

**Synthesis and ^{119}Sn NMR of η^1 -O-coordinated sulphine-dimethyltin dichloride complexes and thermal C=S and S=O bond cleavage reactions.
X-Ray structure (130 K) of $\text{Me}_2\text{SnCl}_2[\eta^1\text{-O-(Me(Ph)NC(Ph)=S=O)}]^\#$**

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Abstract. Aminosulphines $(\text{R}^1\text{R}^2\text{N})(\text{R}^3)\text{C}=\text{S}=\text{O}$ coordinate via the oxygen atom to dimethyltin dichloride. This η^1 -O coordination was established by the X-ray structure of $\text{Me}_2\text{SnCl}_2[\eta^1\text{-O-(Me(Ph)NC(Ph)=S=O)}]$ which consists of monomers connected to dimers with unequal Sn-Cl bridges of 2.544(1) and 3.307(1) Å. The tin centres have a distorted octahedral arrangement. The Sn-O distance is 2.269(3) Å and the Sn-O-S angle is 129.1(2)°. Theoretical calculations showed that the negative charge on the sulphine oxygen atom is enhanced by conjugation of the π -C=S bond with the amino lone pair of the NR^1R^2 group. Of the other sulphines tested, only 9-fluorene S-oxide was found to coordinate to Me_2SnCl_2 , likewise in the η^1 -O coordination mode. The η^1 -O coordination to tin destabilizes the sulphine fragment as was shown by the stoichiometric decomposition of the sulphine into the corresponding ketones and thioketones. A possible route for the decomposition process is proposed involving the formation of an oxathiiran intermediate.

Introduction

In recent years, a considerable amount of research has been carried out on the coordination and reactivity of hetero-olefinic ligands. Our investigations concerned the conjugated 1,4-dihetero-1,3-butadienes with a $\text{N}=\text{C}-\text{C}=\text{N}$ or $\text{N}=\text{C}-\text{C}=\text{O}$ skeleton and heterocumulenes with $\text{N}=\text{S}=\text{N}$, $\text{N}=\text{S}=\text{O}$ or $\text{C}=\text{S}=\text{O}$ skeletons¹⁻⁸. We showed that the coordination modes of hetero-olefines depend upon the nature of the metal¹⁻⁸. Sulphines*** ($\text{RR}'\text{C}=\text{S}=\text{O}$) can coordinate via the S atom (η^1 : e.g. to $\text{Rh}^{\text{I}}\text{Cl}(\text{PCy}_3)_2$), the π -C=S bond (η^2 : e.g. to $\text{Pt}^0(\text{PPh}_3)_2$) or, in a pseudo-allylic mode, via the S-C=S system of $\text{R}(\text{RS})\text{C}=\text{S}=\text{O}$. In the latter case and in the case in which the atom α to the sulphine carbon atom is a chlorine atom, i.e. $\text{R}(\text{Cl})\text{C}=\text{S}=\text{O}$, coordination to the metal is followed by insertion of the metal into the carbon-sulphur or carbon-chlorine bond².

This latter reactivity provided the possibility of developing a catalytic synthetic route for the preparation of new sulphines at a metal centre⁸.

In the present study, we investigate the influence of an amino substituent attached to the sulphine carbon atom

*** IUPAC name: thione oxides.

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[#] This paper is dedicated to Professor Th. J. de Boer on the occasion of his retirement from the University of Amsterdam.

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upon the coordinative properties of the sulphine. In addition to the above-mentioned coordination modes for the C=S=O grouping, coordination of these so-called aminosulphines (thioamide *S*-oxides) via the nitrogen atom could also be expected. Earlier studies suggested that the nitrogen lone pair is not available for coordination since it is delocalised over the N–C=S=O system. In a separate study, we found that only with the monoanionic amido-sulphines, which possess a localized nitrogen lone pair, can N,O chelate bonding [for example to rhodium(I)] be achieved⁹.

In view of the delocalization of negative charge in the N–C=S=O system in the direction of the S=O moiety, the coordinative capacity of the sulphine oxygen atom in aminosulphines was investigated. For this study, the tin centre in Me₂SnCl₂ was selected because it is known that ketones and thioketones can coordinate via the oxygen atom to tin(IV) if it is a strong enough Lewis acid^{10–12}. This approach led to new types of sulphine complexes in which the sulphine is coordinated via the oxygen atom. Furthermore, an interesting C=S and S=O bond cleavage of the η¹-O-coordinated aminosulphines has been found.

Experimental

(i) Apparatus

The IR spectra were recorded on a Perkin-Elmer 283 spectrophotometer. Kinetic measurements were carried out on Beckman IR 4250 and Nicolet FT-IR 7199B spectrophotometers. ¹H NMR spectra were recorded on Varian T60A, Varian XL-100–12" and Bruker WM-250 spectrometers, ¹³C{¹H} on Bruker WM-250 and Bruker WP-80 spectrometers, ³¹P{¹H} on a Bruker WP-80 spectrometer and ¹¹⁹Sn{¹H} on a Bruker WM-250 spectrometer.

(ii) Preparation of the sulphine complexes

The starting complex Me₂SnCl₂ was obtained from Fluka. The sulphines were prepared according to literature procedures^{14–16}. All complexes were prepared using the following general procedure.

The sulphine dissolved in CH₂Cl₂ (1 mmol in 10 ml) was slowly added to an equimolar quantity of Me₂SnCl₂, likewise dissolved in CH₂Cl₂ (1 mmol in 10 ml). Stirring was continued for 15 minutes followed by dropwise addition of *n*-pentane. A white or yellow precipitate was formed, which was filtered off, and then recrystallized from toluene/pentane (1/1 v/v). Elemental analyses were carried out by the Analytical Section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands. For analytical data see Table I.

(iii) Decomposition in the solid state

The decomposition reactions of the sulphine–Me₂SnCl₂ complexes were followed in the solid state by IR and FT-IR spectroscopy. The tin sulphine complex was enclosed in a KBr pellet (2% w/w sulphine–tin complex/KBr). This pellet was heated by the electrical heating mantle of the sample holder. Temperatures were varied over the range ambient to 140°C.

Table I Analyses of compounds.

Compound	Found, calcd. (%)									
	C		H		Cl		N		S	
1b	41.46	41.51	4.17	4.14	15.13	15.31	2.90	3.03	6.99	6.92
2b^a	46.01	40.13	4.01	3.82	14.14	15.79	3.75	3.12	8.60	7.14
3b^a	38.20	36.40	5.04	4.93	15.88	16.53	3.41	3.27	6.99	7.47
4b^a	42.92	42.80	4.53	4.40	15.57	14.88	2.84	2.94	4.81	6.73
5b	41.45	41.67	3.29	3.24	16.65	16.44	–	–	7.27	7.41

^a Analyses of these compounds were difficult to obtain because of decomposition (see text); the ratio C/H/N/Cl was correct.

(iv) Decomposition in solution

The decomposition of the sulphine–Me₂SnCl₂ complexes in solution were followed by ¹H and ¹¹⁹Sn NMR. In order to check the decomposition products formed, an equimolar quantity of a thioamide or amide, having the same α-substituents as the corresponding sulphine, was added to a solution of Me₂SnCl₂ in CDCl₃ or toluene-*d*₈. These reactions were also followed by ¹H and ¹¹⁹Sn NMR.

(v) Structure determination and refinement of C₁₆H₁₉Cl₂NSSnO (130 K)*

The crystal structure of the title compound was solved from a room temperature data set¹⁷ using standard Patterson and Fourier methods. Refinement converged at the unsatisfactorily high *R* value of 0.11 due to severe decay during the data collection. In view of this, a low-temperature (130 K) data set was collected and used for further refinement, the result of which is reported here. Crystal data are given in Table II.

Table II Crystal data for C₁₆H₁₉Cl₂NOSSn (130 K).

Formula	SnC ₁₆ H ₁₉ Cl ₂ NOS
Mol. weight	463.00
Colour	yellow
Crystal system	monoclinic
Space group	C2/c
<i>a</i> (Å)	13.806(1)
<i>b</i> (Å)	9.265(1)
<i>c</i> (Å)	29.221(2)
β (°)	93.48(1)
<i>U</i> (Å ³)	3730.8(6)
<i>Z</i>	8 (monomers)
<i>F</i> (000) (electrons)	1840
<i>D</i> _x (g·cm ⁻³)	1.648
μ(MoKα) (cm ⁻¹)	17.7
Crystal size	0.50 × 0.25 × 0.25 mm

Data were collected on an ENRAF-NONIUS CAD4F diffractometer for a crystal which was mounted on top of a glass fibre. Unit-cell parameters were derived from the diffractometer settings of 21

* Supplementary material. Table containing anisotropic thermal parameters and observed and calculated structure factors are obtainable. Requests should be addressed to Dr. A. L. Spek.

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($26 < \theta < 29^\circ$) reflections. Half a sphere of reflections (16169) was collected (Monochromated MoK α 0.71073 Å, θ -max 35° , $\omega/2\theta$ scan), averaged (R_{av} 4.6%) into a unique set of 8197 reflections and corrected for Lorentz and polarization effects. The correction for absorption was judged to be unnecessary in view of the observed small intensity variation for a $360^\circ \psi$ scan of the close to axial reflection 0 2 0. No correction for decay was necessary at 130 K since the intensities of three standard reflections (2 0 10; 5 1 1; 2 4 - 3) remained constant (r.m.s.d. 0.5%) over the 105 hours of X-ray exposure time. Refinement on F ($w = 1$) converged at $R = 0.0397$ for 228 refined parameters and 6724 reflections with $I > 2.5 \sigma(I)$. The refined parameters included all positional parameters, except for those of the hydrogen atoms of the phenyl groups which were introduced on calculated positions (C-H 1.08 Å) and refined with fixed geometry, anisotropic thermal parameters for the non-hydrogen atoms and two isotropic temperature factors for the phenyl and methyl group hydrogen atoms, respectively. A final difference map showed no significant residual features. Table III lists the positional parameters.

Data on the geometry are given in Table IV

Table III Final positional and equivalent isotropic thermal parameters (with e.s.d.'s in the last digit in parentheses) for $C_{16}H_{19}Cl_2NOSSn$ (130 K).

Atom	x	y	z	U or $U(eq)^a$ (Å ²)
Sn	.21816(2)	-.57670(3)	.54990(1)	.0177(1)
Cl(1)	.27803(8)	-.8352(1)	.55964(4)	.0301(3)
Cl(2)	.21089(8)	-.5378(1)	.63097(3)	.0306(3)
S	.10308(7)	-.2495(1)	.56436(3)	.0221(2)
O	.1739(2)	-.3432(3)	.53800(9)	.0244(6)
N	.2537(2)	-.1496(3)	.6205(1)	.0170(6)
C(1)	.1595(2)	-.1618(4)	.6091(1)	.0181(6)
C(2)	.0885(2)	-.0861(4)	.6367(1)	.0198(6)
C(3)	.0118(3)	-.1602(5)	.6548(2)	.030(1)
C(4)	-.0535(3)	-.0859(6)	.6806(2)	.042(1)
C(5)	-.0425(3)	.0606(6)	.6883(2)	.041(1)
C(6)	.0328(3)	.1351(5)	.6696(2)	.032(1)
C(7)	.0988(3)	.0627(4)	.6441(1)	.0228(6)
C(8)	.2870(2)	-.1095(4)	.6666(1)	.0164(6)
C(9)	.3486(3)	.0080(4)	.6736(1)	.0225(6)
C(10)	.3837(3)	.0417(4)	.7176(1)	.026(1)
C(11)	.3567(3)	-.0404(4)	.7549(1)	.024(1)
C(12)	.2941(3)	-.1562(4)	.7476(1)	.0236(8)
C(13)	.2594(2)	-.1924(4)	.7032(1)	.0199(6)
C(14)	.3303(3)	-.1843(4)	.5894(1)	.0229(8)
C(15)	.0730(3)	-.6389(5)	.5342(2)	.027(1)
C(16)	.3576(3)	-.5121(5)	.5323(2)	.030(1)
H(3)	.0030(3)	-.2748(5)	.6490(2)	.045(4)
H(4)	-.1130(3)	-.1433(6)	.6946(2)	.045(4)
H(5)	-.0927(3)	.1168(6)	.7090(2)	.045(4)
H(6)	.0402(3)	.2500(5)	.6750(2)	.045(4)
H(7)	.1576(3)	.1206(4)	.6296(1)	.045(4)
H(9)	.3690(3)	.0724(4)	.6450(1)	.045(4)
H(10)	.4321(3)	.1323(4)	.7233(1)	.045(4)
H(11)	.3848(3)	-.0141(4)	.7891(1)	.045(4)
H(12)	.2720(3)	-.2182(4)	.7765(1)	.045(4)
H(13)	.2118(2)	-.2840(4)	.6974(1)	.045(4)
H(141)	.381(3)	-.109(4)	.591(2)	.034(4)
H(142)	.359(3)	-.268(4)	.597(2)	.034(4)
H(143)	.302(3)	-.192(4)	.561(2)	.034(4)
H(151)	.026(3)	-.570(4)	.541(2)	.034(4)
H(152)	.060(3)	-.638(4)	.505(2)	.034(4)
H(153)	.058(3)	-.725(4)	.550(2)	.034(4)
H(161)	.399(3)	-.534(4)	.560(2)	.034(4)
H(162)	.389(3)	-.583(4)	.517(2)	.034(4)
H(163)	.356(3)	-.429(4)	.522(2)	.034(4)

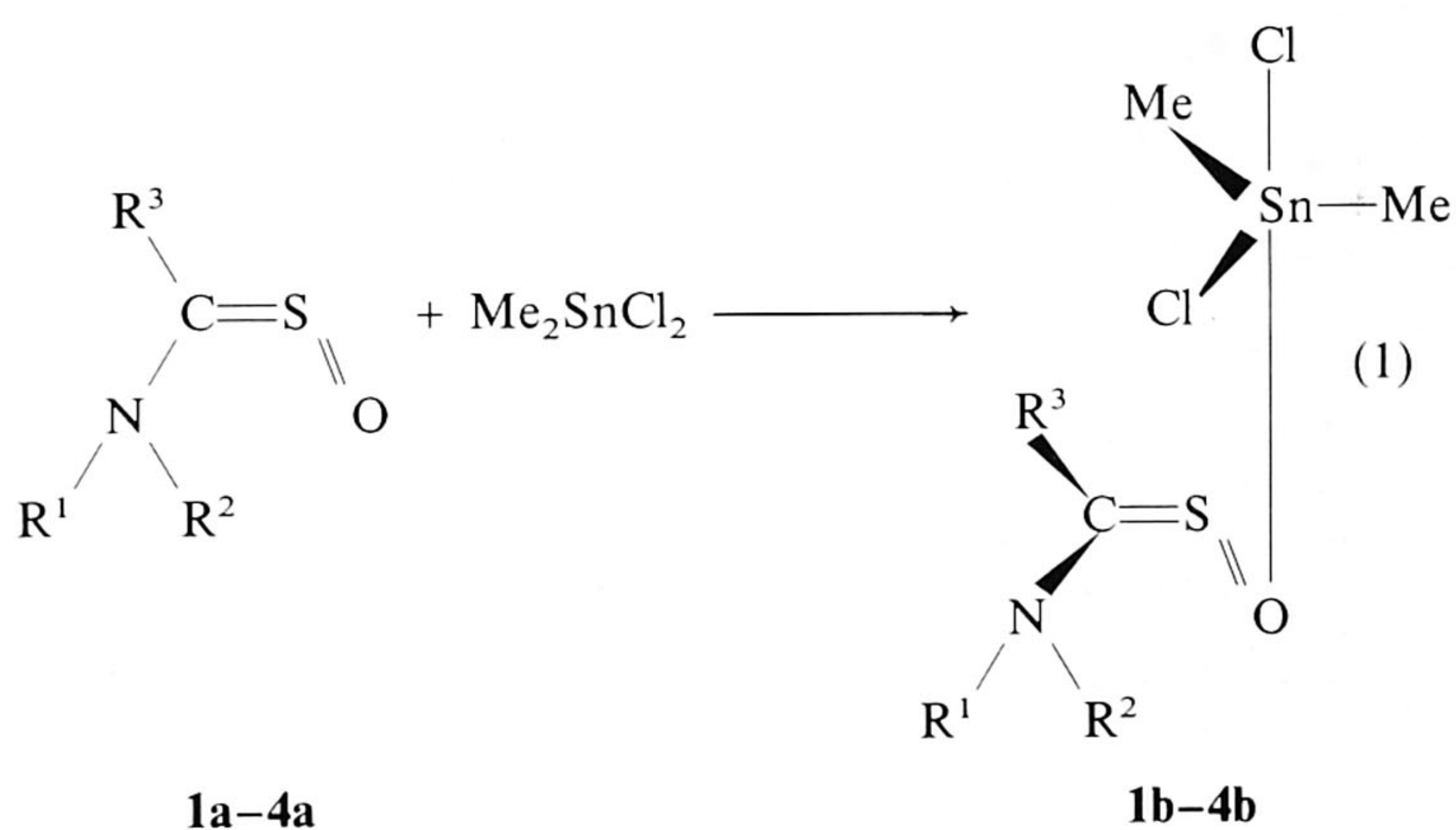
$$^a U(eq) = \frac{1}{3} \sum_i \sum_j (U_{ij} a_i^* a_j \cdot a_j)$$

Scattering factors from refs. 18 and 19, corrected for anomalous dispersion²⁰, were used. The calculations were carried out on an in-house DG-Eclipse S/230 mini-computer with a modified implementation of SHELX-76²¹ or on the CDC CYBER 175 of the University of Utrecht using programmes from the EUCLID package²².

Results and discussion

(i) Synthesis of the aminosulphine- and 9-fluorenothione S-oxide-dimethyltin dichloride complexes

Addition of the aminosulphine (**1a-4a**) to a CH_2Cl_2 solution of an equimolar amount of dimethyltin dichloride resulted in the formation of the 1/1 complexes (**1b-4b**) according to Eqn. 1. A similar reaction was found for 9-fluorenothione S-oxide (**5**). ¹H and ¹³C NMR spectra of the complexes (Tables V and VI, respectively), which were recorded immediately after their preparation, pointed to the 1/1 sulphine/tin stoichiometry indicated in Eqn. 1.



compound	R ¹	R ²	R ³
1	phenyl	methyl	phenyl
2	phenyl	hydrogen	phenyl
3	<i>p</i> -tolyl	hydrogen	isopropyl
4	<i>p</i> -tolyl	hydrogen	<i>p</i> -tolyl

Correct elemental analyses of the products were difficult to obtain because of slow decomposition even at room temperature (*vide infra*). Because the decomposition comprises the liberation of sulfur or oxygen from the complexes, the S and O percentages found in the elemental analyses did not fit with the calculated values. However, the observed C/H/Cl/N ratios were, for all complexes, in accordance with a sulphine/tin ratio of 1/1. Molecular-weight determinations were likewise disturbed by decomposition of the complexes. Unambiguous confirmation, however, of the 1/1 stoichiometry was provided by the X-ray structure determination of $Me_2SnCl_2[Ph(Me)N(Ph)C=S=O]$, for which suitable single crystals could be obtained.

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Table IV Selected data on the geometry of $C_{16}H_{19}Cl_2NOSSn$ (130 K).

(a) Bond distances (\AA)					
Sn–Cl(1)	2.544(1)	N–C(1)	1.328(4)	C(6)–C(7)	1.385(6)
Sn–Cl(2)	2.404(1)	N–C(8)	1.445(4)	C(7)–C(2)	1.401(5)
Sn–Cl(1A) ^a	3.307(1)	N–C(14)	1.469(5)	C(8)–C(9)	1.389(4)
Sn–O	2.269(3)	C(1)–C(2)	1.483(4)	C(9)–C(10)	1.382(4)
Sn–C(15)	2.109(4)	C(2)–C(3)	1.393(6)	C(10)–C(11)	1.398(5)
Sn–C(16)	2.109(4)	C(3)–C(4)	1.392(7)	C(11)–C(12)	1.386(5)
S–O	1.547(3)	C(4)–C(5)	1.383(8)	C(12)–C(13)	1.396(4)
S–C(1)	1.689(3)	C(5)–C(6)	1.387(7)	C(13)–C(8)	1.389(5)
(b) Bond angles ($^\circ$)					
Cl(1)–Sn–Cl(2)	93.54(4)	O–Sn–C(15)	89.1(1)		
Cl(1A)–Sn–Cl(2)	174.15(3)	O–Sn–C(16)	86.2(1)		
Cl(1)–Sn–Cl(1A) ^a	81.47(3)	Sn–O–S	129.1(2)		
Cl(1)–Sn–O	175.86(7)	O–S–C(1)	112.3(2)		
Cl(1)–Sn–C(15)	93.7(1)	S–C(1)–N	129.3(2)		
Cl(1)–Sn–C(16)	90.0(1)	S–C(1)–C(2)	111.1(2)		
Cl(2)–Sn–O	88.92(7)	N–C(1)–C(2)	119.5(3)		
Cl(2)–Sn–C(15)	99.2(2)	C(1)–N–C(8)	120.5(3)		
Cl(2)–Sn–C(16)	106.9(2)	C(1)–N–C(14)	123.8(3)		
Cl(15)–Sn–C(16)	153.4(2)				
(c) Torsion angles ($^\circ$)					
S–C(1)–N–C(14)	14.9(5)	N–C(1)–C(2)–C(7)	53.7(4)		
S–C(1)–N–C(8)	–160.8(3)	C(1)–N–C(8)–C(13)	56.7(4)		
C(2)–C(1)–N–C(8)	22.0(5)	N–C(1)–S–O	8.9(4)		
C(2)–C(1)–N–C(14)	–162.3(3)	Sn–O–S–C(1)	89.5(2)		

^a Atoms related by the symmetry operation $\frac{1}{2}-x, -\frac{3}{2}-y, 1-z$ to the positions in Table III are indicated with A.

Table V 1H NMR of $Me_2SnCl_2 \cdot R^1C(SO)NR^2R^3$ ^a.

R ¹	δR^1	R ²	δR^2	R ³	δR^3	$\delta [Me(Sn)]$	$J(Sn-Me)$
Ph	7.33–6.92	Me	3.67	Ph	7.33–6.92	1.24	81.5
<i>p</i> -Tol	7.76–6.86 2.40/2.32	H	9.8 (broad)	<i>p</i> -Tol	7.76–6.86 2.40/2.32	1.20	70.2
<i>p</i> -Tol	7.62–7.19 2.37	H	5.92 (broad)	<i>i</i> -Pr	4.27 (sept.) 1.24 (d)	1.19	70.2
Ph	7.88–6.93	H	9.6 (broad)	Ph	7.88–6.93	1.29	84.2
Fluorene CSO	8.67–7.16	–	–	–	–	1.19	68.7

^a Spectra recorded in $CDCl_3$. Chemical shifts relative to Me_4Si .

Table VI ^{13}C NMR^a of $Me_2SnCl_2 \cdot R^1C(SO)NR^2R^3$.

R ¹	$\delta(R^1)$	R ²	$\delta(R^2)$	R ³	$\delta(R^3)$	$\delta(CSO)$	$\delta(Me)$	$^1J(Sn-^{13}CMe)$
Ph	132.5–125.3	Me	43.7	Ph	132.5–125.3	188.8	10.0	504
<i>p</i> -Tol	143.8–119.0 21.3/20.6	H	–	<i>p</i> -Tol	143.8–119.0 21.3/20.6	197.4	10.0	536
<i>p</i> -Tol	143.1–126.0 22.5	H	–	<i>i</i> -Pr	43.7/22.5	168.6	10.2	572
Ph	136.9–121.6	H	–	Ph	136.9–121.6	190.7	12.1	490.5
Fluorene CSO	139.3–118.5	–	–	–	–	–	6.8	481.4

^a Spectra recorded in $CDCl_3$. Chemical shifts relative to Me_4Si .

Only for the aminosulphines and 9-fluorene-thione *S*-oxide could stable complexes with diorganotin halides be isolated. It appeared that other types of sulphine, *i.e.* $RR'C=S=O$ and $RXC=S=O$ ($X = Cl$ or SR^2), did not coordinate to tin. Addition of these sulphines to Me_2SnCl_2 resulted, after the usual work-up procedure (see experimental), in the isolation of the starting materials. These observations indicate that the basicities of the sulphine oxygen atoms in the aminosulphine and 9-fluorene-thione *S*-oxide ligands are similar and furthermore that such basicity is a prerequisite if η^1-O coordination is to be observed. In both cases, π -delocalization in the $N-C=S=O$ and 9-fluorene-thione *S*-oxide skeletons, respectively, results in enhanced electron density in the $S=O$ part of the sulphine ligands (*vide infra*). In the $RR'C=S=O$ and $RXC=S=O$ ligands, this enhanced *O* basicity emerging from π -delocalization is not possible.

(ii) *Molecular geometry and crystal structure of $Me_2SnCl_2[Ph(Me)N(Ph)C=S=O]$*

The dimeric structure of *N*-methylthiobenzanilide-*S*-oxide-dimethyltin dichloride consists of two monomers which are connected via two chlorine bridges between the Sn centres around an inversion centre (Fig. 1).

The bridging Cl–Sn distances are different, being 2.544(1) and 3.307(1) Å, respectively, whereas the terminal Sn–Cl(2) distance has a lower value of 2.404(1) Å. It should be noted that the Sn–Cl bridge bond is considerably shorter than the sum of the *van der Waals* radii of Sn and Cl which is 3.85 Å (*vide infra*). The tin centre has a distorted octahedral arrangement with the two methyl groups, the non-bridging and the bridging chlorine atom of the other unit at equatorial positions. The Sn–C bonds are equal, 2.109(4) Å, while the C–Sn–C bond angle amounts to 153.4(2)°. The axial sites are occupied by the oxygen atom of the sulphine ligand [Sn–O, 2.269(3) Å] and the bridging chlorine atom Cl(1).

These structural features indicate that the arrangement around tin is intermediate between trigonal bipyramidal (TBP) and octahedral which are the expected arrangements for five- and six-coordination, respectively. The dimer is in fact formed by distortion of a TBP arrangement of the monomer by the long-range interaction with the chlorine atom of the second monomer. This distortion of geometries by formation of chlorine bridges is commonly met in

organotin halide species^{10-12,23-25}. The values of Sn–Cl bonds observed in the present compound can be compared with 2.40 and 3.54 Å found in Me_2SnCl_2 which forms, in the solid state, linear chains of tin atoms with two tin–chlorine bridges. In this structure, each Sn atom has a distorted octahedral arrangement with four bridging chlorine atoms at unequal distances in the equatorial plane and the methyl groups in axial positions^{11,24}. Another example is the structure, in the solid state (138 K), of trimethyltin chloride which has only one chlorine atom available to form a tin–chlorine bridge. This results in a TBP structure having a linear Cl–Sn–Cl arrangement with Sn–Cl distances of 2.430(2) and 3.269(2) Å, respectively¹². Interestingly, electron diffraction data of Me_3SnCl (at 363 K)²⁵ showed only one type of Sn–Cl bond (2.315 Å), which indicates that the dimeric structure of Me_3SnCl found in the solid state breaks down in the gas phase.

The dichloro bridge in the present compound results in a Sn_2Cl_2 ring which is strictly planar (crystallographic inversion centre) with bond angles at Sn of 81.47(3) and at Cl(1) of 98.53(3)° and a Sn–Sn distance of 4.461(1) Å. The oncoming chlorine atom, Cl(1A), is along the extension of the Sn–Cl(2) vector with a Cl(1A)–Sn–Cl(2) bond angle of 174.15(3)°. The accommodation of a third (bridging) Cl atom in the coordination sphere of Sn(IV) brings about the opening of C–Sn–C angle from the value of 120°, in an ideal TBP arrangement, to 153.4(2)° in the present case; this effect is much more pronounced in the present structure than in the structure of Me_2SnCl_2 polymer, where the C–Sn–C angle amounts 123.5°^{11,24}.

The sulphine ligand coordinates via the oxygen atom in the η^1-O coordination mode, with a Sn–O bond length of 2.269(3) Å; *i.e.* a bond which is considerably longer than the sum of covalent radii of O and Sn (about to 2.05 Å)^{23,26}.

²³ M. Veith and O. Recktenwald, "Structure and Reactivity of Monomeric, Molecular tin(II) Compounds" in "Topics in Current Chemistry – Organotin Compounds" **104**, pp. 7, 9, 13 (1982); Springer Verlag, Berlin.

²⁴ A. G. Davies, H. J. Milledge, D. C. Puxley and P. J. Smith, *J. Chem. Soc.* 2862 (1970).

²⁵ B. Beagle, K. McAloon and J. M. Freeman, *Acta Cryst.* **B30**, 444 (1974).

²⁶ L. E. Sutton, *Interatomic Distances, Supplement*, The Chemical Society, London, 1965.

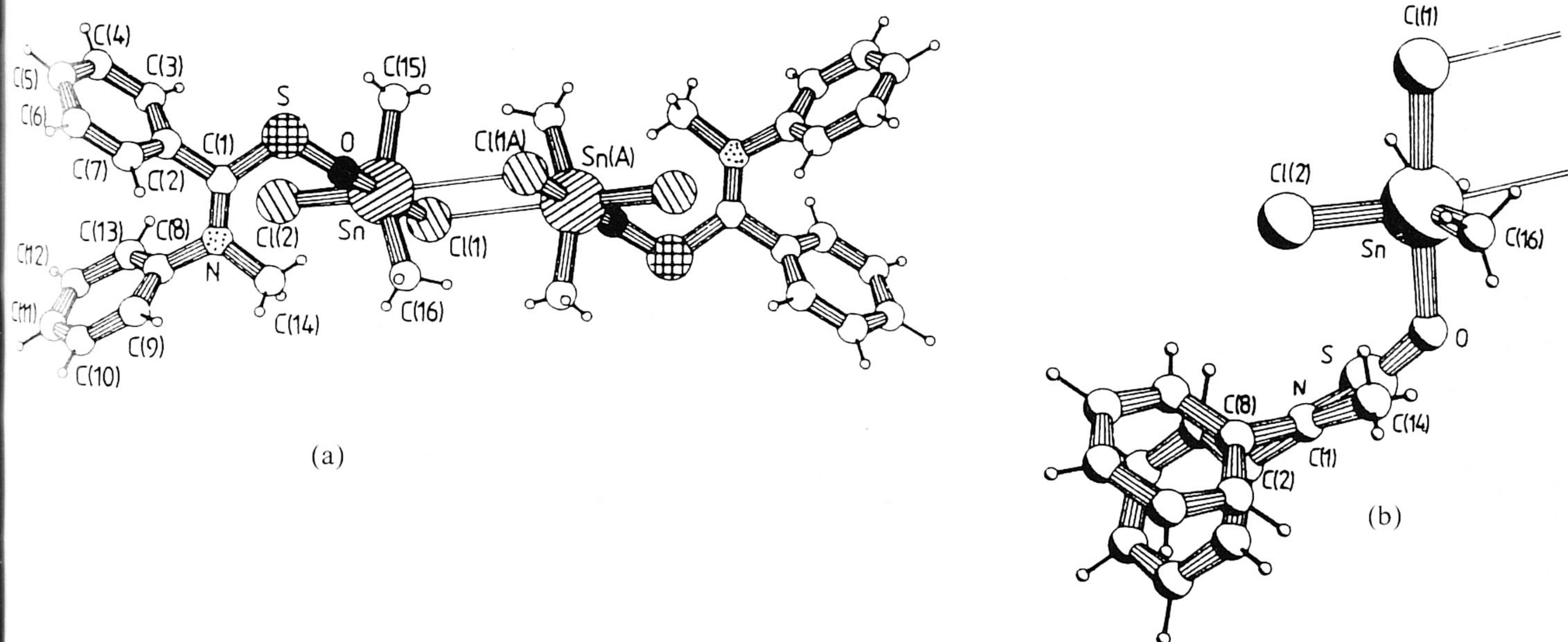


Fig. 1. (a) *Pluto* drawing (*EUCLID* version²²) of the dimeric solid state structure of $C_{16}H_{19}Cl_2NOSSn$ (130 K) with adopted numbering scheme. Atoms related by the inversion symmetry element are indicated with A.

(b) View of the monomeric unit along the C(1)–N bond.

However, trimethyltin sulphinate²⁷, which possesses in the solid state a spiral chain structure of five-coordinated tin centres, has Sn–O distances of 2.209(31) Å and 2.272(19) Å. Similar Sn–O bonds of 2.306(10) Å were found in the polymeric structure of trimethyltin 2-propyne-sulfinato²⁴. The values of the Sn–C bonds (Table IV) are in agreement with those found in other organotin compounds, e.g. in Me₃SnCl (2.119(7) at 138 K and 2.106(5) Å at 363 K)^{12,25}.

The bond lengths in the aminosulphine ligand are clearly affected by the electron delocalization taking place in the N–C=S=O skeleton. The observed C(1)–N(1) bond length is 1.328(4) Å, whereas a value of 1.51 Å would be expected for a single N–C bond, which points to a partial double bond character of the C(1)–N(1) bond. The delocalization also influences the C(1)–C(2) and N(1)–C(8) bond lengths which are 1.483(4) and 1.445(4) Å, respectively. The atoms S(1), C(1), C(2), N(1) and O(1) are coplanar within the limit of 0.01(2) Å (see Fig. 1b), while the O–S–C(1)–N(1) torsion angle amounts to a small value of –8.9(4)°. C(8) and C(14) are also almost in the OSC(1)NC(2) plane with the C(8)–NC(14) group rotated by 17° about the C(1)–N bond out of this plane. Summation of the angles for the respective nuclei in the OSC(1)NC(2) fragment gives values close to 360°, with dihedral angles close 0° or 180°. The structure contains short intramolecular [C(14)–H(143)...O: H(143)...O 2.32(4) Å] and short intermolecular [C(7)–H(7)...Cl(1): H(7)...Cl(1) 2.743(4); C(11)–H(11)...Cl(2): H(11)...Cl(2) 2.761(3) Å] contacts.

(iii) MNDO calculations on the model (*Z*)-sulphine
H₂N(H)C=S=O

The electronic structure of the R₂N–C(R)=S=O ligands has been studied by semi-empirical molecular orbital calculations (MNDO²⁸) based upon the model ligand, (*Z*)-H₂N–(H)C=S=O. The *Z* isomer of the ligand was used, since this has been shown to be the preferred configuration of aminosulphines^{14–16}. In Table VII, the final, optimized geometry of H₂N(H)C=S=O is listed.

Table VII Calculated geometry and charge distribution of H₂N–HC=S=O.

Atom	x	y	z	Charge
O	0.000	0.000	0.000	–0.65
S	1.515	0.000	0.000	0.44
C	2.045	–1.548	0.000	–0.03
N	1.253	–2.648	0.000	–0.29
H	0.261	–2.545	0.000	0.23
H	1.662	–3.555	0.000	0.20
H	3.120	–1.759	0.000	0.09
Calculated bond distances (Å) ^a and angles (°)				
O–S	1.515	O–S–C	108.89	
S–C	1.636	S–C–N	125.33	
C–N	1.354 ^b	H–C–N	120.00	
C–H	1.096	C–N–H	120.00	
N–H	0.997	C–N–H	120.00	
N–H	0.997			

^a Observed O=S bond lengths vary between 1.432(7) and 1.50(1)^{30,32} and C=S bonds between 1.50(1) and 1.640(7) Å³². ^b The CN bond in thioacetanilide *S*-oxide is 1.341 Å³⁰.

The distances in the calculated C=S=O fragment are in agreement with the values reported for other sulphines^{29,30}. The charge distribution over the atoms is listed in Table VII. At this moment, accurate Ultraviolet Photoelectron data are not available. Accordingly, correlation of the calculated

eigenvalues with experimental ionization energies is not possible³¹.

Molecular orbital plots of the five highest occupied and first lowest unoccupied molecular orbitals have been constructed from the calculated eigenvectors by use of the programme PICTOR³², see Fig. 2.

The MO's *B*, *D* and *F* describe the conjugated π system of the N–C=S=O fragment, each with different orbital coefficients due to the different electronegativity of the atoms in this skeleton. MO *C* has the lone pair primarily located on the oxygen atom, while remaining occupied MO *E* comprises mainly contributions from the sulphur and oxygen atoms (50% and 25%, resp.). We were particularly interested in the energy that the MO would have, given a large contribution from the nitrogen atom. The existence of such a MO would indicate that coordination via the nitrogen atom could also be feasible. It appeared, however, that the energy of this MO would be much lower than MO *F* (ca. –20 eV), which is a very unfavourable level for η¹-N coordination. Consequently, it is unlikely that a neutral aminosulphine ligand will be found to form a coordinative bond via the nitrogen atom.

The crystal structure showed that the ligands around tin are arranged in a configuration which is intermediate between an octahedral and a trigonal bipyramidal arrangement. The present calculations suggest that it is MO *B* which interacts with a suitable orbital on Sn. However, it must be noted that, although the C(1)–S–O–Sn torsion angle amounts to 89.5(2)°, it is the S–O–Sn angle which is increased from the expected value of 90° to 129.1(2)°. The latter value is similar to that found for the Sn–O–S angle in *cis*-SnMe₂Cl₂(DMSO)₂ (124.6°)^{33,34}.

(iv) Decomposition of the complexes

The complexes were stable for some time (days) at room temperature and could be stored at low temperatures (–20°C) without decomposition for several weeks. At elevated temperatures, decomposition took place almost immediately (at 70°C, within 15 minutes for **1b**). It appeared that, after some time, (1 day to 2 weeks at room temperature) depending upon the complex, the IR spectra of the tin aminosulphine complexes changed drastically.

A more detailed look at the products formed in the decomposition reaction showed that the sulphine functional group was broken down and that distinct products, *i.e.* the corresponding thioamides and amides, were formed. The latter two products suggested that the decomposition involved elimination of either the sulphur or oxygen atom from the sulphine unit. In each of the complexes described, both eliminations took place. The infrared spectra indicated the presence of a C=O and a C=S bond, while the NMR spectra of the decomposed samples were identical to those of mixtures of Me₂SnCl₂ and the corresponding amide and thioamide compounds. The overall reaction for the decomposition of the sulphine complex into the corresponding amide and thioamide tin complexes, both in the solid and in solution, is shown in Eqn. 2.

²⁷ G. M. Sheldrick and R. Taylor, *Acta Cryst.* **B33**, 135 (1977).

²⁸ M. J. S. Dewar and W. Thiel, *J. Am. Chem. Soc.* **99**, 4633 (1977).

²⁹ O. H. Jarchow, *Acta Cryst.* **B25**, 267 (1969).

³⁰ Th. W. Hummelink, *Cryst. Struct. Commun.* **4**, 441 (1975).

³¹ T. Koopmans, *Physica* **1**, 304 (1934).

³² R. R. Andrea, H. Cerfontain, H. J. A. Lambrechts, J. N. Louwen and A. Oskam, *J. Am. Chem. Soc.* **106**, 2531 (1984).

³³ N. W. Isaacs, C. H. L. Kennard and W. Kitching, *Struc. Rep.* **35**, 735 (1970).

³⁴ N. W. Isaacs, C. H. L. Kennard and W. Kitching, *J. Chem. Soc., Chem. Commun.* 820 (1968).

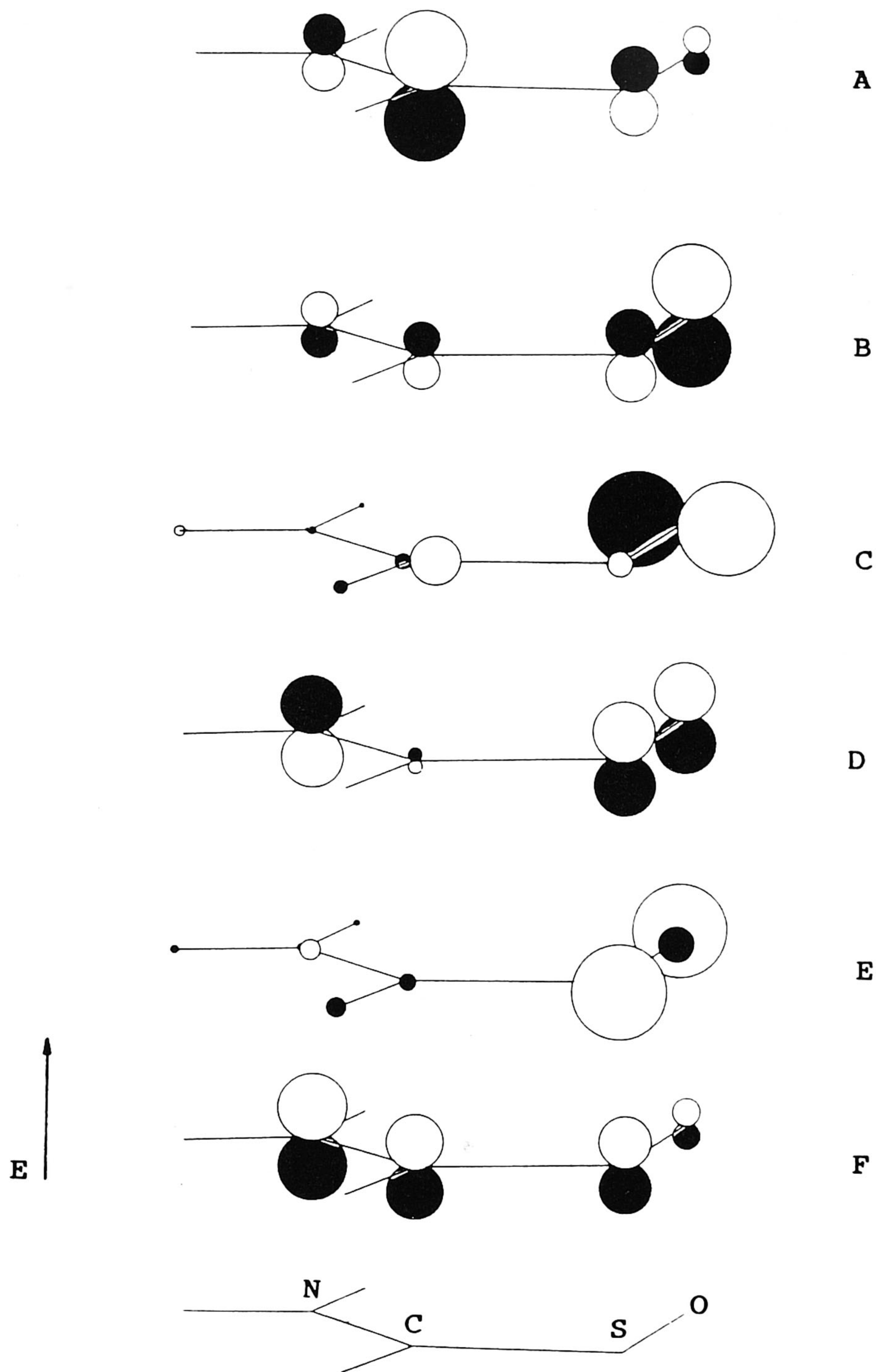
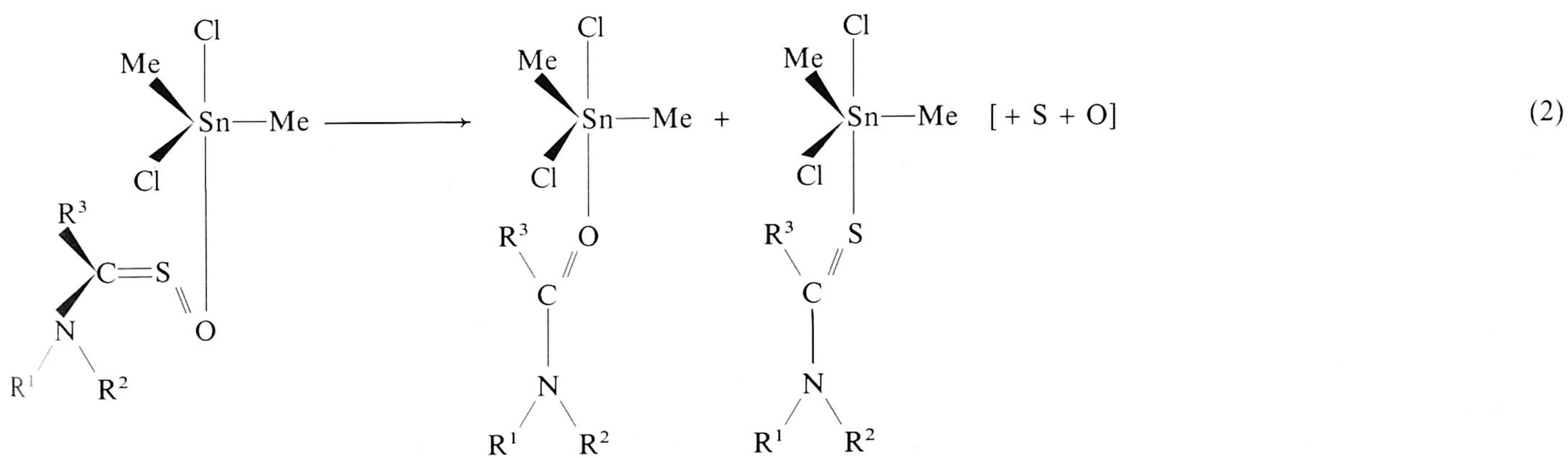


Fig. 2. PICTOR plot of the calculated molecular orbitals. The coefficients of the molecular orbitals are reduced to approximately 30% for clarity.



In order to prove the formation of oxygen and sulphur, the decomposition experiments were also carried out in the presence of PPh_3 in order to trap liberated molecular oxygen as well as sulphur. These reactions were followed by ^{31}P NMR spectrometry. At room temperature, only the signal of free PPh_3 was observed, while resonances belonging to $\text{PPh}_3=\text{O}$ or $\text{PPh}_3=\text{S}$ were absent. The solution was then heated in the NMR tube up to 100°C and the ^{31}P NMR spectrum recorded after 30 minutes, which showed that $\text{Ph}_3\text{P}=\text{O}$ and $\text{Ph}_3\text{P}=\text{S}$ were formed.

The decomposition of the complexes in the solid was followed by IR spectroscopy. Fig. 3 shows the collapse of the sulphine absorptions and the concomitant growth of the amide and thioamide signals in the infrared spectrum of a heated sample of $\text{Me}_2\text{SnCl}_2 \cdot [\text{Ph}(\text{Me})\text{N}(\text{Ph})\text{C}=\text{S}=\text{O}]$.

Because of the presence of isobestic points in the IR spectra, recorded after several time intervals, it is clear that, on the IR time scale, intermediates are not detectable.

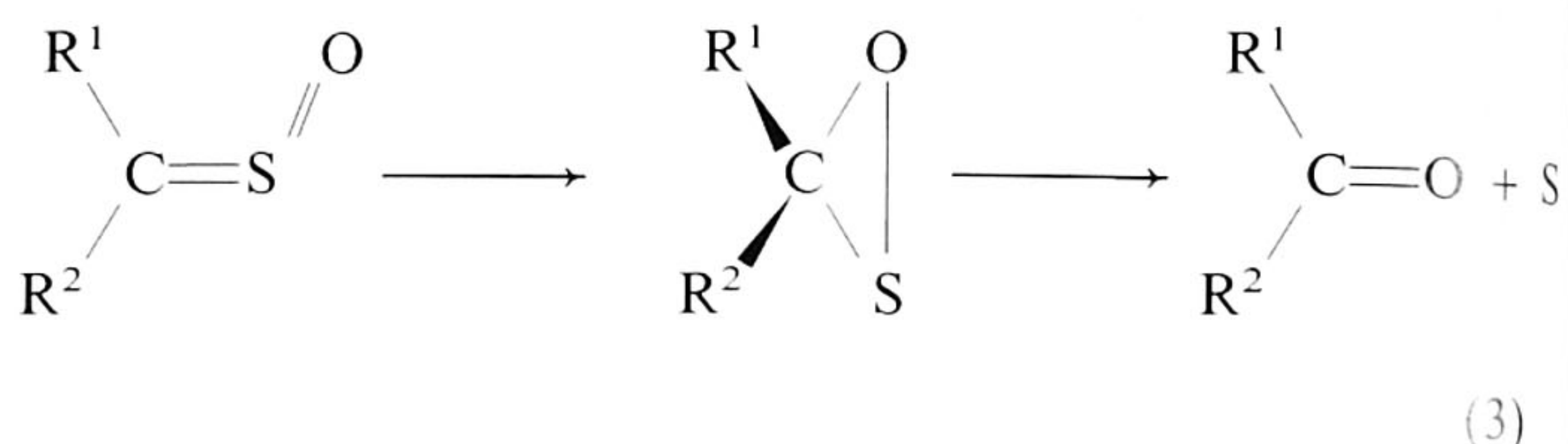
Coordination of the aminosulphine to the tin centre obviously leads to a weakening of both the $\text{C}=\text{S}$ and the $\text{S}=\text{O}$ bond in the sulphine ligand, as is already indicated by the fact that both the $\text{C}=\text{S}$ and the $\text{S}=\text{O}$ bond in **1b** are lengthened upon coordination. The IR stretching frequency of the sulphine unit is shifted to lower frequency by approximately 100 cm^{-1} (Table VIII), which supports the earlier conclusion that the bonding in the $\text{C}=\text{S}=\text{O}$ fragment is weakened upon coordination.

Table VIII Infrared^a.

Compound	$\nu(\text{CSO})$	$\nu(\text{CSO free})$	$\nu(\text{Sn}-\text{Cl})$
1b	903, 949	1008, 992	315, 289
2b	900, 922	1021, 981	317, 294
3b	888, 820	1015, 994	332, 310
4b	898, 936	1015, 1037	333, 306
5b	1002, 1064	1086, 1117	316, 288

^a 2% complex in KBr (w/w).

It is known that sulphines, when exposed to heat or UV radiation, mainly produce the corresponding ketones by elimination of sulphur¹³. This process is thought to take place intramolecularly via an oxathiiran intermediate (see Eqn. 3)³⁵⁻³⁹.



Theoretical calculations have shown that the formation of an oxathiiran intermediate is a thermally and photochemically allowed process. Furthermore, it appeared that the ring closure process to form the oxathiiran is promoted by the presence of a positive charge in the neighbourhood of the oxygen atom³⁵. In view of the $\text{S}=\text{O}$ and $\text{C}=\text{S}$ bond cleavage reactions observed in this study, it is important to note that the free sulphines, when heated at the same temperatures for the same length of time necessary to decompose the tin–aminosulphine complex, did not result in the occurrence of either O or S elimination. Therefore, we can conclude that the tin centre facilitates the formation of the oxathiiran intermediate and, moreover, also affects the subsequent process involving either sulphur elimination (the “normal” thermal process) or oxygen elimination.

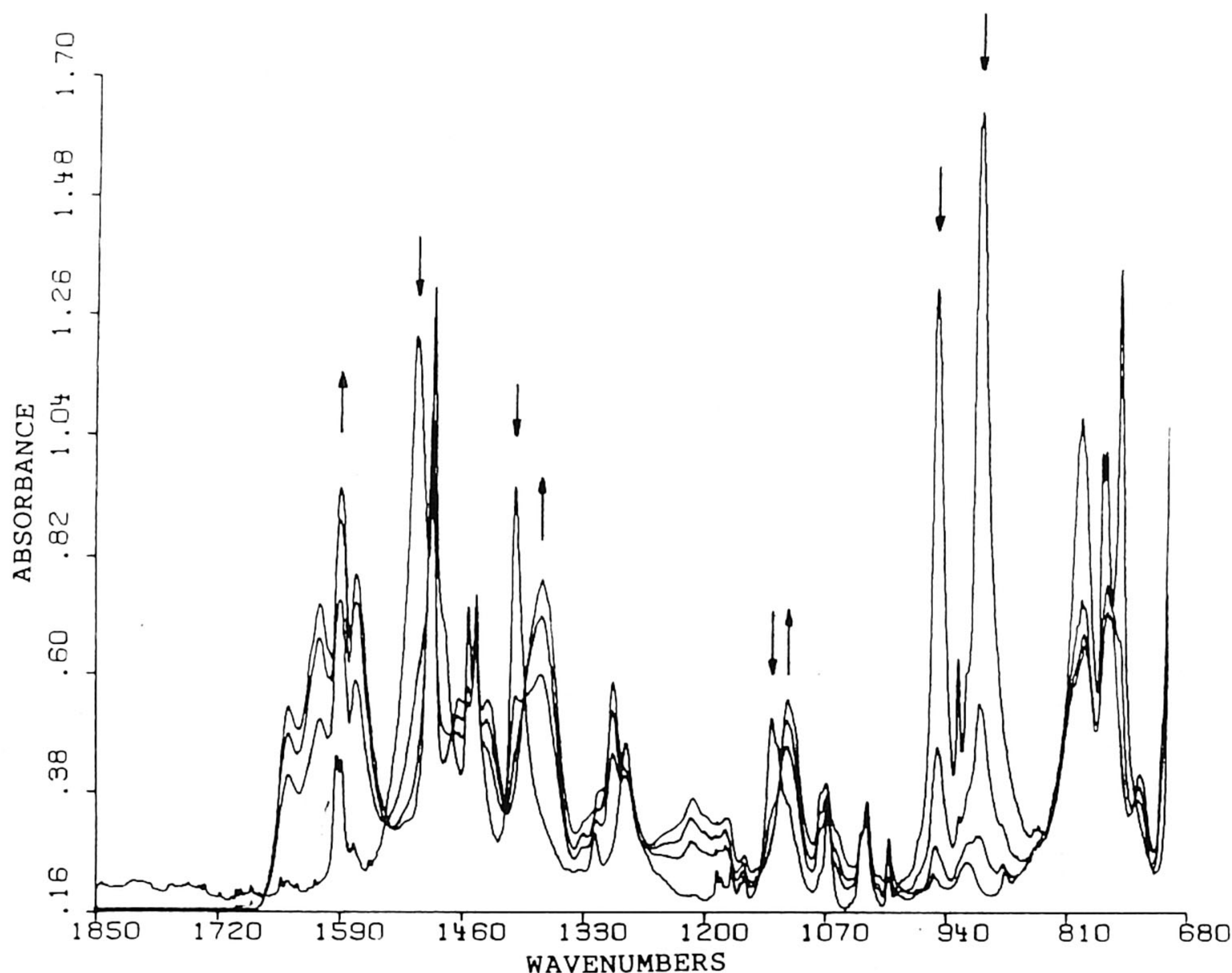


Fig. 3. Infrared spectra of a decomposing sample of $\text{Me}_2\text{SnCl}_2 \cdot [\text{Ph}(\text{Me})\text{N}(\text{Ph})\text{C}=\text{S}=\text{O}]$.

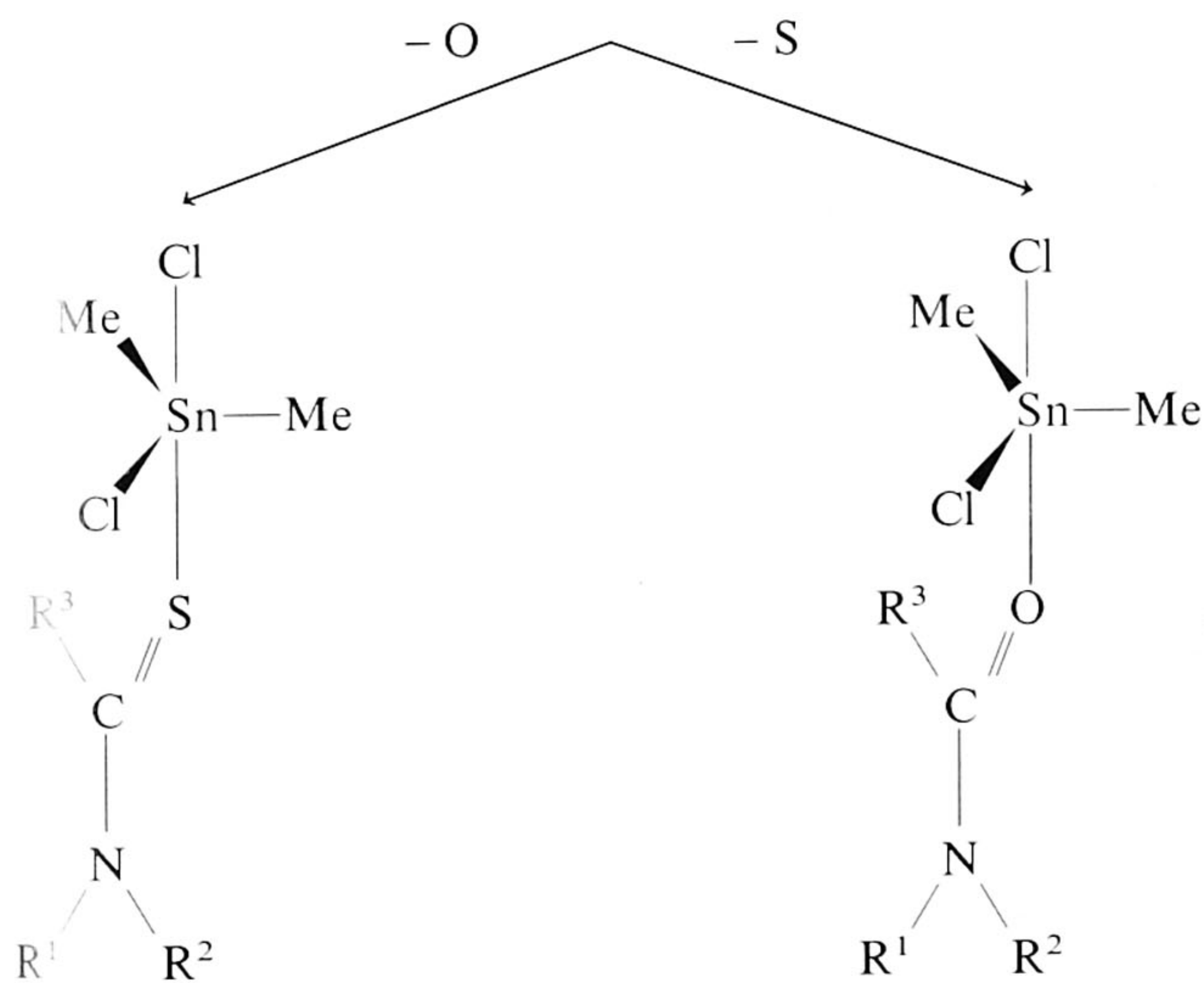
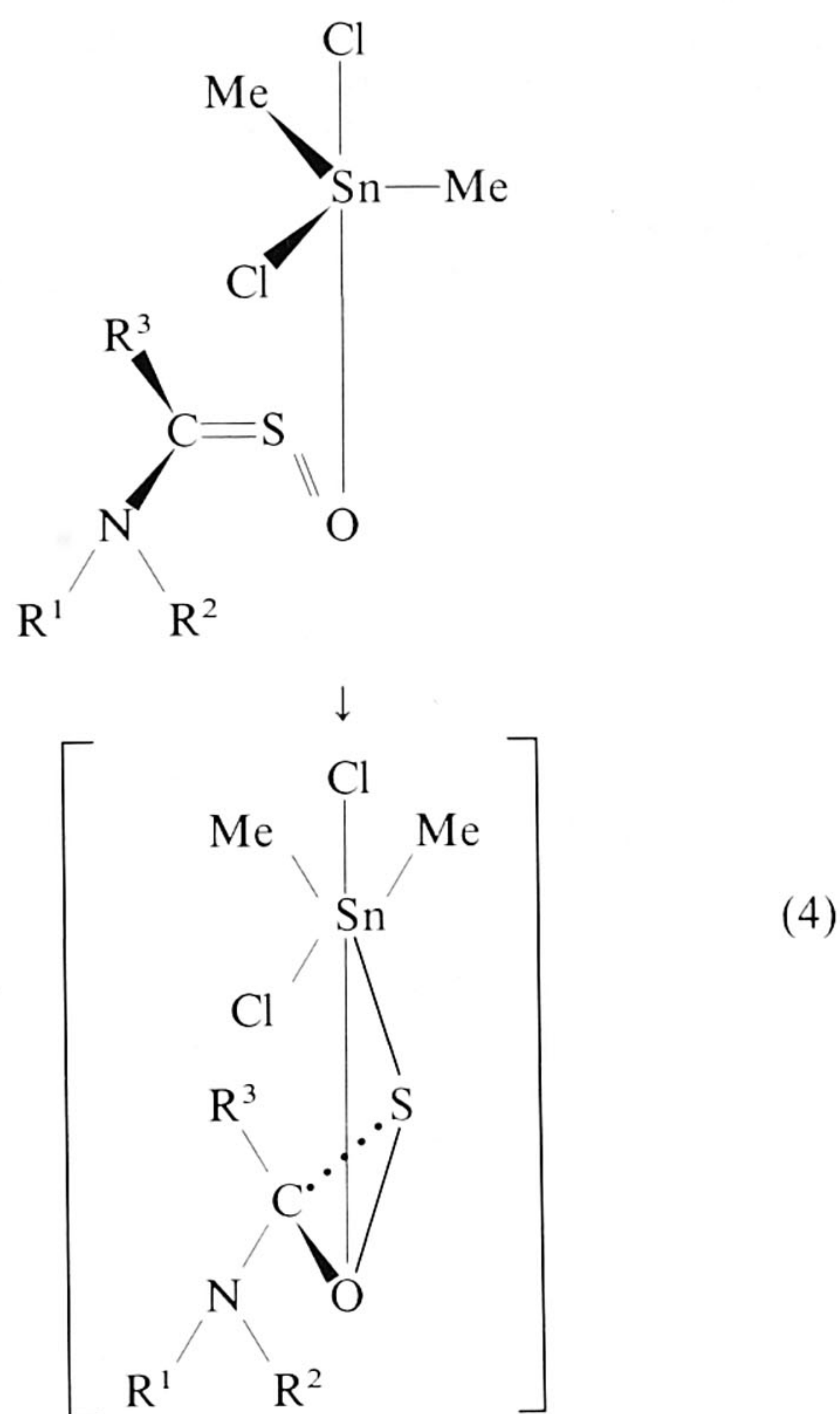
³⁵ J. P. Snyder, J. Am. Chem. Soc. **96**, 5005 (1974).

³⁶ L. Carlsen, N. Harrit and A. Holm, J. Chem. Soc. Perkin I 1404 (1976).

³⁷ L. Carlsen, A. Holm, E. Koch and B. Stilkerieg, Acta Chem. Scand. **B31**, 679 (1977).

³⁸ R. H. Schlessinger and A. G. Schultz, Tetrahedron Lett. **52**, 4513 (1969).

³⁹ J. Silháněk and M. Zbirovský, J. Chem. Soc. Chem. Commun. 878 (1969).



A proposed mechanism for this process, which also accounts for the observed electronic and steric effects of the substituents upon the product formation, is depicted in Eqn. 4. The formation of the oxithiiran intermediate in the decomposition process may account for the somewhat higher stability of the 9-fluorene thione *S*-oxide/tin complex. The process shown in Eqn. 4 would require that, in the transition state the sulphine carbon atom of the 9-fluorene thione *S*-oxide ligand rehybridizes from sp^2 to sp^3 which seems energetically less favourable.

(v) ^{119}Sn NMR of the complexes

In order to obtain more information about both the nature of the tin-sulphine interaction and the factors governing the decomposition reaction, ^{119}Sn NMR spectra of the complexes were recorded. Room temperature spectra of freshly prepared solutions showed one broad ^{119}Sn resonance (100–300 Hz) which shifted continuously, indicating that the nature of the tin-centre-ligand assembly changed gradually during the time necessary for the recording of the spectrum. The δ position of the observed signal appeared to be the average of the signal of the pure tin-aminosulphine complexes (*vide infra*) and the signals of the tin decomposition products. In order to overcome this difficulty, spectra of freshly prepared complexes were recorded at 223 K which resulted in the ^{119}Sn NMR data as listed in Table IX.

Table IX ^{119}Sn NMR spectra^a.

Compound	$\delta(^{119}\text{Sn})$ (ppm)
1b	-70.2
2b	-46.9
3b	-34.0
4b	-15.4
5b	84.6

^a Chemical shifts relative to Me_4Sn . Recorded in CDCl_3 .

Although, under these conditions, the ^{119}Sn resonance was not shifting, a broad resonance (100–150 Hz) was still observed. This is surprising because Sn resonances are generally very narrow. The peak broadening may be due to the quadrupole moment of the chlorine atoms which are attached to the tin centre⁴⁰.

The intermolecular exchange of the aminosulphine ligand and the decomposition products, the thioamides and amides, at the tin-centre was studied by addition of an excess of the corresponding thioamide or amide. This addition of either one of these decomposition products resulted in a shift of $\delta(^{119}\text{Sn})$ value which was indeed dependent upon the amount of amide or thioamide added. However, quantitative data could not be obtained. It can be concluded qualitatively that in solution the sulphine, the amide and the thioamide compete for coordination at the tin centre. Recently, Zuckerman et al. showed that ketones can indeed coordinate via the oxygen atom to the tin-centre^{10,11}.

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⁴⁰ C. Brevard and P. Granger, "Handbook of High Resolution Multinuclear NMR", J. Wiley, N.Y.