REACTIVITY AND CRYSTAL AND MOLECULAR STRUCTURE OF 5-PHENYL-5-PHOSPHA-2,8-DITHIA-1-STANNA(II)BICYCLO[3.3.0^{1,5}]OCTANE

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Summary

5-Phenyl-5-phospha-2,8-dithia-1-stanna(II)bicyclo[3.3.0^{1,5}]octane (**1**) was prepared in good yield by the reaction of tin(II) butoxide with the appropriate mercaptophosphane in toluene. Its crystal and molecular structure was determined by X-ray analysis. Compound **1** crystallizes in the rhombohedral space group $R3$, with 9 molecules in a unit cell of dimensions (referred to hexagonal axis) a 17.218(5) Å, c 10.859(3) Å, and V 2787.9 Å^3. The structure was solved by the Patterson method, and full-matrix least-squares refinement led to a final R value of 0.026. The crystal structure is characterized by parallel infinite spiral chains built up of molecules connected by Sn...S intermolecular contacts of 3.31 Å. The molecules exhibit a strongly distorted ψ-trigonal bipyramidal geometry around the tin atom with the phosphorus atom in an equatorial position and an Sn–P distance of 2.61 Å. The eight-membered ring adopts a boat–boat conformation.

The reaction of compound **1** with $Cr(CO)_6$ in THF under UV irradiation yields the corresponding chromium pentacarbonyl complex.

Introduction

The extent of association of tin(II)-containing bicyclic octanes of the general type $Sn(XCH_2CH_2)_2Y$ in solution depends on the nature of the heteroatoms X and Y. Whereas the ethanolamine derivatives (X = O, Y = NR) are dimeric in solution [1], the corresponding sulphur derivatives (X = S, Y = NR) are monomeric at ambient temperature [2]. However, the X-ray structure of $Sn(SCH_2CH_2)_2NBu^t$ shows that in the solid state two different dimers exist, having different bond lengths and bond angles, and these dimers have been associated with two different geometries along the dissociation inversion pathway [3]. In this connection it seemed of interest to investigate the structure of $Sn(SCH_2CH_2)_2PPh$ in solution and in the solid state and to study the influence of the soft phosphorus atom on the degree of autoassociation of stannabicyclooctanes.

Results and discussion

The title compound **1** was obtained by the reaction of tin(II) butoxide with the appropriate dithiol in toluene [4], as shown in eq. 1.

$$Sn(OBu)_2 + (HSCH_2CH_2)_2PPh \xrightarrow[- \, BuOH]{toluene} Sn(SCH_2CH_2)_2PPh \qquad (1)$$
$$(1),$$
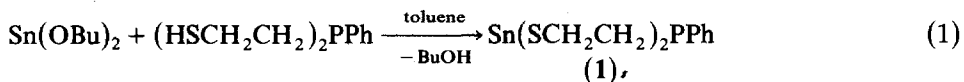
Use of recrystallized tin(II) butoxide in a reaction at room temperature markedly raised the yield of compound **1** compared with that reported previously [4].

The strong donor–acceptor interaction in compound **1** is shown by the large tin–phosphorus coupling constant (Tab. 1), which is comparable with those found in $Sn(PR_2)_2$ and $Sn(Cl)PR_2$ [5,6]. The special electronic situation at the tin atom in the title compound is also evident from its very high field ^{119}Sn NMR chemical shift (Tab. 2) compared with the values found for the nitrogen, sulphur, or oxygen substituted derivatives.

A further difference between $Sn(SCH_2CH_2)_2PPh$ and $Sn(SCH_2CH_2)_2NMe$ concerns their reactions with disulphides. Whereas the nitrogen-substituted compound reacts with dibenzyl disulphide to form the oxidative addition product [7], compound **1** does not react at all even during 10 h in refluxing benzene.

Obviously, the two compounds differ in their stannylene character. Whereas in the N-methyl substituted compound the vacant orbitals of the tin atom are available owing to the dissociation–inversion mechanism [2], in the P-phenyl-substituted compound these orbitals are occupied as a result of the stronger donor–acceptor interaction .

Compound **1** reacts with chromium hexacarbonyl to give the corresponding tin(II) substituted transition metal complex **2** in high yield (eq. 2).
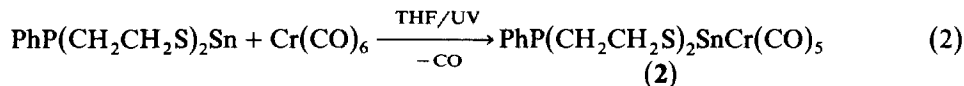
$$PhP(CH_2CH_2S)_2Sn + Cr(CO)_6 \xrightarrow[- \, CO]{THF/UV} PhP(CH_2CH_2S)_2SnCr(CO)_5 \qquad (2)$$
$$(2)$$

TABLE 1

^{13}C AND ^{119}Sn NMR PARAMETERS FOR COMPOUNDS 1 AND 2 AT T 30°C

	1 2 3 4 Sn(S–CH₂–CH₂)₂P–Ph								

Solvent	Chemical shifts δ (ppm)						Coupling constants J (Hz)		
	1	2	3	4	5	6	1–4	2–4	3–4
py-d_5	− 113.55 ^{a}	28.68	35.18	31.19			1244 ^{d}	19.0	21.2

	6 5 1 2 3 4 (CO)(CO)₄CrSn(S–CH₂–CH₂)₂P–Ph								

py-d_5	104.37 ^{b}	27.63	32.24	−8.97	220.45	226.37	1226 ^{d}	18.6	21.5
CD₂Cl₂	264.19 ^{c}	29.33	32.84	18.96	218.78	225.50	1138 ^{d}	11.9	32.5

^{a} Doublet, $J(^{119}Sn-^{31}P)$ 1270 Hz. ^{b} Doublet, $J(^{119}Sn-^{31}P)$ 1222 Hz. ^{c} Doublet, $J(^{119}Sn-^{31}P)$ 1137 Hz. ^{d} Value taken from the ^{31}P NMR spectrum.

TABLE 2

^{119}Sn NMR CHEMICAL SHIFTS FOR VARIOUS STANNA(II)BICYCLOOCTANES Sn(SCH$_2$-CH$_2$)$_2$Y IN PYRIDINE-d_5 AT T 30°C

Y	Chemical shift δ (ppm)	Reference
N−Bu^t	140.10	2
N−Me	91.20	2
O	82.20	2
S	65.80	2
PPh	−113.55	this work

Compound 2 is a yellow, air stable, crystalline solid, soluble in polar organic solvents. That the complexation has taken place at the tin and not at the phosphorus atom is shown by the large low field shift in the ^{119}Sn NMR spectrum of compound 2 compared with that of compound 1 (Tab. 1), and especially by the difference between the isomer shifts in the ^{119}Sn Mössbauer spectra (1, IS 3.01 mm/s; 2, IS 2.11 mm/s), which is typical of transition metal complexes of tin(II) compounds [8]. The ^{31}P NMR chemical shift is markedly different for complex 2 from that for the free ligand 1, whereas the $J(^{119}$Sn–^{31}P) coupling constants are quite similar in the two compounds (Tab. 1); the origin of this ^{31}P chemical shift difference may lie in the different bond angles around the phosphorus atoms in different eight-membered ring conformations. In order to obtain more information relevant to this problem an X-ray study of compound 2 is currently in progress. The strong solvent dependence of the NMR parameters suggests adduct formation in the pyridine solution of compound 2.

Crystal and molecular structure

The structure of Sn(SCH$_2$CH$_2$)$_2$PPh with the atom numbering scheme is shown in Fig. 1, the packing in the unit cell in Fig. 2, and a chain of five molecules in Fig.

TABLE 3

FINAL FRACTIONAL COORDINATES AND EQUIVALENT ISOTROPIC THERMAL PARAMETERS ($\AA^2$). $U_{eq} = (U_{11} \cdot U_{22} \cdot U_{33})^{1/3}$

| Atom	x	y	z	U_{eq}
Sn(1)	0.28211(4)	−0.00343(4)	0.0048(6)	0.0383(2)
S(1)	0.1605(2)	−0.0835(2)	−0.1630(6)	0.0376(9)
S(2)	0.1798(2)	0.0043(2)	0.1656(6)	0.046(1)
P(1)	0.2725(2)	0.1330(2)	−0.0825(6)	0.0322(9)
C(1)	0.1270(8)	−0.0050(8)	−0.210(1)	0.052(4)
C(2)	0.2026(8)	0.0926(8)	−0.220(1)	0.047(4)
C(3)	0.1396(8)	0.0742(9)	0.097(1)	0.060(4)
C(4)	0.2126(7)	0.1583(8)	0.034(1)	0.052(4)
C(5)	0.3684(6)	0.2380(6)	−0.130(1)	0.032(3)
C(6)	0.3699(8)	0.3178(7)	−0.114(1)	0.048(4)
C(7)	0.445(1)	0.3965(9)	−0.159(1)	0.057(5)
C(8)	0.5126(9)	0.3942(8)	−0.219(1)	0.052(5)
C(9)	0.5113(9)	0.315(1)	−0.235(2)	0.071(6)
C(10)	0.4366(8)	0.2347(8)	−0.189(1)	0.054(5)

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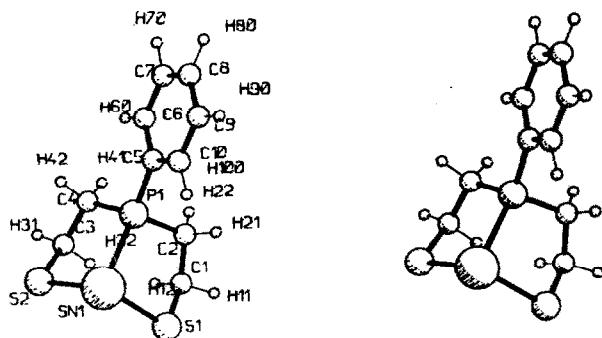
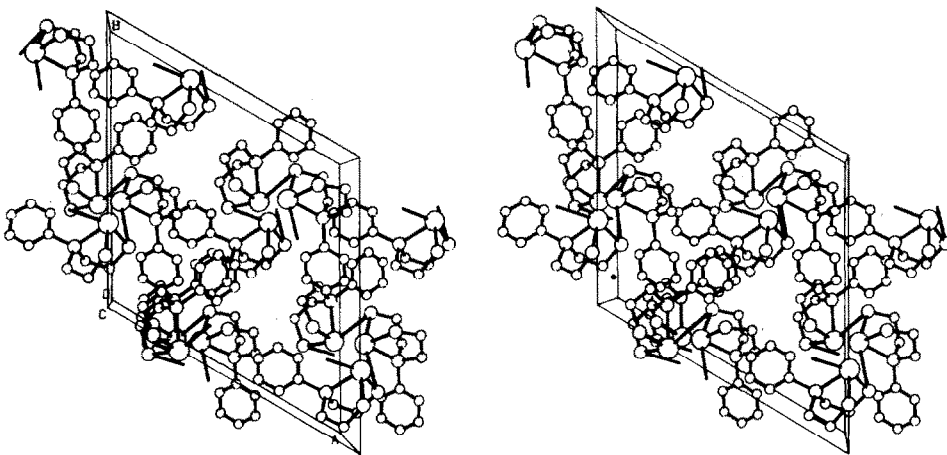Fig. 1. A stereoview of the molecule with the atom-numbering scheme.

Fig. 2. A view of the unit cell.

3. Bond lengths and bond angles are summarized in Tab. 4. The most striking feature of the crystal structure is associated with the threefold screw axis. Molecules related by this symmetry element are packed comparatively closely. The tin–tin contact distances in the region along the screw axis (3.910 Å) are the shortest in the structure, and are somewhat shorter than twice the Van der Waals radius of tin(II) (4.2–4.4 Å) [9]. However, the main intermolecular interaction connecting neighbour-
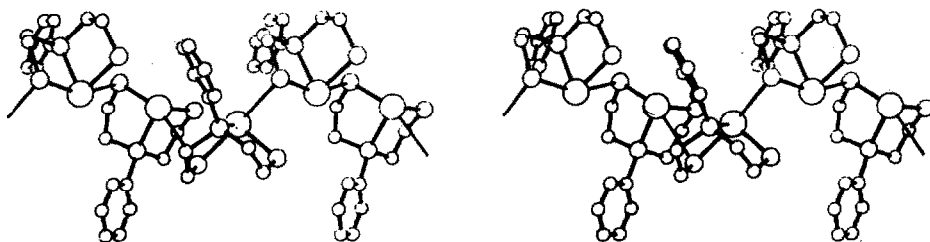

Fig. 3. Chain of five molecules along the screw axis.

TABLE 4

BOND LENGTHS (Å) AND BOND ANGLES (°) WITH STANDARD DEVIATIONS

Sn(1)–S(1)	2.593(7)	S(1)–Sn(1)–S(2)	96.6(2)
Sn(1)–S(2)	2.531(7)	S(1)–Sn(1)–P(1)	80.0(2)
Sn(1)–P(1)	2.614(5)	S(2)–Sn(1)–P(1)	81.0(2)
S(1)–C(1)	1.789(16)	Sn(1)–S(1)–C(1)	106.2(4)
S(2)–C(3)	1.819(18)	Sn(1)–S(2)–C(3)	105.0(5)
P(1)–C(2)	1.824(14)	Sn(1)–P(1)–C(2)	106.3(5)
P(1)–C(4)	1.821(15)	Sn(1)–P(1)–C(4)	105.1(5)
P(1)–C(5)	1.811(9)	Sn(1)–P(1)–C(5)	124.4(5)
		C(2)–P(1)–C(4)	108.5(6)
		C(2)–P(1)–C(5)	104.1(6)
		C(4)–P(1)–C(5-)	107.7(6)
C(1)–C(2)	1.53(2)	S(1)–C(1)–C(2)	115.6(1.0)
C(3)–C(4)	1.52(2)	S(2)–C(3)–C(4)	113.9(1.0)
		P(1)–C(2)–C(1)	113.4(9)
		P(1)–C(4)–C(3)	112.4(1.0)
C(5)–C(6)	1.37(2)	C(5)–C(6)–C(7)	118(2)
C(6)–C(7)	1.41(2)	C(6)–C(7)–C(8)	122(2)
C(7)–C(8)	1.36(3)	C(7)–C(8)–C(9)	121(1)
C(8)–C(9)	1.37(3)	C(8)–C(9)–C(10)	119(2)
C(9)–C(10)	1.42(2)	C(9)–C(10)–C(5)	120(2)
C(10)–C(5)	1.36(2)	C(10)–C(5)–C(6)	121(1)
		P(1)–C(5)–C(6)	121.0(9)
		P(1)–C(5)–C(10)	121.0(9)
Sn(1)...S(1′)	3.310(6)	S(1)–Sn(1)...S(1′)	153.6(2)
Sn(1)...S(2)	3.659(6)	S(2)–Sn(1)...S(1′)	77.7(2)
Sn(1)...Sn(1′)	3.910(8)	P(1)–Sn(1)...S(1′)	73.7(2)

ing molecules along the screw axis arises from contact of the Sn atom of one molecule with the S(1′) atom of the next molecule along the x-direction. This distance Sn...S(1′) of 3.310 Å, is much larger than that in the short Sn...S bridge, viz. 2.709 Å, within the value for dimer a of $Sn(SCH_2CH_2)_2NBu^t$ [3] but markedly shorter than the sum of corresponding Van der Waals radii (4.0 Å) [9]. Thus in the
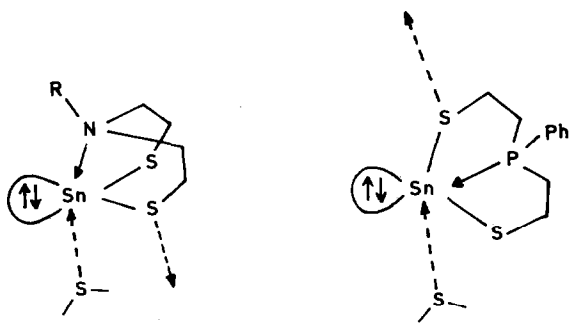

Fig. 4. Schematic representation of the ψ-trigonal bipyramidal geometry around the tin atoms in dimer a of $Sn(SCH_2CH_2)_2NBu^t$ and in compound 1.

crystal the molecules are associated in infinite spiral chains winding around the screw axis (Fig. 3). The most interesting feature of the structure is the very short intramolecular Sn–P distance of 2.614 Å, which is exactly equal to the sum of the covalent radii of tin(II) (1.50 Å) [10] and phosphorus (1.10 Å) [11]. To our knowledge, no other Sn^{II}–P bond lengths have been reported. The Sn–S bond lengths are in the range observed for $Sn(SCH_2CH_2)_2NBu^t$ [3]. The non-equivalence of the Sn(1)–S(1) and Sn(1)–S(2) distances results from the intermolecular interaction with the S(1) atom. When this weak intermolecular Sn(1)...S(1') contact is included, the geometry around the tin atom can be regarded as that of a strongly distorted ψ-trigonal bipyramid, with the tin(II) lone pair in an equatorial position.

The S(1)–Sn(1)...S(1') angle of 153.6° is typical of tin(II) compounds of this geometry, arising from the stereochemical influence of the lone pair, and can be compared with the N(1)–Sn(1)–S(5) angle in dimer a of $Sn(SCH_2CH_2)_2NBu^t$ [3]. The very small S(2)–Sn(1)–P(1) angle of 81.0° is a result of the steric requirement arising from the ligand symmetry. When the structure of compound 1 is compared with that of $Sn(SCH_2CH_2)_2NBu^t$ (dimer a), the intramolecular donor atoms can be seen to occupy different positions in the ψ-trigonal bipyramidal arrangement (Fig. 4). The more electronegative nitrogen atom is located in an apical position whereas the more electropositive phosphorus is bonded equatorially. These results are consistent with the general rules for pentacoordinated molecules [12], which have been shown to apply to five-coordinate organotin(IV) compounds [13–16]. Furthermore it can be shown that the very short intramolecular Sn–P bond results in a marked lengthening of the intermolecular Sn...S distance. The conformation of the eight-membered ring is shown by the torsion angles listed in Tab. 5; the ring adopts a boat–boat conformation, the third example of such a conformation for tin-containing eight-membered rings [17].

Experimental

All manipulations were carried out under dry argon. The NMR spectra were recorded with a Bruker WP 200 spectrometer, ^{13}C at 50.39 MHz, ^{31}P at 81.026 MHz, and ^{119}Sn at 74.64 MHz.

Synthesis of 1

A solution of 4.2 g (18 mmol) of $PhP(CH_2CH_2SH)_2$ [4] in 50 ml of toluene was added dropwise with vigorous stirring to a solution of 4.8 g (18 mmol) of $Sn(OBu)_2$

TABLE 5

SELECTED TORSION ANGLES (°)

S(1)–Sn(1)–S(2)–C(3)	−62.9
Sn(1)–S(2)–C(3)–C(4)	−44.6
S(2)–C(3)–C(4)–P(1)	+55.7
C(3)–C(4)–P(1)–C(2)	+77.5
C(4)–P(1)–C(2)–C(1)	−77.8
P(1)–C(2)–C(1)–S(1)	−51.1
C(2)–C(1)–S(1)–Sn(1)	+39.0
C(1)–S(1)–Sn(1)–S(2)	+67.2

in 800 ml of toluene. After 2 h at 40°C the solvent was evaporated and the residue recrystallized from benzene to give yellow crystals (5.5 g, 88%), m.p. 168–170°C [4]. Analysis: Found: C, 34.52; H, 3.68. $C_{10}H_{13}PS_2Sn$ calcd.: C, 34.61; H, 3.75%.

Synthesis of 2

A mixture of 0.9 g (2.6 mmol) of $Sn(SCH_2CH_2)_2PPh$ and 2.6 mmol of $Cr(CO)_5 \cdot$ THF, generated from $Cr(CO)_6$ by UV-irradiation, was stirred for 5 h in 500 ml of THF. The solvent was then evaporated in vacuum, and the residue kept at 0.2 mmHg to remove unreacted $Cr(CO)_6$. Recrystallisation of the residue from benzene yielded 1.1 g (78.6%) of yellow crystals, m.p. 170–175°C (dec.). Analysis: Found: C, 33.20; H, 2.35. $C_{15}H_{13}PO_5S_2SnCr$ calcd.: C, 33.41; H, 2.41%.

Crystal structure determination

$SnS_2PC_{10}H_{13}$ crystallizes in space group $R3$ with a 17.218(5) Å, c 10.859(3) Å, V 2787.9 Å^3, $Z = 9$ (hexagonal axes), $M_{rel.} = 347.0$, μ(Mo-K_α) 22.9 cm^{-1}, $D_c = 1.860$ g/cm^3, $F(000) = 1092$. A crystal of approximate dimensions $0.34 \times 0.32 \times 0.22$ mm^3 was used, and 857 unique reflections with $1.50° \leq \theta \leq 23.00°$ measured on a CAD4 four-circle diffractometer using graphite-monochromatized Mo-K_α radiation (λ 0.71069 Å). Data reduction was carried out in the usual way without any absorption or extinction correction. The x and y coordinates of Sn were determined by a Patterson synthesis, z was arbitrarily fixed at zero. Two Fourier syntheses were then carried out to complete the analysis of the structure. The positions and thermal parameters of non-hydrogen atoms were refined by least-squares method, whereas the H atom positions were geometrically calculated and not refined. The absolute configuration was not determined. With 7 reflections with high $(F_o - F_c)$ to $\sigma(F_o)$ ratios excluded from the last least-squares cycles, the final R-value was 0.026. The final atomic coordinates for non-hydrogen atoms are listed in Table 3. The structure determination was carried out by use of the SHELX-76 program [18], geometrical calculations by use of the GEOME [19] and PLANE programs [20]. Lists of hydrogen coordinates, thermal parameters and structure factors may be obtained from the authors.

Acknowledgement

References

1 A. Zschunke, G. Mügge, M. Scheer, K. Jurkschat and A. Tzschach, J. Cryst. Spec. Res., 13 (1983) 201.
2 A. Tzschach, M. Scheer, K. Jurkschat, A. Zschunke and C. Mügge, Z. Anorg. Allg. Chem., 502 (1983) 158.
3 K. Jurkschat, M. Scheer, A. Tzschach, J. Meunier-Piret and M. Van Meerssche, J. Organomet. Chem., 281 (1985) 173.
4 A. Tzschach and W. Uhlig, Z. Anorg. Allg. Chem., 475 (1981) 251.
5 W.W. Du Mont and H.J. Kroth, Angew. Chem., 89 (1977) 832.
6 W.W. Du Mont and B. Neudert, Z. Anorg. Allg. Chem., 436 (1977) 270.
7 A. Tzschach, M. Scheer and K. Jurkschat, Z. Anorg. Allg. Chem., 508 (1984) 73.
8 W.W. Du Mont and B. Neudert, Chem. Ber., 111 (1978) 2267.

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9 J.E. Huheey, Inorganic Chemistry, Principles of Structure and Reactivity, p. 184, Harper & Row, New York, 1972.
10 M. Veith and O. Recktenwald, Top. Curr. Chem., 104 (1982) 1.
11 L. Pauling, Die Natur der Chemischen Bindung, Verlag Chemie GmbH, Weinheim/Bergstr., 1962.
12 P. Gillespie, P. Hoffmann, H. Klusacek, D. Marquarding, S. Pfohl, F. Ramirez, A.E. Tsolis and T. Ugi, Angew. Chem., 83 (1971) 691.
13 R. Willem, M. Gielen, J. Meunier-Piret, M. Van Meerssche, K. Jurkschat and A. Tzschach, J. Organomet. Chem., 277 (1984) 335.
14 A. Tzschach and K. Jurkschat, Comments Inorg. Chem., 3 (1983) 35.
15 M. Dräger, J. Organomet. Chem., 251 (1983) 209.
16 R.G. Swisher and R.R. Holmes, Organometallics, 3 (1984) 365.
17 A. Tzschach, K. Jurkschat, M. Scheer, J. Meunier-Piret and M. Van Meerssche, J. Organomet. Chem., 259 (1983) 165.
18 G.M. Sheldrick, SHELX. Program for crystal structure determination, University of Cambridge, England, 1976.
19 M. Jaskólski, GEOME. Program to calculate geometrical features of molecules, University of Poznań, Poland, 1981.
20 M. Jaskólski, PLANE. Program to calculate the mean plane through a set of atoms, University of Poznań, Poland, 1981.