Journal of Organometallic Chemistry, 388 (1990) 259–271
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20726

1,2-Bis(organostannyl)ethanes as powerful bidentate Lewis acids. Crystal structures of $(Ph_2ClSnCH_2)_2 \cdot (Me_2N)_2PO$ and $[Ph_3P{=}N{=}PPh_3][(Ph_2ClSnCH_2)_2 \cdot Cl]$

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(Received November 24th, 1989)

Abstract

The synthesis of bis(organostannyl)ethanes of the types $(Ph_2XSnCH_2)_2$ (**1**, X = Ph; **2**, X = Cl; **3**, X = Br; **4**, X = I) and $(PhX_2SnCH_2)_2$ (**5**, X = Br, **6**, X = I) is described. The compounds have been investigated by means of ^1H, ^{13}C and ^{119}Sn NMR spectroscopy. **2** reacts with HMPA, $[Ph_3P=N=PPh_3]^+ Cl^-$, and Ph_4PBr, respectively, to give the 1/1 complexes $(Ph_2ClSnCH_2)_2 \cdot HMPA$ (**7**), $[Ph_2ClSnCH_2)_2 \cdot Cl]^-[Ph_3P{=}N{=}PPh_3]^+$ (**8**), and $[(Ph_2ClSnCH_2)_2 \cdot Br]^-[Ph_4P]^+$ (**9**). The formation constant K_a for **8** in $CDCl_3$ solution is 2260 M^{-1}. The structures of **7** and **8** have been determined by X-ray diffraction. That of **7** shows that the two tin atoms are pentacoordinate but are inequivalent as a result of having different coordination sphere; one tin atom is coordinated by the monodentate HMPA (Sn–O 2.255(3) Å) whereas the other interacts with a bridging Cl (Sn(1)...Cl(2) 3.000(1) Å). In the anion of **8**, the bis(chlorodiphenylstannyl)ethane may be regarded as an unsymmetrical chelate ligand towards Cl(12) (Sn(1)-Cl(12) 2.83(1), Sn(2)-Cl(12) 2.70(1) Å).

Introduction

In recent years the complexation chemistry of multidentate Lewis acids has attracted increasing interest [1]. Such species include bidentate boron compounds

† Passed away on 6th October 1989.

[3,4], bi- and tetra-dentate mercury derivatives [5], a tridentate silicon ring [6] and a number of bi-, tri- and tetra-dentate organotin compounds [7–12]. Among organotin compounds, methylene as well as propylene and longer alkyl chain-bridged di- and multi-tins have been investigated, but to our knowledge there have been no reports on the complexation behaviour of ethylene-bridged ditins, which is surprising since such systems should be able to form five-membered chelates, which would be expected to be more stable than four-, six- or higher-membered ones. We describe here the synthesis of some phenyl-substituted 1,2-distannaethanes and a study of their complexation with hexamethylphosphoric triamide and with halide ions.

Results and discussion

Syntheses

1,2-Bis(triphenylstannyl)ethane (**1**) was prepared by reaction of triphenylvinyltin with triphenylstannane (eq. 1).

$$Ph_3SnCH{=}CH_2 + Ph_3SnH \xrightarrow[\text{reflux}]{C_6H_6,\ AIBN} (Ph_3SnCH_2)_2 \quad (1)$$
$$(\mathbf{1})$$

Like its methylene bridged analogue $(Ph_3Sn)_2CH_2$ [10], **1** was readily transformed into the bis(halodiphenylstannyl)-ethanes **2**, **3** and **4** by treatment with methanolic HCl, bromine or iodine (eq. 2, 3).

$$(Ph_3SnCH_2)_2 + 2HCl \xrightarrow{MeOH/CHCl_3} (Ph_2ClSnCH_2)_2 + 2PhH \quad (2)$$
$$(\mathbf{2})$$

$$(Ph_3SnCH_2)_2 + 2X_2 \xrightarrow{CH_2Cl_2/MeOH} (Ph_2XSnCH_2)_2 + 2PhX \quad (3)$$
$$(\mathbf{3},\ X = Br;\ \mathbf{4},\ X = I)$$

Removal of four phenyl groups can be brought about by treatment of **1** with four equivalents of bromine or iodine (eq. 4).

$$(Ph_3SnCH_2)_2 + 4X_2 \xrightarrow{CH_2Cl_2/MeOH} (PhX_2SnCH_2)_2 + 4PhBr \quad (4)$$
$$(\mathbf{5},\ X = Br;\ \mathbf{6},\ X = I)$$

The ^{119}Sn NMR spectra of crude **3** and **5** showed additional resonances (see Experimental) indicating the presence of by-products, which were not isolated. Reaction of **2** with hexamethylphosphoric triamide yielded the one-to-one complex **7** (eq. 5). Formation of a 1/2 complex was not observed even when an excess of HMPA was used.

$$(Ph_2ClSnCH_2)_2 + HMPA \xrightarrow{CH_2Cl_2} (Ph_2ClSnCH_2)_2 \cdot HMPA \quad (5)$$
$$(\mathbf{7})$$

Similar behaviour was observed in complexation with chloride and bromide ions, the 1/1 complexes **8** and **9** were the only products isolated when chloride or

bromide ions were introduced into a solution of **2** in methylene chloride (eq. 6, 7).

$$(Ph_2ClSnCH_2)_2 + [Ph_3P{=}N{=}PPh_3]^+ Cl^- \xrightarrow{CH_2Cl_2} \underset{(8)}{[(Ph_2ClSnCH_2)_2 \cdot Cl]^-}[Ph_3P{=}N{=}PPh_3]^+ \quad (6)$$

$$(Ph_2ClSnCH_2)_2 + Ph_4PBr \xrightarrow{CH_2Cl_2} \underset{(9)}{[(Ph_2ClSnCH_2)_2 \cdot Br]^-}[Ph_4P]^+ \quad (7)$$

For purposes of comparison the simple chloride complex $[Ph_2EtSnCl_2]^-[Ph_3P{=}N{=}PPh_3]^+$ (**10**) was also prepared. Compounds **1** to **10** are colourless crystals, soluble in polar organic solvents.

Spectroscopic investigations

The NMR data can in the main be compared with those reported for the methylene bridged analogues of **1** to **9** [8,10]. The ^1H NMR data of **1** to **10** are summarized in Table 1. The methylene protons give the expected singlets, and show a systematic low field shift on going from **1** to **6**. Compared with those in **2** the methylene protons in **7**, **8**, and **9** also exhibit a low field shift. The phenyl signals show a complex pattern for the *ortho* protons and a separate complex pattern for the *meta* and *para* protons together.

The ^{13}C NMR data are listed in Table 2. The methylene carbons appear as singlets with both $^1J(^{119}Sn{-}^{13}C)$ and $^2J(^{119}Sn{-}^{13}C)$ couplings. Again the chemical shift depends on the substituents at the tin atoms.

Table 1

^1H NMR data of **1–10** in $CDCl_3$

Compound	Chemical shifts δ(ppm) ($J(^{119}Sn{-}^1H)$ coupling constants (Hz))		
	CH_2	*o*-Ph	*m*, *p*-Ph
1	1.86 (63.5)	7.50	7.36
2	2.12 (67.2)	7.56	7.42
3	2.12	7.57	7.41
4	2.08	7.61	7.56
5	2.42	7.61	7.49
6	2.36	7.5	7.5
7 [a]	2.20 (76.7)	7.63	7.34
8	2.32 (81.2)	7.58	7.16
9	2.26 (79.0)	[c]	[c]
10 [b]	1.77 (81.1)	7.60	7.23

[a] $\delta(NCH_3)$ 2.48 ppm, $^3J(^{31}P{-}^1H)$ 9.5 Hz. [b] $\delta(CH_3)$ 1.46 ppm. [c] Complex pattern between 7.0 and 8.0 ppm as a result of superposition of the tin and phosphorus phenyl protons.

Table 2

^{13}C and ^{119}Sn NMR data of **1**–**10** in $CDCl_3$

Compound	Chemical shifts δ (ppm) ($J(^{119}Sn-^{13}C)$ and $J(^{119}Sn-^{117}Sn)$ coupling constants (Hz))					
	CH_2	C_i	C_o	C_m	C_p	^{119}Sn
1	7.7	139.0	137.3	128.7	129.1	−104.3
	(367.8; 39.3)	(471.8)	(34.6)	(47.2)	(10.8)	(1318)
2	13.1	138.6	136.1	129.2	130.4	1.8
	(398.5; 43.5)	(530.0)	(47.8)	(60.4)	(11.1)	(1792)
3	13.3	137.6	135.9	129.0	130.2	−5.4
	(379.0; 44.6)	(519.3; 14.4)	(47.1)	(59.5)	(12.4)	(1916)
4	13.6	136.8	136.1	128.9	130.1	−53.8
	(357.5; 45.5)	(491.5)	(46.2)	(57.5)		(2001)
5	21.5	138.2	134.7	129.6	131.6	−6.3
	(429.6; 54.9)	(626.0; 33.7)	(63.2)	(78.5)	(16.9)	(3269)
6	22.1	136.2	134.6	129.2	131.2	−169.0
	(363.2; 56.0)	[a]	(59.8)	(71.7)	(15.6)	(3397)
7	14.8	139.5	136.1	129.2	130.0	−102.6
	[a]	[a]	(47.2)	(60.8)	(13.2)	
8	23.3	145.3	137.1	127.6	128.0	−128.3
	(618.8; 33.8)	(687.2)	(46.7)	(66.1)	[a]	
9	23.5	145.0	137.1	127.7	[c]	−136.5
	[a]	[a]	[a]	[a]		
10	21.2	145.9	137.3	127.5	128.3	−161.3
	(644.0)	(693.0)	(48.3)	(66.8)	[a]	

[a] Not determined. [b] CH_3 10.9 ppm. [c] Probably superimposed on the phenyl signals of the phosphonium ion.

The ^{119}Sn NMR spectra of **1** to **6** (Table 2) exhibit sharp resonances, with chemical shifts somewhat different from those of the bis(stannyl)methanes [10]. These shifts are still, however, in the range for tetracoordinated tin atoms. The $^3J(^{119}Sn-^{117}Sn)$ coupling constants, especially those of **5** and **6** are noteworthy, being to our knowledge the largest of such constants so far reported [13,14]. A marked high field shift is observed for **7**–**10** in comparison with **2** and $Ph_2EtSnCl$ (δ ^{119}Sn 17.2 ppm, $CDCl_3$), respectively, unambiguously indicating the presence of pentacoordinated tin atoms. The signal from **7** is markedly broadened (linewidth about 400 Hz), whereas those from **8** to **10** are sharp (linewidths 10 to 40 Hz). No $^3J(^{119}Sn-^{117}Sn)$ couplings were observed, probably because of exchange processes being fast on the NMR time scale. At −65 °C the spectrum of **7** (in CD_2Cl_2) splits into two sharp resonances, a singlet at −112.1 ppm and a doublet at −174.4 ppm ($^2J(^{119}Sn-^{31}P)$ 138.4 Hz) with a 1/1 intensity ratio.

The results confirm the presence an unsymmetrical structure very similar to that of $(Ph_2ClSn)_2CH_2 \cdot HMPA$ [8], with the HMPA monodentate. The high field signal arises from the tin atom complexed by HMPA, and the low field signal to the tin atom coordinated by the bridging chlorine atom. The formal replacement of the HMPA ligand in **7** by a chloride ion yields compound **8**; the fact that only the 1/1 complex is formed in this reaction even when an excess of chloride ions is used suggests a high stability for **8** and a substantial cooperative binding of both tin atoms. In order to gain some idea about this stability in solution we obtained the ^{119}Sn NMR saturation curve for $[(Ph_2ClSnCH_2)_2 \cdot n[Cl]^-[Ph_3P{=}NPPh_3]^+$ (Fig. 1).

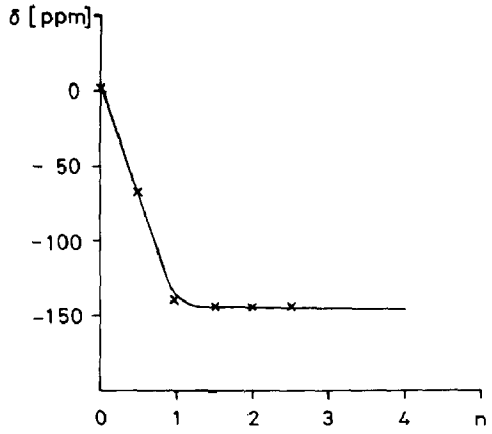

Fig. 1. Plot of the ^{119}Sn chemical shift of $(Ph_2ClSnCH_2)_2 \cdot n[Ph_3P{=}N{=}PPh_3]^+ Cl^-$ versus n (x marks the experimental values, the solid line represents the calculated Hildebrandt–Benesi equation for a K_a of 2260 M^{-1}).

The plot in Fig. 1 shows a large highfield shift of about 145 ppm on going from $n = 0$ to $n = 1$, and almost no change of the chemical shift for higher n values. From this plot a formation constant K_a of 2260 M^{-1} was calculated by use of a modified Hildebrand–Benesi treatment [15,16]. To our knowledge, this is the highest value for a tin-containing Lewis acid so far reported.

For **10** the K_a value was only 71 M^{-1}, which implies that in **8** the 1,2-bis(chlorodiphenylstannyl)ethane (**2**) acts as a true bidentate Lewis acid towards the chloride ion. The same holds for the chloride complex $[(Ph_2ClSn)_2CH_2 \cdot Cl]^-$ (K_a 1560 M^{-1}), whereas for the propylene bridged derivatives $[(Me_2ClSnCH_2)CH_2 \cdot Cl]^-$ and $[Me(Cl)Sn(CH_2)_3SnMe(Cl)(CH_2)_3SnMe(Cl)(CH_2)_3 \cdot Cl]^-$ the K_a values of 23 and 45 M^-, respectively, unambiguously indicate monodentate behaviour. Similar values have been observed previously for $[Bu_3SnCl_2]^-$ (K_a 17 M^{-1}) and $[ClSn[(CH_2)_8]_3SnCl \cdot Cl]^-$ (K_a 7 M^{-1}) [12].

Molecular structures

The molecular structure of **7** is depicted in Fig. 2, and bond lengths and bond angles are listed in Table 3. The results confirm the conclusion drawn from the low temperature NMR measurement. The HMPA molecule acts as a monodentate donor towards the Sn(2) atom whereas the Cl(2) atom bridges the two tin centers unsymmetrically. The two tin atoms are inequivalent and display distorted trigonal bipyramidal geometries. The overall geometry of **7** is very close to that of $(Ph_2ClSn)_2CH_2 \cdot$ HMPA [8], except that **7** forms a five-membered ring instead of the four-membered ring present in the methylene-bridged analogue. Even the bond lengths and bond angles are almost identical. (For a more detailed discussion of these data see ref. 8).

The molecular structure of **8** is shown in Fig. 3, and selected bond lengths and bond angles are listed in Table 4. Although the structure could be refined only to a final R value of 0.21 because of the poor quality of the crystals the essential structure of **8** is unambiguously established. In **8** 1,2-bis(chlorodiphenylstannyl)-ethane (**2**) acts as a bidentate Lewis acid towards a chloride anion. Both tin atoms are in a distorted trigonal bipyramidal environment, with the chlorine atoms Cl(1),

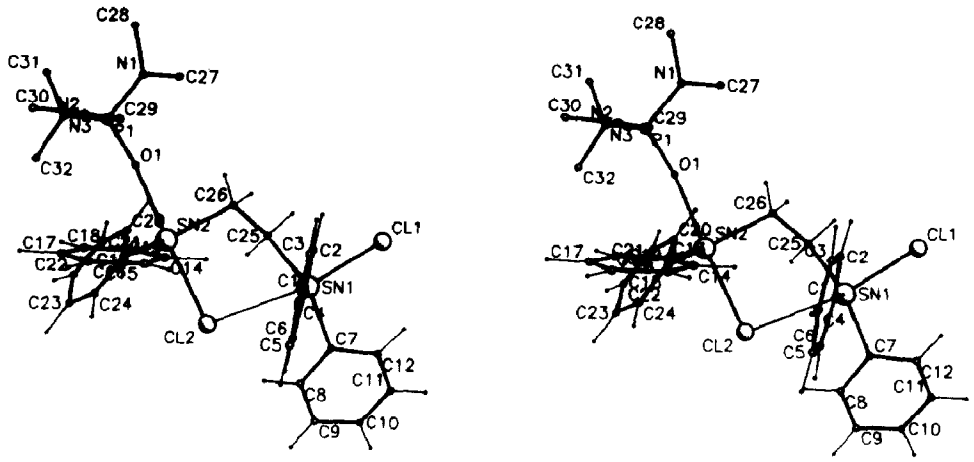

Fig. 2. Stereoscopic view of the molecular structure of $(Ph_2ClSnCH_2)_2 \cdot HMPA$ (7).

Cl(2) and C(12) in the apical positions. The equatorial positions are occupied by the phenyl groups and the ethylene carbons C(1) and C(2), respectively. The Sn(1)–Cl(1) and Sn(2)–Cl(2) distances are typical for pentacoordinated organotin compounds [17]. The intramolecular Sn(1)–Cl(12)–Sn(2) bridge is unsymmetrical, but less so than the bridges in the chloride complexes of 1,1,5,5,9,9-hexachloro-1,5,9-tristannacyclododecane [11] and 1,10-dichloro-1,10-distannabicyclo [8.8.8]-hexacosane [12], for which Sn–Cl...Sn bond lengths of 2.70, 2.906 and 2.61, 3.388 Å were found.

Table 3

Selected bond lengths (Å) and bond angles (°) of 7

Sn(1)–Cl(1)	2.432(1)	Sn(2)–Cl(2)	2.599(1)
Sn(1)–Cl(2)	3.000(1)	Sn(2)–O(1)	2.255(3)
Sn(1)–C(1)	2.122(5)	Sn(2)–C(13)	2.124(5)
Sn(1)–C(7)	2.132(5)	Sn(2)–C(19)	2.109(5)
Sn(1)–C(25)	2.138(4)	Sn(2)–C(26)	2.152(4)
P(1)–O(1)	1.497(3)		
P(1)–N(1)	1.624(4)		
P(1)–N(2)	1.641(5)		
P(1)–N(3)	1.621(6)		
C(25)–C(26)	1.522(6)		
Cl(2)–Sn(1)–Cl(1)	168.5(1)	C(13)–Sn(2)–Cl(2)	92.4(1)
C(1)–Sn(1)–Cl(1)	96.6(1)	C(13)–Sn(2)–O(1)	90.0(2)
C(1)–Sn(1)–Cl(2)	82.5(1)	C(19)–Sn(2)–Cl(2)	91.8(1)
C(7)–Sn(1)–Cl(1)	99.4(1)	C(19)–Sn(2)–O(1)	88.9(2)
C(7)–Sn(1)–Cl(2)	91.3(1)	C(19)–Sn(2)–C(13)	117.3(2)
C(7)–Sn(1)–C(1)	116.2(2)	C(26)–Sn(2)–Cl(2)	92.1(1)
C(25)–Sn(1)–Cl(1)	94.2(1)	C(26)–Sn(2)–O(1)	84.8(2)
C(25)–Sn(1)–Cl(2)	76.7(1)	C(26)–Sn(2)–C(13)	125.8(2)
C(25)–Sn(1)–C(1)	121.1(2)	C(26)–Sn(2)–C(19)	116.5(2)
C(25)–Sn(1)–C(7)	118.7(2)	Sn(2)–Cl(2)–Sn(1)	95.1(1)
O(1)–Sn(2)–Cl(2)	176.8(1)		

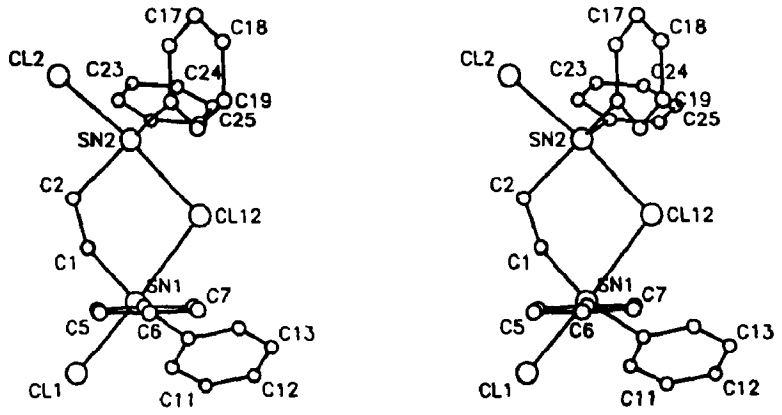

Fig. 3. Stereoscopic view of the molecular structure of $[(Ph_2ClSnCH_2)_2 \cdot Cl]^- [Ph_3P{=}N{=}PPh_3]^+$ (the cationic part is omitted for clarity).

Table 4

Selected bond lengths (Å) and bond angles (°) of **8**

Sn(1)–Cl(1)	2.48(1)	Sn(2)–Cl(2)	2.53(1)
Sn(1)–Cl(12)	2.83(1)	Sn(2)–Cl(12)	2.70(1)
Sn(1)–C(1)	2.07(4)	Sn(2)–C(2)	2.17(4)
Sn(1)–C(3)	2.11(3)	Sn(2)–C(15)	2.13(2)
Sn(1)–C(9)	2.13(2)	Sn(2)–C(21)	2.09(2)
Cl(12)–Sn(1)–Cl(1)	175.1(4)	C(2)–Sn(2)–Cl(2)	86(1)
C(1)–Sn(1)–Cl(1)	96(1)	C(2)–Sn(2)–Cl(12)	88(1)
C(1)–Sn(1)–Cl(12)	80(1)	C(15)–Sn(2)–Cl(2)	93(1)
C(3)–Sn(1)–Cl(1)	94(1)	C(15)–Sn(2)–Cl(12)	88(1)
C(3)–Sn(1)–Cl(12)	90(1)	C(15)–Sn(2)–C(2)	125(1)
C(3)–Sn(1)–C(1)	116(2)	C(21)–Sn(2)–Cl(2)	95(1)
C(9)–Sn(1)–Cl(1)	93(1)	C(21)–Sn(2)–Cl(12)	92(1)
C(9)–Sn(1)–Cl(12)	87(1)	C(21)–Sn(2)–C(2)	121(2)
C(9)–Sn(1)–C(1)	122(2)	C(21)–Sn(2)–C(15)	114(1)
C(9)–Sn(1)–C(3)	120(1)	Sn(1)–Cl(12)–Sn(2)	99.8(4)

Experimental

The solvents were dried by standard methods and freshly distilled before used. The ^1H, ^{13}C and ^{119}Sn NMR spectra were recorded on Bruker AC 80 and WP 200 spectrometers with Me_4Si and Me_4Sn as external standard. Physical constants, yields and analytical data for compounds **1–10** are summarized in Table 5.

1,2-Bis(triphenylstannyl)ethane (1). A solution of 20.4 g (0.058 mol) of triphenylstannane [18], 21.8 g (0.058 mol) of triphenylvinylstannane [19], and a trace of AIBN in 100 ml of benzene was stirred for 6 h at 60 °C, then cooled, and the colourless precipitate of **1** was filtered off.

1,2-Bis(chlorodiphenylstannyl)ethane (2). A solution of 17.2 g (0.024 mol) of **1** in 100 ml of chloroform was treated with two equivalents of methanolic HCl. The mixture was stirred for 24 h at room temperature, then the solvent was removed in vacuo and the residue recrystallized from methylene chloride/hexane to give **2** as

Table 5

Physical data, yields and analytical data of **1–10**

Compound	M.p. (°C)	Yield (%)	Formula	Analysis (Found ((calcd.) (%)		
				C	H	Cl
1	205–207	89	$C_{38}H_{34}Sn_2$	62.45 (62.69)	4.51 (4.67)	
2	159–161	61	$C_{26}H_{24}Cl_2Sn_2$	48.27 (48.43)	3.80 (3.73)	10.91 (11.00)
3	118–120	55	$C_{26}H_{24}Br_2Sn_2$	42.48 (42.55)	3.37 (3.27)	
4	83–85	91	$C_{26}H_{24}I_2Sn_2$	37.53 (37.72)	2.81 (2.90)	
5	101–104	35	$C_{14}H_{14}Br_4Sn_2$	22.87 (22.73)	2.03 (1.89)	
6	137–138	91	$C_{14}H_{14}I_4Sn_2$	18.12 (18.12)	1.73 (1.51)	
7	126–128	90	$C_{32}H_{42}Cl_2N_3OPSn_2$	46.33 (46.64)	5.07 (5.13)	8.75 (8.62)
8	164–165	89	$C_{62}H_{54}Cl_3NP_2Sn_2$	60.99 (61.10)	4.40 (4.71)	8.75 (8.73)
9	229–232	90	$C_{50}H_{44}BrCl_2PSn_2$	56.62 (56.43)	4.20 (4.14)	
10	176–178	91	$C_{50}H_{45}Cl_2NP_2Sn$	66.21 (65.89)	4.85 (4.94)	7.58 (7.79)

colourless needles.

1,2-Bis(bromodiphenylstannyl)ethane (3). A solution of 10 g (0.0137 mol) of **1** in 200 ml of methylene chloride and 20 ml of methanol was cooled to −60 °C and a solution of 1.4 ml of bromine in 20 ml of methanol was added dropwise with stirring. The solvent and the bromobenzene were removed in vacuo and the residue was recrystallized twice from diethyl ether to give **3** as colourless crystals. In addition to the main signal at −5.3 ppm, the ^{119}Sn NMR spectrum ($CDCl_3$) of the crude product showed additional resonances at −0.4, −8.5, −61.2 and −73.3 ppm.

1,2-Bis(iododiphenylstannyl)ethane (4). A solution of 2.2 g (0.003 mol) of **1** in 50 ml of methylene chloride was treated with 1.52 g (0.006 mol) of iodine and the mixture was stirred until the red colour had disappeared. The solvent and the iodobenzene were evaporated in vacuo, to leave **4** as a colourless solid.

1,2-Bis(dibromophenylstannyl)ethane (5). A solution of 10 g (0.0137 mol) of **1** in 200 ml of methylene chloride was cooled to −40 °C and a solution of 2.8 ml of bromine in 20 ml of methanol was added dropwise with stirring. The solvent and the bromobenzene were removed in vacuo and the residue was recrystallized from ether to give **5** as colourless crystals. The ^{119}Sn NMR spectrum ($CDCl_3$) of the crude product showed resonances at −20.7, −75.7 and −248.1 ppm.

1,2-Bis(diiodophenylstannyl)ethane (6). 5 g (0.0069 mol) of **1** and 7 g (0.055 mol) of iodine were dissolved in 80 ml of methylene chloride and stirred at room temperature until the mixture had turned light yellow. The solvent and the iodobenzene were then removed in vacuo and the residue was recrystallized from methylene chloride/diethyl ether to yield **6** as light yellow crystals.

The HMPA complex of 2 (7). A solution of 2 g (0.0031 mol) **2** in 20 ml of methylene chloride was treated with a solution of 0.56 g (0.0031 mol) of HMPA in 10 ml of methylene chloride. The mixture was refluxed for 10 min then cooled, and hexane was added to induce precipitation of a colourless solid. This was filtered off and recrystallized from methylene chloride/hexane to yield **7**.

Chloride complexes of 2, 3 and $Ph_2EtSnCl$ (8, 9, 10). A solution of equimolar quantities of the organotin compound and bis[(triphenylphosphoranylidene)am-

Table 6

Atomic coordinates of **7**

	x	*y*	*z*
Sn(1)	0.16588(3)	0.16335(2)	0.46874(3)
Sn(2)	0.39081(3)	0.26954(2)	0.50990(3)
Cl(1)	0.0995(2)	0.0483(1)	0.6019(2)
Cl(2)	0.2728(1)	0.3003(1)	0.3448(1)
P(1)	0.5430(1)	0.2395(1)	0.7613(1)
O(1)	0.4932(4)	0.2350(2)	0.6546(4)
N(1)	0.5379(4)	0.1575(3)	0.8679(4)
N(2)	0.4624(6)	0.3355(3)	0.8632(6)
N(3)	0.6791(6)	0.2316(5)	0.6844(6)
C(1)	0.0286(4)	0.2792(3)	0.6066(5)
C(2)	−0.0022(6)	0.2768(5)	0.7508(6)
C(3)	−0.0945(8)	0.3576(7)	0.8385(7)
C(4)	−0.1492(8)	0.4336(6)	0.7775(13)
C(5)	−0.1171(8)	0.4361(5)	0.6321(10)
C(6)	−0.0283(6)	0.3604(4)	0.5472(7)
C(7)	0.1477(5)	0.1464(3)	0.2763(6)
C(8)	0.1895(8)	0.1877(5)	0.1567(6)
C(9)	0.1846(10)	0.1714(6)	0.0271(8)
C(10)	0.1393(8)	0.1085(6)	0.0217(9)
C(11)	0.0954(7)	0.0676(5)	0.1393(9)
C(12)	0.0967(6)	0.0880(4)	0.2657(7)
C(13)	0.2860(5)	0.4045(3)	0.6107(5)
C(14)	0.1669(6)	0.4351(4)	0.6841(7)
C(15)	0.0974(8)	0.5234(5)	0.7556(8)
C(16)	0.1601(9)	0.5796(5)	0.7447(8)
C(17)	0.2729(10)	0.5497(5)	0.6777(8)
C(18)	0.3425(7)	0.4621(4)	0.6064(6)
C(19)	0.5516(4)	0.2490(3)	0.3364(5)
C(20)	0.6528(6)	0.1653(5)	0.3155(7)
C(21)	0.7576(6)	0.1498(6)	0.2009(9)
C(22)	0.7687(6)	0.2154(6)	0.1100(8)
C(23)	0.6705(7)	0.2990(5)	0.1259(7)
C(24)	0.5634(5)	0.3132(4)	0.2401(6)
C(25)	0.3398(4)	0.0997(3)	0.4792(5)
C(26)	0.3587(5)	0.1482(3)	0.5830(5)
C(27)	0.5643(7)	0.0670(4)	0.8125(7)
C(28)	0.5344(7)	0.1603(5)	1.0135(6)
C(29)	0.3318(9)	0.3609(5)	0.9401(7)
C(30)	0.5076(12)	0.3993(5)	0.8768(15)
C(31)	0.7752(9)	0.1868(9)	0.7406(14)
C(32)	0.7142(17)	0.2803(16)	0.5530(15)

Table 7

Atomic coordinates of **8**

	x	*y*	*z*
Sn(1)	0.0613(1)	0.0557(3)	0.2758(2)
Sn(2)	0.1624(1)	−0.0109(4)	0.3840(2)
Cl(1)	0.0272(3)	0.2190(16)	0.1675(9)
Cl(2)	0.2135(3)	0.1334(17)	0.3798(9)
Cl(12)	0.1038(2)	−0.1332(15)	0.3880(9)
P(1)	0.8635(2)	0.4669(11)	0.2289(7)
P(2)	0.8714(2)	0.6671(12)	0.0815(7)
N(1)	0.8719(7)	0.5973(41)	0.1816(21)
C(1)	0.1053(11)	0.0995(48)	0.2327(30)
C(2)	0.1352(11)	0.1571(48)	0.3049(30)
C(3)	0.0533(9)	0.1600(39)	0.3970(20)
C(4)	0.0577(9)	0.3039(39)	0.3995(20)
C(5)	0.0529(9)	0.3794(39)	0.4775(20)
C(6)	0.0438(9)	0.3110(39)	0.5531(20)
C(7)	0.0395(9)	0.1670(39)	0.5507(20)
C(8)	0.0442(9)	0.0915(39)	0.4726(20)
C(9)	0.0318(8)	−0.1192(29)	0.2255(22)
C(10)	0.0171(8)	−0.1284(29)	0.1317(22)
C(11)	0.0001(8)	−0.2487(29)	0.0978(22)
C(12)	−0.0022(8)	−0.3598(29)	0.1577(22)
C(13)	0.0125(8)	−0.3506(29)	0.2515(22)
C(14)	0.0294(8)	−0.2303(29)	0.2854(22)
C(15)	0.1726(7)	−0.0242(34)	0.5323(16)
C(16)	0.2054(7)	−0.0402(34)	0.5758(16)
C(17)	0.2137(7)	−0.0412(34)	0.6728(16)
C(18)	0.1891(7)	−0.0262(34)	0.7263(16)
C(19)	0.1563(7)	−0.0101(34)	0.6828(16)
C(20)	0.1480(7)	−0.0091(34)	0.5858(16)
C(21)	0.1786(8)	−0.1820(30)	0.3162(23)
C(22)	0.2013(8)	−0.1593(30)	0.2579(23)
C(23)	0.2151(8)	−0.2721(30)	0.2188(23)
C(24)	0.2062(8)	−0.4075(30)	0.2380(23)
C(25)	0.1835(8)	−0.4302(30)	0.2963(23)
C(26)	0.1697(8)	−0.3174(30)	0.3354(23)
C(27)	0.8406(7)	0.5044(32)	0.3176(18)
C(28)	0.8395(7)	0.6383(32)	0.3537(18)
C(29)	0.8214(7)	0.6639(32)	0.4238(18)
C(30)	0.8044(7)	0.5556(32)	0.4577(18)
C(31)	0.8056(7)	0.4217(32)	0.4216(18)
C(32)	0.8237(7)	0.3961(32)	0.3516(18)
C(33)	0.8397(6)	0.3426(28)	0.1528(18)
C(34)	0.8536(6)	0.2249(28)	0.1196(18)
C(35)	0.8344(6)	0.1397(28)	0.0536(18)
C(36)	0.8014(6)	0.1723(28)	0.0208(18)
C(37)	0.7875(6)	0.2901(28)	0.0541(18)
C(38)	0.8067(6)	0.3752(28)	0.1201(18)
C(39)	0.9015(5)	0.3840(27)	0.2818(17)
C(40)	0.9033(5)	0.3084(27)	0.3641(17)
C(41)	0.9329(5)	0.2474(27)	0.4062(17)
C(42)	0.9609(5)	0.2620(27)	0.3660(17)
C(43)	0.9592(5)	0.3376(27)	0.2837(17)
C(44)	0.9295(5)	0.3986(27)	0.2416(17)
C(45)	0.8973(6)	0.8155(26)	0.0994(19)

Table 7 (continued)

	x	y	z
C(46)	0.9165(6)	0.8484(26)	0.1856(19)
C(47)	0.9377(6)	0.9625(26)	0.1941(19)
C(48)	0.9398(6)	1.0438(26)	0.1162(19)
C(49)	0.9206(6)	1.0109(26)	0.0300(19)
C(50)	0.8994(6)	0.8968(26)	0.0215(19)
C(51)	0.8868(6)	0.5551(26)	0.0001(17)
C(52)	0.9188(6)	0.5706(26)	−0.0173(17)
C(53)	0.9304(6)	0.4810(26)	−0.0791(17)
C(54)	0.9101(6)	0.3758(26)	−0.1235(17)
C(55)	0.8781(6)	0.3603(26)	−0.1062(17)
C(56)	0.8665(6)	0.4499(26)	−0.0444(17)
C(57)	0.8305(5)	0.7215(30)	−0.0277(17)
C(58)	0.8215(5)	0.7414(30)	−0.0682(17)
C(59)	0.7901(5)	0.7903(30)	−0.1061(17)
C(60)	0.7676(5)	0.8192(30)	−0.0480(17)
C(61)	0.7765(5)	0.7993(30)	0.0479(17)
C(62)	0.8080(5)	0.7504(30)	0.0858(17)

monium] chloride $[Ph_3P{=}N{=}PPh_3]^+Cl^-$ in methylene chloride was refluxed for 5 min. The solutions were cooled to room temperature and hexane was added, but only to an extent that the solution remained clear. Slow evaporation of the solvent resulted in precipitation of the required complex as colourless crystals.

Structural data

The fractional atomic coordinates for **7** and **8** are listed in Tables 6 and 7, respectively. Details of the X-ray studies are summarized in Table 8.

The space group and approximate cell constants of **7** were obtained from oscillation and Weissenberg photographs. Accurate cell constants were determined by least squares refinement of 2θ for 15 reflections in the range of $10 < 2\theta < 25°$ on an automatic Syntex $P2_1$ diffractometer using graphite monochromated Mo-K_α radiation by the ω-scan technique of 1.7° to $2\theta_{max} = 50°$ (range of h, k, l: −13 to 15, −18 to 18, 0 to 11), minimum scan rate 1.2°/min. One standard reflection was monitored every 50 reflections.

Structure solution was carried out by direct methods [20]. Structure refinement was carried out anisotropically by full-matrix least squares [21] with weighting scheme $w = 1/(\sigma^2(F) + 0.032F^2)$. 24 H atoms were located by difference Fourier synthesis. No hydrogen atoms were introduced for the methyl groups. H-atoms (were refined using a riding model with a common isotropic thermal parameter. Except for some peaks around the tin atom the final difference map was featureless. The final $R(R_w)$ was 0.045 (0.055), $S = 1.221$.

In the case of **8**, a suitable crystal could not be obtained. However the crystallographic study was undertaken in an attempt to establish the rough geometry of the anion $[(Ph_2ClSnCH_2)_2 \cdot Cl]^-$. Colourless and transparent crystals, but with internal cracks were used. Unit-cell parameters were derived from least-squares treatment of the angular setting of 15 reflections with $6° < 2\theta < 26°$. 69988 reflections were collected on Syntex $P2_1$ (Mo-K_α) to $2\theta_{max}$ 44°, in ω-scan mode of 1.3°. One

Table 8

Details of X-ray structure determination

	7	8
Formula	$C_{32}H_{42}N_3OPSn_2Cl_2$	$C_{62}H_{54}NP_2Sn_2Cl_3$
M	823.97	1218.82
System	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a	13.221(3) Å	41.27(4) Å
b	15.947(5) Å	9.61(1) Å
c	10.248(4) Å	14.61(2) Å
α	84.26(4)°	–
β	67.58(3)°	100.6(1)°
γ	65.64(3)°	–
V	1815(1) Å^3	5696(16) Å^3
Z	2	4
$F(000)$	824	2456
D_c	1.507 g cm^{-3}	1.421 g cm^{-3}
λ (Mo-K_α)	0.71069 Å	0.71069 Å
μ	14.65 cm^{-1}	10.14 cm^{-1}
Unique reflections	6375	6988
Observed reflections ($I \geq 2.5(I)$)	5558	3514
Crystal size	0.30×0.18×0.15 mm^3	0.20×0.20×0.17 mm^3
No absorption corrections		

standard reflection was observed per 50 reflections. The position of two tin and one chlorine atoms was found from a three-dimensional Patterson map [20], and remaining atoms were located by successive Fourier synthesis. In order to reduce the number of variable parameters Sn, Cl, P and N atoms were allowed to vibrate anisotropically and phenyl rings placed in calculated positions [21]. Weighting $w = 1/\sigma^2(F) = 0.1325F^2$. The final R (R_w) value was 0.21 (0.206), $S = 0.706$.

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