ELSEVIER

Journal of Organometallic Chemistry 492 (1995) 145–150

Journal of Organo metallic Chemistry

Synthesis, NMR studies and molecular structures of $[(PhSSn)_2(CH_2)_3]_2$ and $[PhSn(S_2CNEt_2)]_2(S)(CH_2)_3$

Dainis Dakternieks [a,*], Klaus Jurkschat [a,*], Dieter Schollmeyer [b], Hong Wu [a]

[a] *School of Biological and Chemical Sciences, Deakin University, Geelong 3217, Australia*

[b] *Institut für Organische Chemie der Johannes Gutenberg-Universität, Johann Joachim Becher-Weg, D-6500 Mainz, Germany*

Received 21 July 1994

Abstract

Reaction of bis(dichlorophenylstannyl)propane $(PhCl_2Sn)_2(CH_2)_3$ with Na_2S gives the dimeric compound $[(PhSSn)_2(CH_2)_3]_2$ (**1**) which has been shown by X-ray crystallography to contain six-membered SnC_3SnS rings as well as eight-membered Sn_4S_4 rings. NMR studies show that **1** is stable in toluene solution with the same structure as that in the solid state, but addition of chloride ion brings about exchange, resulting in the formation of other geometrical isomers. The compound $[PhSn(S_2CNEt_2)]_2(S)(CH_2)_3$ (**2**) exists as the *cis*-isomer and contains six-membered SnC_3SnS rings in the solid state. In solution, **2** exists as a mixture of *cis*-and *trans*-isomers.

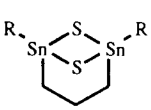
Keywords: Tin; Diorganotin sulphides; Crystal structure; Isomerism

1. Introduction

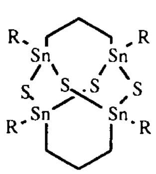
Structural studies of diorganotin(IV) sulphides show that a variety of structures exist in the solid state depending on the organic groups bonded to the tin atom. For example, $(Me_2SnS)_3$ [1] and $(PhSnS)_3$ [2] are cyclic trimers containing a six-membered Sn_3S_3 ring, whereas $({}^t\mathrm{Bu}_2\mathrm{SnS})_2$ and $({}^t\mathrm{Am}_2\mathrm{SnS})_2$ [3,4] are cyclic dimers containing a four-membered Sn_2S_2 ring. Four-membered rings can also be stabilized by incorporation of an intramolecular functionality into the ligand [5,6]. Adamantane-like structures containing six-membered SnSSnCSnS rings have been observed for several diorganotin(IV) sulphides $[(RSSn)_2CH_2]_2$ in which two tin atoms are bridged by a single methylene carbon atom [7]. Different structural possibilities exist (**I**–**VI**) for the propylene-bridged analogues $[(RSSn)_2(CH_2)_3]_2$ depending on the stability of various rings sizes and on the degree of oligomerization. We now report the synthesis, NMR studies and molecular structures of $[PhSSn)_2(CH_2)_3]_2$ (**1**) and $[(PhSn(S_2CNEt_2)]_2(S)(CH_2)_3$ (**2**).

2. Results and discussion

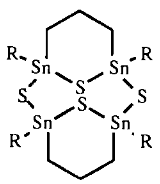
Treatment of bis(dichlorophenylstannyl)propane $(PhCl_2Sn)_2(CH_2)_3$ with two molar equivalents of sodium sulphide at 0°C in acetone/water gave a white solid product with an elemental analysis consistent



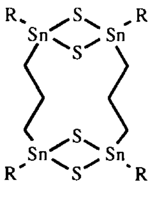
I



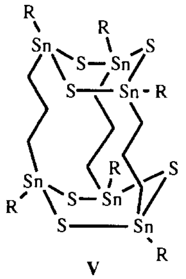
II



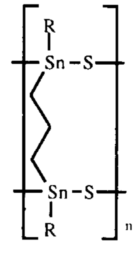
III



IV



V



VI

---

* Corresponding author.

Elsevier Science S.A.
SSDI 0022-328X(94)05303-0

with the empirical formula $(PhSSn)_2(CH_2)_3$. The X-ray structural determination showed it to be a dimeric species $[(PhSSn)_2(CH_2)_3]_2$ (**1**).

$$2(PhCl_2Sn)_2(CH_2)_3 + 4Na_2S \rightarrow \underset{(\mathbf{1})}{[(PhSSn)_2(CH_2)_3]_2} + 8NaCl$$

Treatment of bis(dichlorophenylstannyl)propane $(PhCl_2Sn)_2(CH_2)_3$ with two molar equivalents of sodium diethyldithiocarbamate at room temperature in dichloromethane/ethanol yielded $[PhClSn(S_2CNEt_2)]_2(CH_2)_3$ as an oil which upon treatment with one molar equivalent of sodium sulphide at 0°C in acetone/water gave a white solid product with satisfactory elemental analyses for $[PhSn(S_2CNEt_2)]_2(S)(CH_2)_3$ (**2**).

$$(PhCl_2Sn)_2(CH_2)_3 + 2NaS_2CNEt_2 \rightarrow [Ph(Cl)Sn(S_2CNEt_2)]_2(CH_2)_3 + 2NaCl$$

$$[Ph(Cl)Sn(S_2CNEt_2)]_2(CH_2)_3 + Na_2S \rightarrow \underset{(\mathbf{2})}{[PhSn(S_2CNEt_2)]_2(S)(CH_2)_3} + 2NaCl$$

The ^{119}Sn NMR spectrum at room temperature of a toluene solution of **1** (recrystallized from toluene) consists of a single resonance at δ 53.9 ppm with $^2J(^{119}Sn{-}S{-}^{117}Sn) = 183$ Hz. It is interesting that a solution of the same product in dichloromethane solution shows additional, weak, ^{119}Sn resonances at δ 64.0, 69.0, 74.0 and 74.5 ppm. Moreover the ^{119}Sn NMR spectrum in dichloromethane solution is very similar to that of the compound in toluene solution to which has been added a catalytic amount of Cl^- as Bu_4NCl. These observations indicate that the single isomer of **1** isolated from toluene is stable in toluene solution but that other structural isomers may be formed in dichloromethane solution. Furthermore, it appears that the addition of a Lewis base such as chloride ion may catalyze the formation of other structural isomers (**I**, **II**, **IV–VI**) in solution. We have found earlier that the addition of chloride ion also catalyzed exchange reactions between stannaadamantanes, possibly via formation of a hypervalent tin intermediate [7]. The ^{119}Sn MAS NMR spectrum of **1** displays a broad resonance at δ 68 ppm which is close to the signal observed for the toluene solution.

The ^{119}Sn NMR spectrum of $[PhClSn(S_2CNEt_2)]_2(CH_2)_3$ in dichloromethane shows only one singlet resonance at δ −272.6 ppm, which is assigned to a five-coordinated tin atom [9–11]. The ^{119}Sn NMR spectrum of **2** in dichloromethane shows two resonances of equal intensity at δ −144.5 ppm $[^2J(^{119}Sn{-}S{-}^{117}Sn) = 117$ Hz] and at δ −147.5 ppm $[^2J(^{119}Sn{-}S{-}^{117}Sn) = 105$ Hz]. The ^{119}Sn MAS NMR spectrum of **2** shows two signals at δ −149 and −169 ppm. The molecular structure of **2** (see below) shows a *cis*-configuration containing a Sn_2C_3S six-membered ring and the two ^{119}Sn resonances are assigned to *cis*- and *trans*-isomers, respectively. This assignment is confirmed by the ^{13}C NMR spectrum, which shows that the resonances attributed to $Sn{-}CH_2$, $-CH_2-$, $N{-}CH_2$, $-CH_3$ and CS_2 all appear as pairs. For the phenyl groups, only the resonance attributed to *o*-C is split. Furthermore, ^1H NMR data are also consistent with the presence of *cis*- and *trans*-isomers in solution.

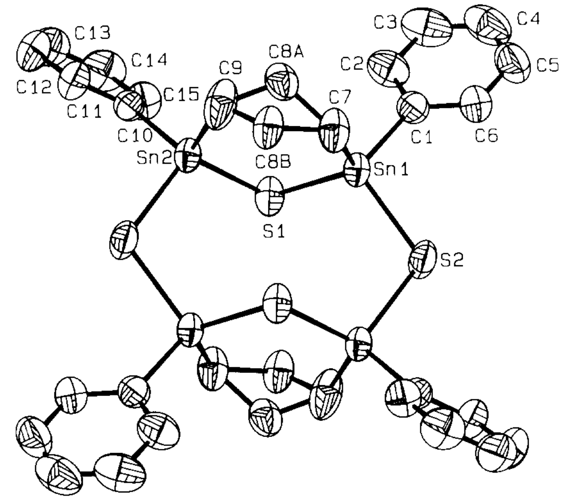
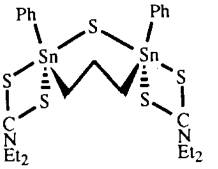
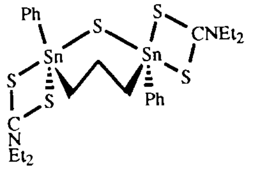


Fig. 1. The molecular structure of $[(PhSSn)_2(CH_2)_3]_2$ showing the numbering scheme.



cis-



trans-

2.1. The molecular structure of 1 and 2

The molecular structure of **1** is depicted in Fig. 1. Selected bond distances and bond angles are listed in Table 1, and selected torsion angles in Table 2. The molecule contains an Sn_4S_4 eight-membered ring and two $SnSSnC_3$ six-membered rings. The C_3 parts of these six-membered rings are *trans* with respect to each other. The Sn_4S_4 eight-membered ring shows a twisted-chair conformation that is comparable to that observed in 1,3,5,7-tetrathiocane [8a]. A six-membered $SnSSnC_3$ ring is also found in the tristannaadamantane $C_4H_7(PhSnS)_3$ [8b]. The shorter Sn–C distance (2.143 Å) and larger Sn–S–Sn angle (99.62°) in $[(PhSSn)_2(CH_2)_3]_2$ compared with those in $C_4H_7(PhSnS)_3$ (2.154 Å and 94.3°) may indicate less strain in the former

Table 1
Selected bond distances (Å) and bond angles (°) in **1**

Sn1–S1	2.407(1)	Sn1–S2	2.397(1)
Sn1–C1	2.135(5)	Sn1–C7	2.142(4)
Sn2–S1	2.407(1)	Sn2–S2	2.402(1)
Sn2–C9	2.144(5)	Sn2–C10	2.129(4)
C7–C8A	1.549(9)	C7–C8B	1.534(13)
C8B–C9	1.372(15)	C8A–C9	1.415(9)
S1–Sn1–S2	108.26(4)	S1–Sn2–S2	109.47(4)
S1–Sn1–C1	107.00(13)	S1–Sn2–C9	113.01(14)
S1–Sn1–C7	114.92(12)	S1–Sn2–C10	105.25(11)
S2–Sn1–C1	100.71(12)	S2–Sn2–C9	108.94(19)
S2–Sn1–C7	113.66(13)	S2–Sn2–C10	103.18(11)
C1–Sn1–C7	111.17(18)	C9–Sn2–C10	116.42(20)
Sn1–S1–Sn2	99.62(4)	Sn1–S2–Sn2	105.89(4)
Sn1–C7–C8A	112.18(35)	Sn1–C7–C8B	123.53(50)
C7–C8A–C9	116.92(51)	C7–C8B–C9	120.78(78)
Sn2–C9–C8	120.70(60)	Sn2–C9–C8A	123.50(41)

compound. The propyl chain is disordered at atom C8 (ratio 0.65 : 0.35). The elongation of C8 from the plane of the five-membered ring Sn1–C7–C8–C9–Sn2 results in relief of strain. Because an inversion of C8 through this plane is very unlikely, a statistical disorder can be assumed.

The molecular structure of **2** is presented in Fig. 2. Selected bond distances and bond angles are listed in Table 3 and selected torsion angles in Table 4. The molecular structure of **2** shows a *cis*-configuration with a boat Sn–S–Sn–CH_2–CH_2–CH_2 six-membered ring. Each tin atom in the molecule is penta-coordinated, with a trigonal-bipyramidal geometry, owing to the bidentate bonding of the diethyldithiocarbamate ligand to the tin atom, with two C[C1, C4 for Sn1; C3, C10 for Sn2] and one S[S2 for Sn1; S4 for Sn2] occupying the equatorial positions and two S[S1, S3 for Sn1; S1, S5 for Sn2] the axial ones. The Sn–S bond distances for Sn1–S3 and Sn2–S5 (average 2.925 Å) are longer than the sum of the covalent radii of Sn and S (2.44 Å) but shorter than the sum of van der Waals radii (3.97 Å)

Table 2
Torsion angles (°) for the eight-membered Sn_4S_4 and the six-membered Sn_2SC_3 rings in **1**

S2–Sn1–S1–Sn2	133.66(5)
Sn1–S1–Sn2–S2′	−115.13(5)
S1–Sn2–S2′–Sn1′	29.40(5)
Sn2–S2′–Sn1′–S1′	54.05(5)
S2′–Sn1′–S1′–Sn2′	−133.66(5)
Sn1′–S1′–Sn2′–S2	115.13(5)
S1′–Sn2′–S2–Sn1	−29.40(5)
Sn2′–S2–Sn1–S1	−54.05(5)
S1–Sn2–C9–C8A	17.4(6)
S1–Sn2–C9–C8B	−44.6(8)
Sn2–C9–C8A–C7	−66.3(6)
Sn2–C9–C8B–C7	69.6(9)
C9–C8A–C7–Sn1	78.6(7)
C9–C8B–C7–Sn1	−50 (1)
C8A–C7–Sn1–S1	−43.3(4)
C8B–C7–Sn1–S1	8.4(8)
C7–Sn1–S1–Sn2	5.4(2)
Sn1–S1–Sn2–C9	6.5(2)

Table 3
Selected bond distances (Å) and bond angles (°) in **2**

Sn1–S1	2.434(2)	Sn1–S2	2.465(2)
Sn1–S3	2.957(2)	Sn1–C1	2.141(6)
Sn1–C4	2.146(6)	Sn2–S1	2.447(1)
Sn2–S4	2.459(2)	Sn2–S5	2.894(2)
Sn2–C3	2.145(6)	Sn2–C10	2.132(5)
S2–C16	1.760(6)	S3–C16	1.668(6)
S4–C21	1.764(6)	S5–C21	1.688(7)
N1–C16	1.398(9)	N1–C17	1.587(12)
N1–C19	1.549(9)	N2–C21	1.326(8)
N2–C22	1.478(9)	N2–C24	1.477(11)
C1–C2	1.539(8)	C2–C3	1.514(8)
S1–Sn1–S2	95.54(5)	S1–Sn1–S3	160.60(5)
S1–Sn1–C1	108.23(16)	S1–Sn1–C4	98.02(16)
S2–Sn1–S3	65.41(5)	S2–Sn1–C1	113.42(16)
S2–Sn1–C4	117.80(16)	S3–Sn1–C1	84.07(16)
S3–Sn1–C4	88.48(16)	C1–Sn1–C4	118.81(22)
S1–Sn2–S4	93.90(5)	S1–Sn2–S5	160.42(5)
S1–Sn2–C3	105.82(16)	S1–Sn2–C10	99.06(14)
S4–Sn2–S5	66.67(5)	S4–Sn2–C3	117.01(16)
S4–Sn2–C10	115.09(15)	S5–Sn2–C3	82.39(16)
S5–Sn2–C10	91.83(14)	C3–Sn2–C10	119.52(21)
Sn1–S1–Sn2	101.45(5)	Sn1–S2–C16	94.71(21)
Sn1–S3–C16	80.43(22)	Sn2–S4–C21	93.21(21)
Sn2–S5–C21	80.69(21)		

Table 4
Torsion angles (°) for the six-membered ring in **2**

S1–Sn1–C1–C2	−7.3(4)
Sn1–C1–C2–C3	73.5(5)
C1–C2–C3–Sn2	−82.3(4)
C2–C3–Sn2–S1	19.4(4)
C3–Sn2–S1–Sn1	29.6(2)
Sn2–S1–Sn1–C1	−34.6(2)

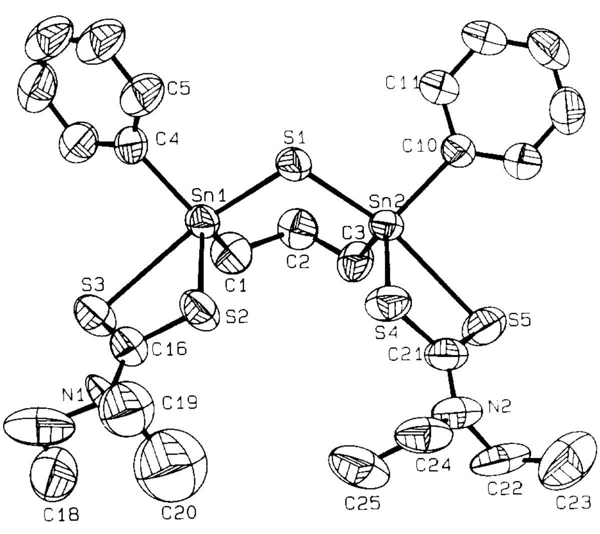


Fig. 2. The molecular structure of $[Ph(Et_2NCS_2)SnCH_2]_2CH_2$ showing the numbering scheme.

[12]. The longer bond distances for Sn1–S3 and Sn2–S5 compared with Sn1–S2 and Sn2–S4 (average 2.462 Å) are attributed to their axial bonding positions, and are in agreement with a general structural principle concerning trigonal–bipyramidal molecular geometry [13–16]. The Sn–S bond distances [Sn1–S1, 2.434 Å; Sn2–S1, 2.447 Å] involved in the Sn–S–Sn–CH_2CH_2–CH_2 six-membered ring are longer than the corresponding Sn–S bond distances (2.403 Å) in the six-membered ring of the tetracoordinated compound **1**.

3. Experimental details

3.1. Physical measurements

Tin-119 NMR spectra were recorded at 100.75 MHz with broad-band proton-decoupling an a JEOL GX 270 MHz spectrometer, and referenced against external Me_4Sn. Phosphorus-31 spectra were recorded at 109.38 MHz and referenced against external 85% phosphoric acid. Carbon-13 spectra were recorded at 67.94 MHz and referenced against internal TMS. Temperatures were maintained using a JEOL GTV3 control system. Solid-state ^{119}Sn NMR spectra were recorded by Dr. T.J. Bastow (CSIRO Division of Materials Science and Technology) using a Bruker MSL-400 at 149.21 MHz. The pulse width was 2.5 μs and spinning frequencies for MAS ranged between 4.1–4.8 kHz.

3.2. Preparation of compounds

3.2.1. Synthesis of 1,3-bis(triphenylstannyl)propane, $(Ph_3Sn)_2(CH_2)_3$

A solution of 1,3-dichloropropane (22.0 g, 0.12 mol) in 30 ml of dry THF, was added dropwise to a mechanically stirred solution of 0.39 mol of Ph_3SnNa in 500 ml of liquid ammonia at −78°C. The mixture was stirred for 1 h and the ammonia then allowed to evaporate slowly. Ether (200 ml) was added, the mixture stirred for 10 min, and the solution filtered to remove the NaCl. The filtrate was evaporated, the oily residue dissolved in ether and Ethanol added. Slow evaporation of the solvent yielded colourless crystals of $(Ph_3Sn)_2(CH_2)_3$, m.p. 80–85°C; yield, 92 g. ^1H NMR ($CDCl_3$)δ: 1.66 ($SnCH_2$); 2.14 (CH_2); 7.45 (*o*-Ph) 7.33 (*m,p*-Ph) ppm. ^{119}Sn NMR (CH_2Cl_2)δ: −103.3 ppm. Anal. Calc. for $C_{39}H_{36}Sn_2$ (742.14): C, 63.12; H, 4.89%. Found: C, 62.4; H, 4.80%.

3.2.2. Synthesis of $[(PhSSnCH_2)_2CH_2]_2$ (1)

A solution of 1,3-bis(dichlorostannyl)propane, $(PhCl_2SnCH_2)_2CH_2$, (2.0 g, 3.48 mmol) (prepared from 1,3-bis(triphenylstannyl)propane and mercuric chloride) in 15 ml acetone was added dropwise to a mag-

Table 5
Summary of crystallographic data for compound **1** and **2**

Compound	**1**	**2**
Mol. formula	$C_{30}H_{32}S_2Sn_4$	$C_{25}H_{36}N_2S_5Sn_2$
Mol. wt.	931.17	762.22
Cryst. system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/n$
CAD4 diffractometer		
radiation	Mo Kα radiation (0.71069 Å), graphite monochromator	
temp., θ range, scan	298 K, 1.5–30.0°, ω/2θ	
a (Å)	13.009(5)	15.330(2)
b (Å), β(°)	9.039(1), 105.70(2)°	9.8123(8), 89.68(2)°
c (Å)	15.238(2)	21.202(7)
V (Å³)	1725.0(8)	3189(1)
Z	2	4
D_{calc} (g cm^{-3})	1.800	1.594
F(000)	880.0	1528
Range of *hkl*	+19, +13, ±22	+22, −13, ±30
Ref. reflns.	3, every 4000 s	
Loss of intensity (%)	10	20
Correction	linear fit	cubic spline fit
No. of reflns.: measd.	5516, 4318 (0.017)	12474, 7944 (0.011)
Indep. (int *R*)		
no. of reflns. used, limit	3351, $I > 1.96\sigma I$	5857, $I > 1.96\sigma I$
μ, (cm^{-1})	27.8 (num. abs. corr.)	17.62 (num. abs. corr.)
Trans. factors	0.736, 0.549	0.789, 0.719
Variables, ratio refl./var.	185, 18	303, 19
Final *R*, R_w	0.0288, 0.0296	0.0484, 0.0413
Weighting scheme	$1/(\sigma^2(F_o) + 0.000311F^2)$	$1/(\sigma^2(F_o))$

netically stirred, ice-cooled, solution of $Na_2S \cdot 9H_2O$ (1.67 g, 6.96 mmol) in a mixture of 10 ml methanol and 5 ml water. The mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed in vacuo, 20 ml of dichloromethane were added, and the mixture was stirred for 15 min and the solution was then filtered to remove sodium chloride. The filtrate was evaporated and the residue recrystallized from toluene to give **1** (1.47 g, 85%) as colourless crystals, m.p. 190°C. Anal. Calc. for $C_{30}H_{32}S_4Sn_4$ (995.69): C, 36.19; H, 3.24%. Found: C, 36.24; H, 3.14%.

3.2.3. *Synthesis of* $[PhSn](Et_2NCS_2)(CH_2)_3$ *(2)*

A solution of $Et_2NCS_2Na \cdot 3H_2O$ (0.87 g, 3.86 mmol) in 25 ml ethanol was added dropwise to a magnetically stirred solution of $(PhCl_2SnCH_2)_2CH_2$ (1.11 g, 1.93 mmol) in 30 ml of dichloromethane. The mixture was stirred for 2 h and the solvent then evaporated. The residue was stirred for 15 min with 25 ml of dichloromethane and the solution was filtered to remove the sodium chloride. The filtrate was evaporated in vacuo to yield $[PhClSn(Et_2NCS)_2]_2(CH_2)_3$ as a colourless oil. ^{13}C NMR ($CDCl_3$) ($J(^{119}Sn-^{13}C)$, Hz) δ: 32.4 ($SnCH_2$, (597)); 22.5 (CH_2, (31)); 50.4 (NCH_2); 11.8 (CH_3); 142.2 (C_i); 135.7 (C_o, (62)); 129.8 (C_m, (68)); 128.5 (C_p); 194.8 (CS_2) ppm.

A solution of $Na_2S \cdot 9H_2O$ (0.46 g, 1.93 mmol) in 15 ml of water was added dropwise to a magnetically stirred, ice-cooled, solution of $[PhClSn(Et_2NCS)_2]_2(CH_2)_3$ (1.54 g, 1.93 mmol) in 30 ml of dichloromethane. The mixture was allowed to warm to room temperature and stirred for a further 3 h. The solvents were removed under reduced pressure and the residue stirred with 30 ml of dichloromethane for 15 min. The mixture was filtered to remove sodium chloride and diethyl ether (30 ml) was added to the filtrate. Slow evaporation of the solution yielded **2** (1.32 g, 90%) as colourless crystals; m.p. 169–170°C. Anal. Calc. for $C_{25}H_{36}N_2S_5Sn_2$ (762.32): C, 39.39; H, 4.76; N, 3.67%. Found: C, 39.45, H, 5.11; N, 3.54%. ^1H NMR ($CDCl_3$) δ: 2.57, 2.61 ($SnCH_2$); 2.03, 2.08 (CH_2); 3.61, 3.72 (NCH_2); 1.15, 1.24 (CH_3) ppm. ^{13}C NMR ($CDCl_3$) ($J(^{119}Sn-13C)$, Hz) δ: 28.7, 28.8 ($SnCH_2$, (538)); 22.9, 23.2 (CH_2); 50.4, 50.5 (NCH_2); 12.0, 12.1 (CH_3); 145.2 (C, (694)); 135.9, 136.2 (C_o); 129.5 (C_m); 128.5 (C_p); 196.1, 196.4 (CS_2) ppm.

Table 6
Fractional atomic coordinates and estimated standard deviations for **1**

Atom	*x*	*y*	*z*
Sn1	0.36016(2)	0.11849(3)	0.06463(2)
Sn2	0.36777(2)	−0.24582(3)	−0.04095(2)
S1	0.3378(1)	0.0102(1)	−0.08369(7)
S2	0.47335(9)	0.3311(1)	0.0767(1)
C1	0.2122(4)	0.22123(5)	0.0639(3)
C2	0.1157(4)	0.1705(7)	0.0096(3)
C3	0.0200(5)	0.2386(8)	0.0139(4)
C4	0.0220(6)	0.3537(7)	0.0712(5)
C5	0.1156(6)	0.4051(6)	0.1250(5)
C6	0.2119(5)	0.3394(5)	0.1228(4)
C7	0.4102(4)	−0.0324(5)	0.1764(3)
C8A	0.3495(8)	−0.1816(8)	0.1577(5)
C8B	0.445(1)	−0.192(1)	0.1661(8)
C9	0.3834(6)	−0.2838(5)	0.1009(3)
C10	0.2439(3)	−0.3640(5)	−0.1348(3)
C11	0.2422(4)	−0.5164(5)	−0.1337(3)
C12	0.1647(5)	−0.5940(6)	−0.1981(4)
C13	0.0885(5)	−0.5174(8)	−0.2627(4)
C14	0.0884(4)	−0.3679(8)	−0.2634(4)
C15	0.1666(4)	−0.2900(6)	−0.2005(3)

Table 7
Fractional atomic coordinates and estimated standard deviations for **2**

Atom	*x*	*y*	*z*
Sn1	0.44433(2)	0.21525(4)	0.22008(2)
Sn2	0.26563(3)	0.08598(4)	0.11365(2)
S1	0.3597(1)	0.2847(1)	0.12879(7)
S2	0.5511(1)	0.0785(2)	0.15998(7)
S3	0.5869(1)	0.0993(2)	0.29664(8)
S4	0.3693(1)	−0.0295(2)	0.04264(8)
S5	0.2072(1)	−0.1806(2)	0.07357(9)
N1	0.6921(4)	−0.0308(7)	0.2097(3)
N2	0.3461(4)	−0.2919(5)	0.0175(2)
C1	0.3620(4)	0.0956(6)	0.2803(3)
C2	0.2649(4)	0.0878(6)	0.2625(3)
C3	0.2472(4)	−0.0011(6)	0.2056(3)
C4	0.4836(4)	0.4143(6)	0.2510(3)
C5	0.4788(5)	0.5216(7)	0.2086(3)
C6	0.4948(5)	0.6532(7)	0.2284(4)
C7	0.5135(5)	0.6766(8)	0.2910(5)
C8	0.5197(4)	0.5734(9)	0.3323(4)
C9	0.5046(4)	0.4384(7)	0.3124(3)
C10	0.1588(4)	0.1833(5)	0.0681(3)
C11	0.1334(4)	0.3112(6)	0.0905(3)
C12	0.0599(5)	0.3746(7)	0.0671(4)
C13	0.0123(5)	0.3154(8)	0.0200(4)
C14	0.0376(5)	0.1912(8)	−0.0033(3)
C15	0.1100(4)	0.1249(6)	0.0208(3)
C16	0.6173(4)	0.0436(6)	0.2255(3)
C17	0.7596(7)	−0.0456(9)	0.2658(5)
C18	0.7394(7)	−0.165(1)	0.2914(5)
C21	0.3086(4)	−0.1821(6)	0.0421(3)
C22	0.3026(6)	−0.4261(6)	0.0208(4)
C23	0.2570(7)	−0.4618(9)	−0.0403(4)
C24	0.4346(6)	−0.2894(7)	−0.0104(3)
C25	0.5047(6)	−0.3145(8)	0.0389(4)

3.3. *Crystal structure determinations*

Colourless crystals of **1** (hexagonal prismatic) and **2** (rectangular) were obtained from toluene solution. Crystallographic and refinement data are given in Table 5. Final fractional atomic coordinates are given in Tables 6 and 7. Data were corrected for Lorentz polarization. The Patterson methods option from SHELX86

[17] revealed the locations of all non-hydrogen atoms. The structures were refined by full-matrix least-squares methods, including positional and anisotropic displacement parameters for non-H atoms. The H atoms were located in difference Fourier maps and refined as riding atoms isotropic displacement parameters. The ethylenic group C19–C20 in compound **2** and the C8 atom in compound **1** are disordered.

Acknowledgements

We are grateful to the Australian Research Council (A.R.C.) and to the Stifterverband für die Deutsche Wissenschaft for financial assistance.

References

[1] (a) H.-J. Jacobsen and B. Krebs, *J. Organomet. Chem., 136* (1977) 333; (b) B. Menzcbach and P. Bleckmann, *J. Organomet. Chem., 91* (1975) 291.

[2] B.M. Schmidt and M. Dräger, *J. Organomet. Chem., 399* (1990) 63.

[3] H. Puff, G.B. Ebeling, M. Franken, R. Gattermayer, R. Hundt, W. Schuh and R. Zimmer, *J. Organomet. Chem., 379* (1989) 235.

[4] H. Puff, A. Bongartz, R. Sievers and R. Zimmer, *Angew. Chem., Int. Ed. Engl., 17* (1978) 939.

[5] (a) B.M. Schmidt, M. Dräger and K. Jurkschat, *J. Organomet. Chem., 410* (1991) 43; (b) K. Jurkschat, S. van Dreumel, G. Dyson, D. Dakternieks, T.J. Bastow, M.E. Smith and M. Dräger, *Polyhedron, 11* (1992) 2747; (c) D. Schollmeyer, J. Kalbitz, H. Hartung, A. Tzschach and K. Jurkschat, *Bull. Soc. Chim. Belg., 97* (1988) 1075.

[6] O.S. Jung, J.H. Jeong and Y.S. Sohn, *Polyhedron, 8* (1989) 2557.

[7] D. Dakternieks, K. Jurkschat, H. Wu and E.R.T. Tiekink, *Organometallics, 12* (1993) 2788.

[8] (a) G.W. Frank, P.J. Degen and F.A.L. Anet, *J. Am. Chem. Soc., 94* (1972) 4792; (b) A.I. Beauchamp, S. Lalour, M.J. Olivier and J.D. Wuest, *J. Am. Chem. Soc., 105* (1988) 7778.

[9] J. Otera, *J. Organomet. Chem., 221* (1981) 57.

[10] D. Dakternieks, H. Zhu, D. Masi and C. Mealli, *Inorg. Chem., 31* (1992) 3601.

[11] A.G. Davies, P.G. Harrison, J.D. Kennedy, R.J. Puddephatt, T.N. Mitchell and W. McFarlane, *J. Chem. Soc. A*, (1969) 1136.

[12] J.E. Huheey, *Inorganic Chemistry, Principles of Structure and Reactivity*, Harper and Row, New York, 1972, p. 184.

[13] R.S. McDowell and A.J. Streitiwieser, *J. Am. Chem. Soc., 107* (1985) 5849.

[14] J.A. Deiters and R.R. Holmes, *J. Am. Chem. Soc., 109* (1987) 1686; J.A. Deiters and R.R. Holmes, *J. Am. Chem. Soc., 109* (1987) 1692.

[15] K.C. Molloy, S.J. Blunden and R. Hill, *J. Chem. Soc., Dalton Trans.*, (1988) 1259.

[16] R.R. Holmes, *Prog. Inorg. Chem., 32* (1984) 119.

[17] G.M. Sheldrick, SHELX86 *Program*, University of Göttingen, Germany, 1986.