirmed by numerous vibrational [6] and Mössbauer [7] spectroscopic studies as well as X-ray structural determinations [8].

Thiirane-1-oxide has been used by us [9] and others [10] as an SO-transfer reagent in the synthesis of transition metal complexes of sulphur monoxide [11]. The participation of two rather unstable intermediates in this reaction, probably tautomeric O- and S-bonded complexes of **1**, has been inferred from low-tempera-

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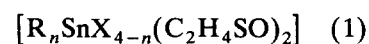
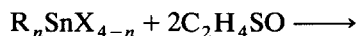
* For Part XIX, see ref. 1.

ture NMR observations (Scheme 1) [9b]. Uncoordinated **1** releases SO only at temperatures above 100°C [12] in a non-concerted reaction [13]. It seems safe to assume that the rapid SO-transfer occurs from the S-bonded complex. Indeed, electrophilic attack at oxygen by HX [12a,14*] or CuX₂ [15] leads to formation of β-substituted sulphenic acids XC₂H₄SOH, which are unstable and undergo further reactions (see below).

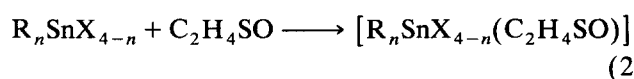
In order to gain a better understanding of the different reaction paths that thiirane-1-oxide can take, we planned to attempt the isolation and characterization of O-bonded complexes. Organotin halides R_nSnX_{4-n} seemed to offer the best chances for success owing to their relatively mild Lewis acidity and the possibility of fine-tuning their properties by judicious choice of R, X and *n*. Part of this work has already been described in preliminary form [16].

2. Results

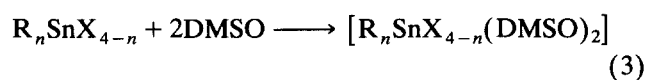
The 1:2 adducts of tin halides R_nSnX_{4-n} (*n* = 0, 1, 2) and thiirane-1-oxide are readily obtained by combining solutions of the reactants at low temperature (eqn. (1)). As mentioned in Section 1, the preferential isolation of 1:2 adducts is mainly due to their lower solubility. With the appropriate choice of stoichiometry, solvent and temperature, we should thus also be able to obtain 1:1 adducts. This has indeed been achieved in the isolation of compounds **7–9** (eqn. (2)). In **10** the bulk of the ^tBu groups probably precludes hexa-coordination of tin; this compound also stands out in being exceptionally unstable. For Lewis base adducts of triorganotin halides a 1:1 stoichiometry is regularly observed, and **11a–c** conform to this expectation. Analogous 1:2 and 1:1 adducts of dimethylsulphoxide (DMSO) which were needed for comparison, were obtained in much the same way (eqns. (3), (4)); of these, **12a**, **13a**, **14a** and **17a** have been described previously [6a,b]. Compounds **13b,c** were reported while the present work was in progress [7g].



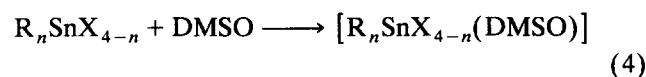
R	X	<i>n</i>	
	Cl	0	1
	Br	0	2
Ph	Cl	1	3a
4-MeC ₆ H ₄	Cl	1	3b
4-FC ₆ H ₄	Cl	1	3c
Ph	Cl	2	4a
4-MeC ₆ H ₄	Cl	2	4b
4-FC ₆ H ₄	Cl	2	4c
Ph	Br	2	5a
4-MeC ₆ H ₄	Br	2	5b
4-FC ₆ H ₄	Br	2	5c
Me	Cl	2	6



R	X	<i>n</i>	
4-MeC ₆ H ₄	Cl	2	7
4-MeC ₆ H ₄	Br	2	8
Me	Cl	2	9
^t Bu	Cl	2	10
Ph	Cl	3	11a
4-MeC ₆ H ₄	Cl	3	11b
4-FC ₆ H ₄	Cl	3	11c

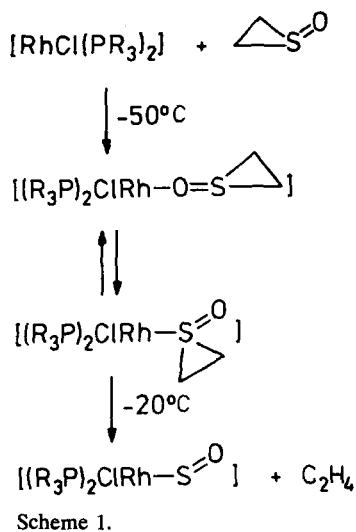


R	X	<i>n</i>	
Ph	Cl	1	12a
4-MeC ₆ H ₄	Cl	1	12b
4-FC ₆ H ₄	Cl	1	12c
Ph	Cl	2	13a
4-MeC ₆ H ₄	Cl	2	13b
4-FC ₆ H ₄	Cl	2	13c
Ph	Br	2	14a
4-MeC ₆ H ₄	Br	2	14b
4-FC ₆ H ₄	Br	2	14c



R	X	<i>n</i>	
4-MeC ₆ H ₄	Cl	2	15
4-MeC ₆ H ₄	Br	2	16
Ph	Cl	3	17a
4-MeC ₆ H ₄	Cl	3	17b
4-FC ₆ H ₄	Cl	3	17c

* Reference number with asterisk indicates a note in the list of references.



Characterization of the adducts rests primarily on elemental analyses, IR spectroscopy and an X-ray structural study of **4c**. Characteristic features of the IR spectra of all thiirane-1-oxide adducts are two strong $\nu(\text{C}-\text{H})$ absorptions that, relative to those of uncoordinated C₂H₄SO (3100,3000 cm⁻¹), are shifted only slightly to lower frequency. This provides unambiguous proof that the three-membered ring is still intact. The S–O stretching frequency, at 1060 cm⁻¹ in the free ligand, is shifted to distinctly lower values on complexation, a clear indication of O-coordination of the sulphoxide [5,6]. This shift is largest for the tetra-halide adducts **1** and **2**, and decreases with increasing number of carbon substituents at tin. Similar trends have long been observed for analogous DMSO adducts [6], and have been interpreted as reflecting the decreasing Lewis acidity of the tin compound. A strong absorption that appears at *ca.* 440 cm⁻¹ in **1** and **2** is shifted to progressively lower frequencies with increasing *n*, and can be assigned as the Sn–O vibration. Throughout the series S–O stretching frequencies of thiirane-1-oxide adducts are higher and Sn–O stretching frequencies lower than those of analogous DMSO adducts [17*]. The Sn–Cl vibrations are found within their normal range, while Sn–Br vibrations in penta- and hexa-coordinated tin complexes usually appear below 200 cm⁻¹ [6c,7a,7f,18], and were outside the range of our instruments. Since the adducts dissociate rapidly, ¹H- and ¹³C-NMR spectra of dilute solutions are more or less undisturbed superpositions of the spectra of the components (see below). The reappearance in the ¹H-NMR spectra of the typical AA'BB' multiplet of C₂H₄SO at 1.8–2.6 ppm can, nevertheless, be taken as another indication of the intact nature of the cyclic sulphoxide

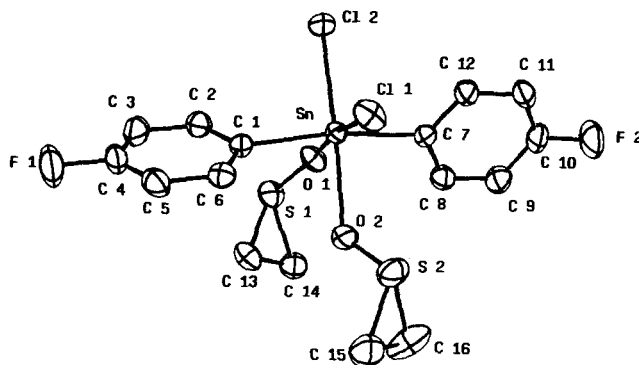


Fig. 1. ORTEP drawing of [(4-FC₆H₄)₂SnCl₂(C₂H₄SO)₂] (**4c**) (50% probability level). Hydrogen atoms are omitted.

ligand. Integration of the ¹H-NMR signals provided independent proof of the composition of the samples.

A determination of the molecular structure of **4c** finally confirmed the geometry of these compounds (Fig. 1). The coordination around tin is almost perfectly octahedral with the Cl(1)–Sn–Cl(2) angle slightly above and the O(1)–Sn–O(2) angle slightly below 90° (Table 1). The fact that the aryl substituents are bent towards the oxygen atoms indicates that these distortions are mainly caused by the bulkiness of the chlorine atoms. Packing forces are certainly also responsible for the different rotational arrangements of the thiirane-1-oxide ligands. In all, the structure of **4c** is very similar to that of [Ph₂SnCl₂(DMSO)₂] [8b]. Notable, however, are the geometrical changes on coordination within the thiirane-1-oxide ligand [19]. As expected the S–O bond is slightly lengthened, by 0.04 Å, while within the ring the C–S and C–C bonds are shortened by a similar amount. Bond angles, including that between the S–O

TABLE 1. Selected bond distances (Å) and angles (°) for [(4-FC₆H₄)₂SnCl₂(C₂H₄SO)₂] (**4c**)

Bond distances			
Sn–C(1)	2.136(2)	S(2)–O(2)	1.509(2)
Sn–C(7)	2.138(2)	S(1)–C(13)	1.805(4)
Sn–Cl(1)	2.4678(7)	S(1)–C(14)	1.796(4)
Sn–Cl(2)	2.4730(7)	S(2)–C(15)	1.760(5)
Sn–O(1)	2.3082(8)	S(2)–C(16)	1.778(4)
Sn–O(2)	2.3274(9)	C(13)–C(14)	1.445(5)
S(1)–O(1)	1.522(2)	C(15)–C(16)	1.420(6)
Bond angles			
Cl(1)–Sn–Cl(2)	94.78(3)	Sn–O(1)–S(1)	139.5(1)
O(1)–Sn–O(2)	84.09(3)	Sn–O(2)–S(2)	126.3(1)
C(1)–Sn–C(7)	168.30(9)	O(1)–S(1)–C(13)	111.1(2)
Cl(1)–Sn–O(1)	172.31(3)	O(1)–S(1)–C(14)	109.4(2)
Cl(2)–Sn–O(2)	176.04(3)	O(2)–S(2)–C(15)	109.0(2)
Cl(1)–Sn–O(2)	88.70(3)	O(2)–S(2)–C(16)	108.9(2)
Cl(2)–Sn–O(1)	92.52(3)	C(13)–S(1)–C(14)	47.3(2)
		C(15)–S(2)–C(16)	47.3(2)

TABLE 2. Observed coupling constant 2J (${}^{119}\text{Sn}-{}^1\text{H}$) (Hz) of Me_2SnCl_2 at various concentrations of thiirane-1-oxide^a, and the calculated equilibrium constant K (eqn. (5))

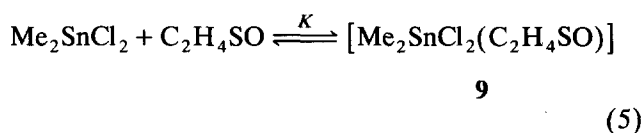
T (°C)	${}^2J({}^{119}\text{Sn}-{}^1\text{H})$ at $[\text{C}_2\text{H}_4\text{SO}]$			K
	0.04 M	0.06 M	0.10 M	
-43.5	79.29	80.31	81.70	107.0
-35.5	78.38	79.66	81.07	74.6
-27.5	77.49	78.90	80.44	54.5
-19.6	76.47	78.01	79.66	39.2
-11.7	75.58	77.12	78.90	29.4
-3.8	74.94	76.34	78.14	23.3
+4.0	74.04	75.45	77.36	17.7
+11.7	73.28	74.69	76.68	14.0
+19.4	72.78	73.92	75.84	11.2
+27.0	72.13	73.15	74.94	8.6
+34.5	71.62	72.52	74.34	7.0

^a $[\text{Me}_2\text{SnCl}_2] = 0.02$ M in all experiments.

bond and the vector bisecting the C-S-C angle, remain essentially constant.

In order to compare the base properties of thiirane-1-oxide with those of DMSO, we studied the complex formation between Me_2SnCl_2 and $\text{C}_2\text{H}_4\text{SO}$ (eqn. (5)) by ${}^1\text{H-NMR}$ spectroscopy. Only averaged signals are observed, since even at low temperature there is fast exchange between the various species in solution. Of the available data the coupling constant ${}^2J({}^{119}\text{Sn}-{}^1\text{H})$ of the methyl groups at tin provides the best measure of K . Concentrations were kept as low as possible in order to avoid complications arising from the formation of the 1:2 adduct **6**. In a very careful study Yoder *et al.* [4c] have shown that with DMSO concentrations up to 1 M formation of the 1:2 adduct plays no significant role, and even with the stronger base Ph_3PO the equilibrium constant for the 1:2 adduct is about two orders of magnitude smaller than that for the 1:1

complex. Therefore, a simplified treatment could be used to obtain K from the coupling constant data listed in Table 2. If $c(\text{AB})$ is the concentration of adduct **9** in solution, and $c_0(\text{A})$, $c_0(\text{B})$ are the initial concentrations of acid and base respectively, then the mass action law for eqn. (5) can be written as in eqn. (6).



$$K(T) = \frac{c(\text{AB})}{[c_0(\text{A}) - c(\text{AB})][c_0(\text{B}) - c(\text{AB})]} \quad (6)$$

On the assumption that, at the low concentrations employed in this study, formation of the 1:2 adduct **6** plays no significant role, the observed tin-proton coupling is a weighted average of ${}^2J({}^{119}\text{Sn}-{}^1\text{H})$ of Me_2SnCl_2 (J_{A} , 68.65 Hz) and of **9** (J_{AB}) (eqn. (7)).

$$J_{\text{obs}} = \frac{c_0(\text{A}) - c(\text{AB})}{c_0(\text{A})} J_{\text{A}} + \frac{c(\text{AB})}{c_0(\text{A})} J_{\text{AB}} \quad (7)$$

Equation (7) may be rearranged to give an expression for $c(\text{AB})$ (eqn. (8)).

$$c(\text{AB}) = c_0(\text{A}) \frac{J_{\text{obs}} - J_{\text{A}}}{J_{\text{AB}} - J_{\text{A}}} \quad (8)$$

Since J_{AB} is not directly accessible, the following iterative procedure was employed. For each individual temperature J_{AB} was varied in steps of 0.1 Hz within a reasonable range of 75–90 Hz and K calculated until the sum of the squared relative deviations reached a minimum. This gave J_{AB} values between 82 and 85 Hz. In a final cycle this procedure was repeated with the entire set of data, with J_{AB} varied between 81 and 85 Hz in steps of 0.01 Hz until the total sum of the squared relative deviations was minimized. This procedure also gave ${}^2J({}^{119}\text{Sn}-{}^1\text{H}) = 83.08$ Hz for **9**, in very good agreement with the value reported for $[\text{Me}_2\text{SnCl}_2(\text{DMSO})]$ (83.5 Hz) [4b]. Deviations occurred only at temperatures below 230 K and at higher concentrations of thiirane-1-oxide, indicating that some 1:2 adduct might perhaps be formed under these conditions. A van't Hoff plot of $\ln K$ over $1/T$ in the temperature range between 230 and 310 K (Fig. 2) was linear giving $\Delta H^{\text{R}} = -20.4$ kJ mol⁻¹ and $\Delta S^{\text{R}} = -50$ J mol⁻¹ K⁻¹.

When subjected to differential thermal analysis (DTA), the thiirane-1-oxide adducts all undergo exothermic decomposition at slightly elevated temperatures. Indeed, some of them are so thermally labile that IR spectra could only be obtained when samples were placed between silicon discs and mounted in a

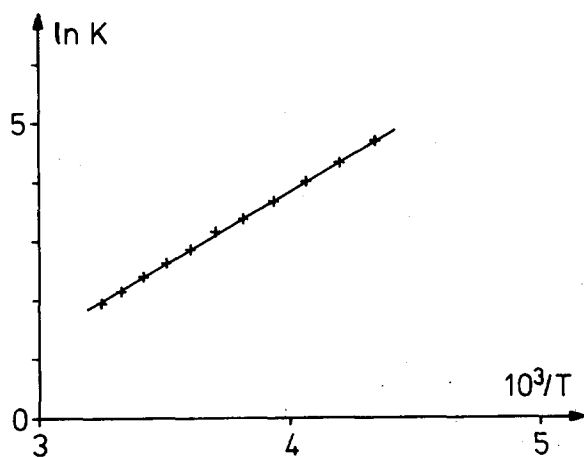


Fig. 2. Temperature dependence of K during formation of **9** (eqn. (5)).

pre-cooled sample holder [20]. In the IR spectra of decomposed samples the characteristic two $\nu(\text{C-H})$ absorptions of the three-membered ring at 3100 and 3000 cm^{-1} were absent, and had been replaced by the typical bands of aliphatic hydrocarbon chains. Obviously ring opening of thiirane-1-oxide had occurred. When solutions of the adducts were allowed to stand at room temperature, rapid decomposition occurred with the formation of white precipitates. Workup of the soluble part by column chromatography gives thiosulphinic acid esters $\text{XC}_2\text{H}_4\text{S(O)SC}_2\text{H}_4\text{X}$ ($\text{X} = \text{Cl}$: **18a**, Br : **18b**) in *ca.* 30% and 90% yields respectively. The yield of **18a** can be improved to more than 80% by adding Et_4NCl to the reaction mixture. A control experiment showed that thiirane-1-oxide and Et_4NX ($\text{X} = \text{Cl}$, Br) alone do not interact. Addition of HX to NMR samples of **18a,b** led to immediate disproportionation into the thiosulphinic acid esters $\text{XC}_2\text{H}_4\text{S(O)}_2\text{SC}_2\text{H}_4\text{X}$ (**19a,b**) and the corresponding disulphides.

3. Discussion

The rapid formation of adducts between organotin halides and thiirane-1-oxide shows that this particular ligand has Lewis base properties similar to those of DMSO and other sulfoxides. This is borne out by the molecular structure of **4c**, which is very similar to those of $[\text{Ph}_2\text{SnCl}_2(\text{DMSO})_2]$ [8b] and $[\text{Me}_2\text{SnCl}_2(\text{DMSO})_2]$ [8a]. All the intricate details, such as the lengthening of the S–O bond on coordination, the bending away of the Sn–C bonds from the Cl atoms and the deviations of the Cl–Sn–Cl and O–Sn–O angles from 90°, are also seen in those structures. As far as we know the molecular geometry of the other thiirane-1-oxide adducts is also similar to those of their DMSO analogues. Thus $[\text{SnCl}_4(\text{DMSO})_2]$ [8d] and $[\text{SnBr}_4(\text{DMSO})_2]$ [8f] are both octahedral, with a *cis* arrangement of the donor ligands. Adduct **1** certainly has a similar structure, since for the *trans* isomer only one Sn–Cl stretching vibration would be observable in the IR spectrum. Less certain conclusions can be reached in respect of the structures of adducts **3** and **12**. In solution different isomers may coexist, as was found in the systems $\text{RSnX}_3\text{-Bu}_3\text{PO}$ [21], with the least soluble isomer finally being isolated. The 1:1 adducts $[\text{R}_3\text{SnX(L)}]$ are, on the basis of simple VSEPR rules, expected to have trigonal bipyramidal geometries, with the electronegative groups X and L occupying axial positions. This is supported by a number of structural determinations [8h,22], and we have no reason to assume that adducts **11** and **17** would be an exception. Within the relatively rare class of complexes $[\text{R}_2\text{SnX}_2(\text{L})]$, however, there arises some ambiguity.

TABLE 3. Comparison of spectroscopic and thermodynamic data for adducts of Me_2SnCl_2 with thiirane-1-oxide and DMSO

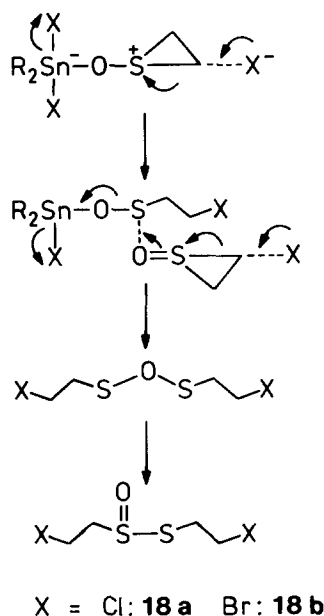
Type of compound	Property (unit)	L = C ₂ H ₄ SO	L = DMSO
L	IP (eV)	9.66 ^a	9.01 ^a
$[\text{Me}_2\text{SnCl}_2\text{L}_2]$	$\nu(\text{Sn-O})$ (cm^{-1})	378	415 ^b
$[\text{Me}_2\text{SnCl}_2\text{L}_2]$	$\Delta\nu(\text{S-O})$ (cm^{-1})	-79	-114 ^b
$[\text{Me}_2\text{SnCl}_2\text{L}]$	$K(300\text{ K})$ (M^{-1})	8.6	90 ^c
$[\text{Me}_2\text{SnCl}_2\text{L}]$	ΔH^R (kJ mol^{-1})	-20.4	-31.8 ^c
$[\text{Me}_2\text{SnCl}_2\text{L}]$	ΔS^R ($\text{J mol}^{-1} \text{K}^{-1}$)	-50	-70 ^c
$[\text{Me}_2\text{SnCl}_2\text{L}]$	$^2J(^{119}\text{Sn-}^1\text{H})$ (Hz)	83.08	83.5 ^d

^a Ref. 24 ^b Ref. 7a. ^c Calculated from data of refs. 4b,c. ^d Ref. 4b. IP, ionization potential.

Depending on their nature, the ligands around tin might adopt either truly trigonal bipyramidal geometries, as in the case of $[\text{Me}_2\text{SnCl}_2\{(\text{PhCH}_2)_2\text{SO}\}]$ [8g], or binuclear structures in which the coordination of tin is raised to six by dimerization via unsymmetrical halide bridges [8g,23]. It is tempting to ascribe the appearance of two widely separated Sn–Cl stretching vibrations in **7**, **9** and **15** to the latter type of structure.

Two sets of vibrational spectroscopic data can be taken as measures of the strength of the acid–base interaction in complexes of the type described here, namely: (i) the frequency of the Sn–O stretching vibration, and (ii) the frequency shift $\Delta\nu = \nu(\text{S-O})(\text{complex}) - \nu(\text{S-O})(\text{free})$. Within both series of compounds $\nu(\text{Sn-O})$ increases and $\Delta\nu$ decreases (becomes more negative), as expected, with increasing Lewis acidity of the tin compound. A comparison of analogous thiirane-1-oxide and DMSO complexes reveals that the acid–base interaction is consistently weaker in the thiirane-1-oxide adducts. In order to support this by thermodynamic data we have determined K for equilibrium (5) at various temperatures by $^1\text{H-NMR}$ spectroscopy. Similar studies were previously carried out on the analogous $\text{Me}_2\text{SnCl}_2\text{-DMSO}$ system by Fujiwara *et al.* [4a,b], and later in more detail by Yoder *et al.* [4c]. Pertinent data are compared in Table 3. The K value for thiirane-1-oxide is indeed smaller, by a factor of ten, the difference being due to a correspondingly smaller ΔH^R . This lower thermodynamic basicity may be traced back to a higher first ionization potential, which largely represents the oxygen lone pair energy, the difference being caused by the narrowing of the C–S–C angle [24].

Small ring heterocycles are highly susceptible to ring opening via electrophilic addition to the heteroatom followed by nucleophilic attack at carbon [25]. Thus it is not surprising that the adducts described here are thermally labile. Controlled decomposition leads to thiosulphinic acid esters **18a,b** (Scheme 2) in a reaction very similar to the ring opening of thiirane-1-oxide by



Scheme 2.

Brönsted acids [12a,14,26*]. If moisture is carefully excluded the products are stable, and may be isolated in high yield. Compounds **18a,b** had previously been judged to be intermediates in the hydrogen halide-promoted ring opening of thiirane-1-oxide, but were considered to be unstable with respect to disproportionation into $\text{XC}_2\text{H}_4\text{S}(\text{O})_2\text{SC}_2\text{H}_4\text{X}$ (**19a,b**) and the corresponding disulphides [14b]. Indeed, under more acidic conditions (if the tetra-halides SnX_4 are used or traces of HX are present) rapid disproportionation occurs.

In recent years thiosulphinic acid esters have attracted attention due to their wide range of reactions as well as their biological properties [28]. The ring opening reaction outlined here may open up another simple route to this interesting class of compounds.

The results presented here demonstrate that thiirane-1-oxide behaves as a ligand like almost any other sulphoxide, in that it forms O-bonded five- and six-coordinate adducts with organotin halides. Thiirane-1-oxide is distinctly less basic than DMSO. The reactivity of these adducts is clearly dominated by the facile unsymmetrical opening of the three-membered ring. In that respect O-bonded complexes of thiirane-1-oxide are different from S-bonded complexes, the latter being cleaved symmetrically into ethylene and sulphur monoxide, which in favourable circumstances remains coordinated to the metal fragment.

4. Experimental section

All manipulations were carried out under nitrogen using Schlenk-type glassware. Solvents were dried and

distilled under nitrogen prior to use. NMR solvents were degassed and stored under nitrogen over molecular sieves. NMR spectra were recorded on a Jeol FX 90 Q instrument. IR spectra were recorded with a Perkin-Elmer 283 spectrometer using polyethylene ($3200\text{--}600\text{ cm}^{-1}$) and water vapour ($600\text{--}200\text{ cm}^{-1}$) as wavenumber standards; samples were prepared as Nujol or Teflon oil mulls and placed between caesium iodide or silicon windows. Melting and decomposition points were determined by DTA on a DuPont 990 instrument. Electron impact mass spectra were recorded using Varian Mat CH 7 and Finnigan Mat 8200 instruments at an ionization energy of 70 eV; assignments given are based on the isotopes ^{32}S , ^{35}Cl and ^{79}Br . Elemental analyses (C,H) were carried out by the analytical service of the Institut für Anorganische Chemie. Sulphur was estimated, after combustion under O_2 and oxidation with H_2O_2 , by titration with 0.01 M $\text{Ba}(\text{ClO}_4)_2$. For tin analyses, samples were digested with aqua regia and the solutions subjected to atomic absorption spectrometry using a Perkin-Elmer 1100 instrument.

The following starting materials were prepared by published procedures: thiirane-1-oxide [29], Ph_4Sn [30], Ph_3SnCl [31], Ph_2SnCl_2 [32], Ph_2SnBr_2 [33a], PhSnCl_3 [32], $(4\text{-MeC}_6\text{H}_4)_4\text{Sn}$ [34], $(4\text{-MeC}_6\text{H}_4)_3\text{SnCl}$ [35], $(4\text{-MeC}_6\text{H}_4)_2\text{SnCl}_2$ [34], $(4\text{-MeC}_6\text{H}_4)_2\text{SnBr}_2$ [33b], $(4\text{-MeC}_6\text{H}_4)\text{SnCl}_3$ [34], $(4\text{-FC}_6\text{H}_4)_4\text{Sn}$ [36], $(4\text{-FC}_6\text{H}_4)_3\text{SnCl}$ [37], $(4\text{-FC}_6\text{H}_4)_2\text{SnCl}_2$ [38], $(4\text{-FC}_6\text{H}_4)\text{SnCl}_3$ [38], $(\text{tBu})_2\text{SnCl}_2$ [39], $[\text{PhSnCl}_3(\text{DMSO})_2]$ (**12a**) [6a], $[\text{Ph}_2\text{SnCl}_2(\text{DMSO})_2]$ (**13a**) [6a] and $[\text{Ph}_3\text{SnCl}(\text{DMSO})]$ (**17a**) [6a].

4.1. Improved synthesis of diphenyltin dibromide

A mixture of tetraphenyl tin (4.27 g, 10.0 mmol) and tin tetrabromide (4.38 g, 10.0 mmol) was slowly heated to 190°C and kept at this temperature for 2 h. The resulting yellow oil was dissolved in hexane (100 ml), slight turbidity was removed by filtration, and the solution was cooled to -78°C . (If necessary crystallization can be induced by brief chilling in liquid nitrogen.) The product was filtered off and rapidly washed with cold hexane. A second crop was isolated by evaporating the mother liquor. Combined yield 8.50 g (98%), colourless crystals, m.p. 36°C (Lit. 38°C [33c]). IR: 254(vs), 237(s) cm^{-1} (Sn-Br). Anal. Found: C, 33.01; H, 2.28; Sn, 27.20. $\text{C}_{12}\text{H}_{10}\text{Br}_2\text{Sn}$ calcd.: C, 33.31; H, 2.33; Sn, 27.43%.

4.2. Improved synthesis of bis(paratolyl) tin dibromide

Treatment of a mixture of $\text{Sn}(\text{C}_6\text{H}_4\text{CH}_3)_4$ (2.51 g, 5.20 mmol) and SnBr_4 (2.28 g, 5.20 mmol) as above gave 4.31 g (90%) $(\text{C}_6\text{H}_4\text{CH}_3)_2\text{SnBr}_2$ as colourless crystals, m.p. 75°C (Lit. 74°C [33c]). IR: 248 (vs,br)

cm⁻¹ (Sn–Br). Anal. Found: C, 36.27; H, 3.00; Sn, 26.20. C₁₄H₁₄Br₂Sn calcd.: C, 36.49; H, 3.06; Sn, 25.76%.

4.3. Synthesis of bis(parafluorophenyl) tin dibromide

Treatment of a mixture of Sn(C₆H₄F)₄ (3.00 g, 6.00 mmol) and SnBr₄ (2.63 g, 6.00 mmol) for 2 h at 170–180°C and workup as described above gave 5.20 g (92%) (C₆H₄F)₂SnBr₂ as colourless crystals, mp. 50°C. IR: 243(vs), 238(vs) cm⁻¹ (Sn–Br). Anal. Found: C, 30.70; H, 1.61; Sn, 24.95. C₁₂H₈Br₂F₂Sn calcd.: C, 30.75; H, 1.72; Sn, 25.33%.

4.4. Improved synthesis of bis(parafluorophenyl) tin dichloride

Treatment of a mixture of Sn(C₆H₄F)₄ (3.00 g, 6.00 mmol) and SnCl₄ (1.57 g, 6.03 mmol) for 2 h at 190°C and 40 min at 205°C and workup as described for Ph₂SnBr₂ gave 4.35 g (95%) (C₆H₄F)₂SnCl₂ as colourless crystals, m.p. 52°C (Lit. 51°C [38]). IR: 355(vs), 342(s) cm⁻¹ (Sn–Cl). Anal. Found: C, 37.66; H, 2.13; Sn, 31.25. C₁₂H₈Cl₂F₂Sn calcd.: C, 37.95; H, 2.12; Sn, 31.25%.

4.5. Improved synthesis of tris(parafluorophenyl) tin chloride

A mixture of Sn(C₆H₄F)₄ (3.00 g, 6.00 mmol), SnCl₄ (0.52 g, 2.00 mmol) and AlCl₃ (0.06 g, 0.45 mmol) was slowly heated to 210°C, kept at this temperature for 4 h and then cooled to room temperature. Diethyl ether (10 ml) was added and the solution filtered to remove an insoluble impurity. Cooling to 0°C produced large quantities of off-white crystals, which were recrystallized from hexane. Workup of the mother liquor gave additional material. Combined yield 2.81 g (80%), colourless crystals, m.p. 122°C (Lit. 118.2–120.5°C [37]). IR: 335(s) cm⁻¹ (Sn–Cl). Anal. Found: C, 48.98; H, 2.72; Sn, 27.48. C₁₈H₁₂ClF₃Sn calcd.: C, 49.20; H, 2.75; Sn, 27.01%.

4.6. Preparation of thiirane-1-oxide adducts 1–3

Cold (0°C) solutions of thiirane-1-oxide (76 mg, 1.00 mmol) in dichloromethane (1 ml) and the tin compound (0.50 mmol) in the same solvent (2–3 ml) were combined. The precipitate which formed immediately was filtered off, washed with hexane and vacuum dried.

4.6.1. [SnCl₄(C₂H₄SO)₂] (1)

Yield 175 mg (85%), colourless crystals, dec. 49°C. IR: 3090(s), 2993(s) (C–H), 915(vs) (S–O), 446(s,br) (Sn–O), 322(vs,br), 310(sh), 280(w) cm⁻¹ (Sn–Cl). Anal. Found: C, 11.08; H, 2.13; S, 15.80; Sn, 29.00. C₄H₈Cl₄O₂S₂Sn calcd.: C, 11.64; H, 1.95; S, 15.54; Sn, 28.76%.

4.6.2. [SnBr₄(C₂H₄SO)₂] (2)

Yield 265 mg (90%), colourless crystals, dec. 56°C. IR: 3084(s), 2988(s) (C–H), 910(vs) (S–O), 437(s) (Sn–O), 235(vs,br) cm⁻¹ (Sn–Br). Anal. Found: C, 8.01; H, 1.48; S, 11.87; Sn, 19.43. C₄H₈Br₄O₂S₂Sn calcd.: C, 8.14; H, 1.37; S, 10.86; Sn, 20.10%.

4.6.3. [PhSnCl₃(C₂H₄SO)₂] (3a)

Yield 220 mg (97%), colourless crystals, dec. 30°C. IR: 3090(s), 2990(s) (C–H), 950(vs) (S–O), 425(s) (Sn–O), 290(vs,br) cm⁻¹ (Sn–Cl). Anal. Found: C, 26.20; H, 3.23; S, 14.20; Sn, 25.20. C₁₀H₁₃Cl₃O₂S₂Sn calcd.: C, 26.43; H, 2.88; S, 14.11; Sn, 26.12%.

4.6.4. [(4-MeC₆H₄)SnCl₃(C₂H₄SO)₂] (3b)

Yield 225 mg (96%), colourless crystals, dec. 23°C. IR: 3082(s), 2980(s) (C–H), 953(vs) (S–O), 294(vs,br) cm⁻¹ (Sn–Cl). Anal. Found: C, 27.76; H, 3.05; S, 13.68; Sn, 24.07. C₁₁H₁₅Cl₃O₂S₂Sn calcd.: C, 28.21; H, 3.23; S, 13.69; Sn, 25.34%.

4.6.5. [(4-FC₆H₄)SnCl₃(C₂H₄SO)₂] (3c)

The product was precipitated by adding hexane. Yield 225 mg (96%), colourless crystals, dec. 61°C. IR: 3092(s), 2975(s) (C–H), 956(vs) (S–O), 414(m) (Sn–O), 289(vs,br) cm⁻¹ (Sn–Cl). Anal. Found: C, 24.96; H, 2.52; S, 13.42; Sn, 23.59. C₁₀H₁₂Cl₃FO₂S₂Sn calcd.: C, 25.43; H, 2.56; S, 13.57; Sn, 25.13%.

4.7. Preparation of thiirane-1-oxide adducts 4 and 5

Cold (0°C) solutions of thiirane-1-oxide (152 mg, 2.00 mmol) in toluene (1 ml) and the tin compound (1.00 mmol) in the same solvent (3 ml) were combined. The product was precipitated by addition of hexane (5 ml), filtered off, washed with cold hexane and vacuum dried.

4.7.1. [Ph₂SnCl₂(C₂H₄SO)₂] (4a)

Yield 415 mg (84%), colourless crystals, dec. 84°C. IR: 3090(s), 2998(s) (C–H), 967(vs) (S–O), 382(m) (Sn–O), 284(s), 258(s) cm⁻¹ (Sn–Cl). Anal. Found: C, 38.46; H, 3.46; S, 12.70; Sn, 23.74. C₁₆H₁₈Cl₂O₂S₂Sn calcd.: C, 38.74; H, 3.66; S, 12.93; Sn, 23.93%.

4.7.2. [(4-MeC₆H₄)₂SnCl₂(C₂H₄SO)₂] (4b)

Yield 480 mg (92%), colourless crystals, dec. 150°C. IR: 3089(s), 2987(s) (C–H), 968(vs) (S–O), 360(s) (Sn–O), 264(s), 236(s) cm⁻¹ (Sn–Cl). Anal. Found: C, 41.57; H, 4.30; S, 12.36; Sn, 23.25. C₁₈H₂₂Cl₂O₂S₂Sn calcd.: C, 41.25; H, 4.23; S, 12.23; Sn, 22.65%.

4.7.3. [(4-FC₆H₄)₂SnCl₂(C₂H₄SO)₂] (4c)

Yield 505 mg (95%), colourless crystals, dec. 93°C. IR: 3094(s), 2995(s) (C–H), 978(vs) (S–O), 388(m) (Sn–

O), 259(vs), 250(sh) cm^{-1} (Sn–Cl). Anal. Found: C, 36.24; H, 3.13; S, 12.23; Sn, 21.58. $\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{F}_2\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 36.12; H, 3.03; S, 12.05; Sn, 22.31%.

4.7.4. $[\text{Ph}_2\text{SnBr}_2(\text{C}_2\text{H}_4\text{SO})_2]$ (5a)

Yield 445 mg (76%), colourless crystals, dec. 51°C. IR: 3083(s), 2985(s) (C–H), 964(vs) (S–O), 384(m) cm^{-1} (Sn–O). Anal. Found: C, 32.33; H, 3.10; S, 11.27; Sn, 20.00. $\text{C}_{16}\text{H}_{18}\text{Br}_2\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 32.85; H, 3.10; S, 10.96; Sn, 20.29%.

4.7.5. $[(4\text{-MeC}_6\text{H}_4)_2\text{SnBr}_2(\text{C}_2\text{H}_4\text{SO})_2]$ (5b)

Yield 560 mg (91%), colourless crystals, dec. 49°C. IR: 3094(s), 2990(s) (C–H), 957(vs) (S–O), 375(m) cm^{-1} (Sn–O). Anal. Found: C, 35.33; H, 3.70; S, 10.55; Sn, 19.14. $\text{C}_{18}\text{H}_{22}\text{Br}_2\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 35.27; H, 3.62; S, 10.46; Sn, 19.37%.

4.7.6. $[(4\text{-FC}_6\text{H}_4)_2\text{SnBr}_2(\text{C}_2\text{H}_4\text{SO})_2]$ (5c)

Yield 510 mg (82%), colourless crystals, dec. 47°C. IR: 3096(s), 2994(s) (C–H), 974(vs) (S–O), 382(m) cm^{-1} (Sn–O). Anal. Found: C, 31.02; H, 2.67; S, 10.44; Sn, 19.14. $\text{C}_{16}\text{H}_{16}\text{Br}_2\text{F}_2\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 30.95; H, 2.60; S, 10.33; Sn, 19.12%.

4.8. $[\text{Me}_2\text{SnCl}_2(\text{C}_2\text{H}_4\text{SO})_2]$ (6)

To a cold (0°C) solution of Me_2SnCl_2 (440 mg, 2.00 mmol) in carbon disulphide (25 ml) was added a solution of thiirane-1-oxide (305 mg, 4.00 mmol) in the same solvent (2 ml). On storage overnight at –20°C a white solid separated, which was filtered off, washed with carbon disulphide and vacuum dried. Yield 670 mg (90%), colourless microcrystalline solid, dec. 33°C. IR: 3090(s), 2991(s) (C–H), 981(vs) (S–O), 378(m) (Sn–O), 275(sh), 258(s) cm^{-1} (Sn–Cl). Anal. Found: C, 18.87; H, 3.85; S, 19.96; Sn, 28.99. $\text{C}_6\text{H}_{14}\text{Cl}_2\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 19.38; H, 3.79; S, 17.24; Sn, 31.92%.

4.9. Preparation of thiirane-1-oxide adducts 7, 8 and 11a–c

Cold (0°C) solutions of thiirane-1-oxide (76 mg, 1.00 mmol) in toluene (1 ml) and the tin compound (1.00 mmol) in the same solvent (4 ml) were combined. The product was precipitated by addition of hexane (5 ml), filtered off, washed with cold hexane and vacuum dried.

4.9.1. $[(4\text{-MeC}_6\text{H}_4)_2\text{SnCl}_2(\text{C}_2\text{H}_4\text{SO})]$ (7)

Yield 420 mg (94%), colourless crystals, dec. 70°C. IR: 3092(s), 2998(s) (C–H), 986(vs) (S–O), 356(s) (Sn–O), 326(vs), 260(vs) cm^{-1} (Sn–Cl). Anal. Found: C, 42.36; H, 4.35; S, 7.09; Sn, 26.59. $\text{C}_{16}\text{H}_{18}\text{Cl}_2\text{OSSn}$ calcd.: C, 42.90; H, 4.05; S, 7.16; Sn, 26.50%.

4.9.2. $[(4\text{-MeC}_6\text{H}_4)_2\text{SnBr}_2(\text{C}_2\text{H}_4\text{SO})]$ (8)

Yield 170 mg (32%), colourless crystals, dec. 50°C. IR: 3089(s), 2989(s) (C–H), 960(vs) (S–O), 377(m) cm^{-1} (Sn–O). Anal. Found: C, 35.52; H, 3.60; S, 6.10; Sn, 22.95. $\text{C}_{16}\text{H}_{18}\text{Br}_2\text{OSSn}$ calcd.: C, 35.79; H, 3.38; S, 5.97; Sn, 22.11%.

4.9.3. $[\text{Ph}_3\text{SnCl}(\text{C}_2\text{H}_4\text{SO})]$ (11a)

Yield 350 mg (76%), colourless crystals, dec. 80°C. IR: 3091(s), 2990(s) (C–H), 987(vs) (S–O), 338(m) (Sn–O), 270(vs) cm^{-1} (Sn–Cl). Anal. Found: C, 51.97; H, 4.29; S, 6.65; Sn, 25.35. $\text{C}_{20}\text{H}_{19}\text{ClOSSn}$ calcd.: C, 52.04; H, 4.15; S, 6.95; Sn, 25.72%.

4.9.4. $[(4\text{-MeC}_6\text{H}_4)_3\text{SnCl}(\text{C}_2\text{H}_4\text{SO})]$ (11b)

Yield 380 mg (75%), colourless crystals, dec. 70°C. IR: 3090(s), 3005(s) (C–H), 993(s) (S–O), 332(m) (Sn–O), 251(s) cm^{-1} (Sn–Cl). Anal. Found: C, 54.29; H, 5.06; S, 6.48; Sn, 24.00. $\text{C}_{23}\text{H}_{25}\text{ClOSSn}$ calcd.: C, 54.85; H, 5.00; S, 6.37; Sn, 23.57%.

4.9.5. $[(4\text{-FC}_6\text{H}_4)_3\text{SnCl}(\text{C}_2\text{H}_4\text{SO})]$ (11c)

Yield 460 mg (89%), colourless crystals, dec. 66°C. IR: 3090(s), 2980(sh) (C–H), 994(s) (S–O), 343(m) (Sn–O), 263(s) cm^{-1} (Sn–Cl). Anal. Found: C, 46.66; H, 3.13; S, 6.28; Sn, 22.73. $\text{C}_{20}\text{H}_{16}\text{ClF}_3\text{OSSn}$ calcd.: C, 46.59; H, 3.13; S, 6.22; Sn, 23.03%.

4.10. $[\text{Me}_2\text{SnCl}_2(\text{C}_2\text{H}_4\text{SO})]$ (9)

To a cold (–78°C) solution of Me_2SnCl_2 (220 mg, 1.00 mmol) in toluene (10 ml) was added a solution of thiirane-1-oxide (76 mg, 1.00 mmol) in the same solvent (1 ml). On addition of pentane (2 ml) a white precipitate formed, which was filtered off, washed with cold pentane and vacuum dried. Yield 265 mg (90%), colourless crystals, dec. 52°C. IR: 3090(s), 2993(s) (C–H), 979(vs) (S–O), 378 (m) (Sn–O), 314(s), 246(s) cm^{-1} (Sn–Cl). Anal. Found: C, 16.77; H, 3.63; S, 10.98; Sn, 41.67. $\text{C}_4\text{H}_{10}\text{Cl}_2\text{OSSn}$ calcd.: C, 16.24; H, 3.41; S, 10.84; Sn, 40.13%.

4.11. $[(^i\text{Bu})_2\text{SnCl}_2(\text{C}_2\text{H}_4\text{SO})]$ (10)

This compound was prepared from $(^i\text{Bu})_2\text{SnCl}_2$ (304 mg, 1.00 mmol) and thiirane-1-oxide (76 mg, 1.00 mmol) by the procedure described for 9. The product must be kept below 0°C in order to avoid rapid decomposition. Yield 325 mg (86%), colourless crystals, dec. 26°C. The IR spectrum could not be obtained. Anal. Found: C, 32.19; H, 6.44; S, 8.36. $\text{C}_{10}\text{H}_{22}\text{Cl}_2\text{OSSn}$ calcd.: C, 31.61; H, 5.84; S, 8.44%.

4.12. Preparation of DMSO adducts 12b,c

Cold (0°C) solutions of DMSO (78 mg, 1.00 mmol) in dichloromethane (1 ml) and the tin compound (0.50

mmol) in the same solvent (2 ml) were combined. The product, which crystallized on addition of a few millilitres of pentane, was filtered off, washed with pentane, and vacuum dried.

4.12.1. $[(4\text{-MeC}_6\text{H}_4)_2\text{SnCl}_3(\text{DMSO})_2]$ (12b)

Yield 230 mg (97%), colourless crystals, m.p. 157°C. IR: 935(vs) (S–O), 452(s) (Sn–O), 345(m), 275(s), 258(s) cm^{-1} (Sn–Cl). Anal. Found: C, 27.97; H, 3.90; S, 13.72; Sn, 24.71. $\text{C}_{11}\text{H}_{19}\text{Cl}_3\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 27.96; H, 4.05; S, 13.57; Sn, 25.12%.

4.12.2. $[(4\text{-FC}_6\text{H}_4)_2\text{SnCl}_3(\text{DMSO})_2]$ (12c)

Yield 230 mg (97%), colourless crystals, m.p. 248°C. IR: 936(vs) (S–O), 451(s) (Sn–O), 340(m), 272(s), 243(m) cm^{-1} (Sn–Cl). Anal. Found: C, 25.06; H, 3.29; S, 13.33; Sn, 24.91. $\text{C}_{10}\text{H}_{16}\text{Cl}_3\text{FO}_2\text{S}_2\text{Sn}$ calcd.: C, 25.21; H, 3.38; S, 13.46; Sn, 24.92%.

4.13. Preparation of DMSO adducts 13 and 14

Cold (0°C) solutions of DMSO (78 mg, 1.00 mmol) in toluene (1 ml) and the tin compound (0.50 mmol) in the same solvent (2 ml) were combined. The product crystallized out within a few minutes and was filtered off, washed with pentane and dried. While this work was in progress a similar preparation of 13b,c was reported [7g].

4.13.1. $[(4\text{-MeC}_6\text{H}_4)_2\text{SnCl}_2(\text{DMSO})_2]$ (13b)

Yield 250 mg (95%), colourless crystals, m.p. 148°C (Lit. 144–145°C [7g]). IR: 949(vs) (S–O), 422(s) (Sn–O), 264(s), 224(s) cm^{-1} (Sn–Cl). Anal. Found: C, 41.17; H, 4.87; S, 12.22; Sn, 22.55. $\text{C}_{18}\text{H}_{26}\text{Cl}_2\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 40.94; H, 4.96; S, 12.14; Sn, 22.48%.

4.13.2. $[(4\text{-FC}_6\text{H}_4)_2\text{SnCl}_2(\text{DMSO})_2]$ (13c)

Yield 260 mg (97%), colourless crystals, m.p. 132°C (Lit. 132–133°C [7g]). IR: 946(vs) (S–O), 428(m) (Sn–O), 260(sh), 251(vs) cm^{-1} (Sn–Cl). Anal. Found: C, 35.69; H, 3.69; S, 12.13; Sn, 21.04. $\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{F}_2\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 35.85; H, 3.76; S, 11.96; Sn, 22.14%.

4.13.3. $[\text{Ph}_2\text{SnBr}_2(\text{DMSO})_2]$ (14a)

Yield 180 mg (61%), colourless crystals, m.p. 147°C. IR: 936(vs) (S–O), 418(s), 403(sh) cm^{-1} (Sn–O). Anal. Found: C, 32.61; H, 3.78; S, 10.80; Sn, 20.00. $\text{C}_{16}\text{H}_{22}\text{Br}_2\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 32.63; H, 3.76; S, 10.89; Sn, 20.16%.

4.13.4. $[(4\text{-MeC}_6\text{H}_4)_2\text{SnBr}_2(\text{DMSO})_2]$ (14b)

Yield 280 mg (91%), colourless crystals, m.p. 165°C. IR: 943(s) (S–O), 415(m), 403(sh) cm^{-1} (Sn–O). Anal. Found: C, 35.27; H, 4.23; S, 10.43; Sn, 19.20. $\text{C}_{18}\text{H}_{26}\text{Br}_2\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 35.04; H, 4.25; S, 10.39; Sn, 19.24%.

4.13.5. $[(4\text{-FC}_6\text{H}_4)_2\text{SnBr}_2(\text{DMSO})_2]$ (14c)

Yield 305 mg (98%), colourless crystals, m.p. 161°C. IR: 950(vs) (S–O), 414(s) cm^{-1} (Sn–O). Anal. Found: C, 31.24; H, 3.25; S, 10.12; Sn, 18.75. $\text{C}_{16}\text{H}_{20}\text{Br}_2\text{F}_2\text{O}_2\text{S}_2\text{Sn}$ calcd.: C, 30.75; H, 3.23; S, 10.26; Sn, 18.99%.

4.14. $[(4\text{-MeC}_6\text{H}_4)_2\text{SnCl}_2(\text{DMSO})]$ (15)

To a cold (0°C) solution of $(4\text{-MeC}_6\text{H}_4)_2\text{SnCl}_2$ (186 mg, 0.50 mmol) in toluene (2 ml) was added a pre-cooled solution of DMSO (40 mg, 0.51 mmol) in the same solvent (1 ml). On addition of pentane (2 ml) and cooling to –78°C, colourless crystals formed, which were filtered off, washed with pentane and dried. Yield 215 mg (96%), m.p. 78°C. IR: 952(vs) (S–O), 421(s) (Sn–O), 349(s), 262(vs) cm^{-1} (Sn–Cl). Anal. Found: C, 42.38; H, 4.64; S, 7.22; Sn, 26.40. $\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{OSSn}$ calcd.: C, 42.70; H, 4.48; S, 7.13; Sn, 26.38%.

4.15. $[(4\text{-MeC}_6\text{H}_4)_2\text{SnBr}_2(\text{DMSO})]$ (16)

This compound was prepared from $(4\text{-MeC}_6\text{H}_4)_2\text{SnBr}_2$ (424 mg, 0.92 mmol) and DMSO (72 mg, 0.92 mmol) following the procedure described for 15. Yield 300 mg (60%), colourless crystals, dec. 39°C. IR: 946(vs) (S–O), 415(m) cm^{-1} (Sn–O). Anal. Found: C, 35.63; H, 4.25; S, 6.06; Sn, 21.72. $\text{C}_{16}\text{H}_{20}\text{Br}_2\text{OSSn}$ calcd.: C, 35.66; H, 3.74; S, 5.95; Sn, 22.03%.

4.16. $[(4\text{-MeC}_6\text{H}_4)_3\text{SnCl}(\text{DMSO})]$ (17b)

To a cold (0°C) solution of $(4\text{-MeC}_6\text{H}_4)_3\text{SnCl}$ (110 mg, 0.26 mmol) in ether (2 ml) was added a solution of DMSO (40 mg, 0.51 mmol) in the same solvent (1 ml). On addition of pentane (2 ml) a colourless precipitate formed, which was filtered off and recrystallized from benzene–pentane. Yield 110 mg (84%), m.p. 43°C. IR: 952(vs) (S–O), 403(s) (Sn–O), 246(vs) cm^{-1} (Sn–Cl). Anal. Found: C, 54.57; H, 5.51; S, 6.45; Sn, 22.30. $\text{C}_{23}\text{H}_{27}\text{ClOSSn}$ calcd.: C, 54.63; H, 5.38; S, 6.34; Sn, 23.47%.

4.17. $[(4\text{-FC}_6\text{H}_4)_3\text{SnCl}(\text{DMSO})]$ (17c)

To a cold (0°C) solution of $(4\text{-FC}_6\text{H}_4)_3\text{SnCl}$ (100 mg, 0.23 mmol) in toluene (2 ml) was added a solution of DMSO (36 mg, 0.46 mmol) in the same solvent (1 ml). On addition of pentane (3 ml) and chilling to –78°C colourless crystals separated, which were filtered off, washed with pentane and vacuum dried. Yield 95 mg (81%), m.p. 116°C. IR: 948(s) (S–O), 412(vs) (Sn–O), 263(s) cm^{-1} (Sn–Cl). Anal. Found: C, 46.41; H, 3.56; S, 6.26; Sn, 22.93. $\text{C}_{20}\text{H}_{18}\text{ClF}_3\text{OSSn}$ calcd.: C, 46.41; H, 3.51; S, 6.19; Sn, 22.94%.

4.18. $\text{ClC}_2\text{H}_4\text{S(O)SC}_2\text{H}_4\text{Cl}$ (18a)

Caution: 18–20 bear some resemblance to the Mustard Gas family. Although we have not experienced any

adverse effects, materials such as these should be handled with due care.

To a stirred solution of Ph₂SnCl₂ (3.44 g, 10.0 mmol) in dichloromethane (20 ml) were added Et₄NCl (0.25 g, 1.50 mmol) and C₂H₄SO (0.76 g, 10.0 mmol). Within a few minutes a white precipitate began to appear. After 52 h the solution was filtered through Celite and the solids washed repeatedly with ethanol. The combined filtrates were evaporated to dryness and the residue chromatographed on silica using dichloromethane–pentane (2:1) as eluent. Evaporation of the solvent gave the product as a colourless oil. Yield 0.86 g (83%). IR: 1078(s) cm⁻¹ (S–O). ¹H-NMR (CDCl₃): δ 3.4–4.0 (m, br). ¹³C-NMR (CDCl₃): δ 35.0, 37.1, 43.1, 57.6. MS: 206 (7.0%, M⁺), 158 (11.0%, M⁺–SO), 144 (7.8%, M⁺–C₂H₃Cl), 143 (18.4%, M⁺–C₂H₄Cl), 111 (5.3%, M⁺–SC₂H₄Cl), 108 (10.1%, C₂H₄S₂O⁺), 95 (9.9%, SC₂H₄Cl⁺), 83 (11.6%, SOCl⁺), 63 (100%, C₂H₄Cl⁺), 59 (27.4%, C₂H₃S⁺), 49 (9.9%, CH₂Cl⁺), 48 (6.4%, SO⁺), 45 (23.6%, CHS⁺), 27 (65.3%, C₂H₃⁺). Anal. Found: C, 23.31; H, 4.08. C₄H₈Cl₂OS₂ calcd.: C, 23.19; H, 3.89%.

4.19. BrC₂H₄S(O)SC₂H₄Br (18b)

This compound was obtained similarly from Ph₂SnBr₂ (4.33 g, 10.0 mmol) and C₂H₄SO (0.76 g, 10.0 mmol) without the addition of a halide salt. Yield 2.78 g (94%), colourless crystals, m.p. 56°C. IR: 1064(s) cm⁻¹ (S–O). ¹H-NMR (CDCl₃): δ 3.5–3.9 (m, br). ¹³C-NMR (CDCl₃): δ 23.6, 30.2, 35.0, 57.8. MS: 294 (0.8%, M⁺), 266 (2.8%, M⁺–C₂H₄), 246 (1.3%, M⁺–SO), 215 (3.7%, M⁺–Br), 187 (9.1%, M⁺–C₂H₄Br), 167 (4.1%, M⁺–SOBr), 155 (5.2%, M⁺–SC₂H₄Br), 139 (6.5%, SC₂H₄Br⁺), 127 (10.1%, SOBr⁺), 107 (100%, C₂H₄Br⁺), 93 (3.9%, CH₂Br⁺), 59 (46.2%, C₂H₃S⁺), 48 (13.0%, SO⁺), 45 (30.8%, CHS⁺), 27 (81.7%, C₂H₃S⁺). Anal. Found: C, 16.70; H, 2.53. C₄H₈Br₂OS₂ calcd.: C, 16.23; H, 2.72%.

4.20. ClC₂H₄S(O)₂SC₂H₄Cl (19a)

This compound was prepared from C₂H₄SO (0.35 g, 4.00 mmol) and CuCl₂ (0.54 g, 4.00 mmol) as described by Kondo *et al.* [15]. Yield 0.22 g (49%, Lit. 65.5% [15]), colourless crystals, m.p. 30°C (Lit. 33°C [15]). IR: 1332(vs), 1126(vs) cm⁻¹ (S–O). ¹H-NMR (CDCl₃): δ 3.4–4.0 (m, br). ¹³C-NMR (CDCl₃): δ 35.7, 38.3, 42.4, 64.0. (No spectroscopic data were given in the original publication.) Anal. Found: C, 21.92; H, 3.82. C₄H₈Cl₂O₂S₂ calcd.: C, 21.53; H, 3.61%.

4.21. BrC₂H₄S(O)₂SC₂H₄Br (19b)

The bromo derivative was obtained analogously from C₂H₄SO (0.35 g, 4.00 mmol) and CuBr₂ (0.89 g, 4.00 mmol). Yield 0.36 g (58%, Lit. 64.2% [15]), colourless

crystals, m.p. 34°C (Lit. 43°C [15]; the melting point remained constant after repeated crystallizations from toluene–pentane). IR: 1314(vs), 1128(vs) cm⁻¹ (S–O). ¹H-NMR (CDCl₃): δ 3.5–4.0 (m, br). ¹³C-NMR (CDCl₃): δ 20.7, 29.3, 37.9, 64.9. (No spectroscopic data were given in the original publication.) Anal. Found: C, 15.81; H, 2.74. C₄H₈Br₂O₂S₂ calcd.: C, 15.40; H, 2.58%.

4.22. NMR study of adduct formation between Me₂SnCl₂ and C₂H₄SO

The temperature readout of the NMR instrument was calibrated using the shift difference between the OH and CH signals of methanol (210–330 K) and ethylene glycol (310–340 K) [40]. Reproducibility between consecutive measurements was better than ±0.3 K, and disagreement between the two methods in the overlapping temperature range was less than 0.2 K. Temperature readings should thus be accurate to ±0.5 K. The 0.2 M stock solutions of Me₂SnCl₂ and C₂H₄SO were made by weighing appropriate amounts of the two compounds in volumetric flasks and adding CDCl₃ to 10 ml. Individual samples were then prepared by transferring aliquots of both solutions into a 1 ml volumetric flask using a precision microlitre syringe and adding CDCl₃. Flasks and syringes had previously been calibrated by weighing the water they contained or delivered. NMR measurements were carried out in precision 5 mm tubes; 5 to 10 min were allowed for temperature equilibration before data collection (usually 64 pulses). The ¹¹⁹Sn and ¹¹⁷Sn satellites were well resolved in all cases. Each individual entry in Table 2 is the average of at least two measurements, which agreed to within ±0.2 Hz.

4.23. X-Ray structure determination of [(4-FC₆H₄)₂SnCl₂(C₂H₄SO)₂] (4c)

Diffraction measurements were carried out on a Nonius CAD4 diffractometer with monochromated Mo Kα radiation, 4° take-off and 0.8 mm collimator diameter. A colourless crystal (0.3 × 0.4 × 0.5 mm³) suitable for data sampling was obtained from a saturated toluene solution at –20°C. Orientation photographs around the three crystallographic axes and a least-squares calculation based on 25 well centred reflections with 22° < 2θ < 26° led to a monoclinic cell with dimensions given in Table 4. On the basis of systematic absences of *h*0*l*: *l* = 2*n* + 1 and 0*k*0: *k* = 2*n* + 1 and the successful solution and refinement of the structure, the space group was determined to be P2₁/c (No. 14). Data were collected in a quadrant of the reflection sphere (*h*: 0 < *h* < 15, *k*: 0 < *k* < 12, *l*: –18 < *l* < 17) using the ω/θ scan technique (Δω = 0.8°) with a range of 3° < 2θ < 50°. An empirical absorption correction

TABLE 4. Crystal data and collection details for compound 4c

Compound	$\text{SnCl}_2(\text{C}_6\text{H}_4\text{F})_2 \cdot 2\text{C}_2\text{H}_4\text{SO}$
Empirical formula	$\text{C}_{16}\text{H}_{16}\text{Cl}_2\text{F}_2\text{O}_2\text{S}_2\text{Sn}_2$
Formula weight	532.03
Crystal colour	Colourless
Space group	$P2_1/c$ (No. 14)
Temperature	223 K
Wavelength λ	0.7093 Å
Lattice parameters	
a	13.072(2) Å
b	10.445(3) Å
c	15.813(2) Å
β	114.13(1)°
V	1970(1) Å ³
Z	4
D_{calc}	1.793 mg mm ⁻³
$\mu(\text{Mo K}\alpha)$	1.8 mm ⁻¹
Range of transmission	0.926–1.0
Range of 2θ	3°–50°
Data measured	3832
Unique	3675
Data observed ($I_o > 3\sigma(I_o)$)	3147
No. of parameters varied	227
R	0.025
R_w	0.031
Error in an obs. of unit weight	1.53

TABLE 5. Atomic coordinates and their estimated standard deviations

Atom	x	y	z	B_{eq} (Å ²)
Sn	0.24412(2)	0.18062(2)	0.90801(1)	1.925(4)
Cl(1)	0.43827(7)	0.1979(1)	1.02625(6)	3.10(2)
Cl(2)	0.15930(7)	0.28693(9)	1.00357(6)	2.76(2)
S(1)	-0.00332(8)	0.0561(1)	0.72268(6)	3.10(2)
S(2)	0.42162(8)	0.0985(1)	0.80491(7)	4.04(2)
F(1)	0.1753(2)	-0.3615(2)	1.0410(2)	5.21(7)
F(2)	0.2998(3)	0.6845(3)	0.7193(2)	5.97(7)
O(1)	0.0731(2)	0.1602(2)	0.7833(2)	2.76(6)
O(2)	0.3124(2)	0.0728(3)	0.8130(2)	3.12(6)
C(1)	0.2161(3)	-0.0064(3)	0.9489(2)	2.21(7)
C(2)	0.1132(3)	-0.0418(4)	0.9462(2)	2.68(8)
C(3)	0.0976(3)	-0.1625(4)	0.9764(3)	3.27(9)
C(4)	0.1889(3)	-0.2434(4)	1.0095(3)	3.29(9)
C(5)	0.2920(3)	-0.2125(4)	1.0135(3)	3.15(9)
C(6)	0.3061(3)	-0.0921(4)	0.9820(2)	2.62(8)
C(7)	0.2567(3)	0.3522(3)	0.8391(2)	2.32(7)
C(8)	0.2217(3)	0.3599(4)	0.7445(2)	2.87(8)
C(9)	0.2351(3)	0.4713(4)	0.7026(3)	3.50(9)
C(10)	0.2843(3)	0.5739(4)	0.7588(3)	3.59(9)
C(11)	0.3202(4)	0.5716(4)	0.8528(3)	3.73(9)
C(12)	0.3063(3)	0.4595(4)	0.8938(2)	3.14(8)
C(13)	0.0770(4)	-0.0776(4)	0.7103(3)	3.7(1)
C(14)	0.0427(4)	0.0120(4)	0.6341(3)	4.2(1)
C(15)	0.4551(4)	-0.0344(5)	0.7526(4)	5.6(1)
C(16)	0.4039(4)	0.0666(6)	0.6893(3)	5.5(1)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(1/8\pi^2) (4/3) [a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos \gamma)\beta(1,2) + ac(\cos \beta)\beta(1,3) + bc(\cos \alpha)\beta(2,3)]$.

was made on the basis of eight ψ -scans; 3675 of the collected 3832 reflections were unique; equivalent reflections were merged (agreement factor on F for merged reflections: 0.026). The structure was solved by direct methods (program SHELXS 86). Further calculations were performed using the SDP program package from Enraf Nonius. After anisotropic least-squares refinement (the function minimized was $\sum W(|F_o| - |F_c|)^2$ with unit weights) of the non-hydrogen atoms, hydrogen atoms were included in the structure factor calculation at idealized positions ($d_{\text{C-H}} = 0.95$ Å). Further least-squares cycles with isotropic hydrogen atoms riding on the carbon atoms to which they are bonded led to $R = 0.031$. There were three (five) highest (lowest) peaks on the final difference Fourier map in the range of $(-0.5$ to -0.71 e Å⁻³ respectively. Positional parameters of the non-hydrogen atoms are given in Table 5. Further details of the structure determination are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, Germany, on quoting the depository number CSD 54751, the names of the authors and the journal citation.

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