

## Crystal structure of pentacarbonyl-5-phenyl-5-phospha-2,8-dithia-1-stannabicyclo[3.3.0]<sup>1,5</sup>octanechromium(0) · pyridine

**K. Jurkschat, A. Tzschach,**

*Martin-Luther-Universität Halle-Wittenberg, Sektion Chemie, WB Allgemeine und Anorganische Chemie, Halle/(S.)/Postfach, DDR-4010 (German Democratic Republic)*

**J. Meunier-Piret and M. Van Meerssche**

*Laboratoire de Chimie Physique et de Cristallographie, Université de Louvain, Bâtiment Lavoisier, Place L. Pasteur 1, B-1348 Louvain-la-Neuve (Belgium)*

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### Abstract

The compound  $\text{PhP}(\text{CH}_2\text{CH}_2\text{S})_2\text{SnCr}(\text{CO})_5 \cdot \text{C}_5\text{H}_5\text{N}$  crystallizes in the triclinic space group  $P\bar{1}$  with two molecules in a unit cell of dimensions  $a$  10.654(2),  $b$  10.146(3),  $c$  12.448(3) Å,  $\alpha$  85.31(2),  $\beta$  79.66(2),  $\gamma$  65.53(2)°,  $V$  1204.8 Å<sup>3</sup>. The structure was solved by the Patterson method. The full matrix refinement with the 4456 observed reflections gave a final  $R$  value of 0.034. The tin atom is pentacoordinated by 2S, Cr, N and P. The Sn–Cr distance is 2.618 Å, and the Sn–N and Sn–P donor–acceptor interactions are 2.514 and 2.756 Å, respectively. The eight-membered ring adopts a boat-chair conformation.

### Introduction

In previous papers we have described a number of stannylene complexes of the general types  $(\text{CO})_5\text{MSn}(\text{XCH}_2\text{CH}_2)_2\text{E}$  (I, M = Cr, Mo, W; X = O, S; E = NR, PPh, O, S),  $(\text{CO})_5\text{WSn}(\text{SCH}_2\text{CH}_2)_2\text{E} \cdot \text{Py}$  (II, E = NMe, O, S) and  $[o\text{-C}_6\text{H}_4\text{CH}_2\text{E}]_2\text{Sn}-\text{W}(\text{CO})_5$  (III: E = NMe<sub>2</sub>, PPh) [1–4]. The compounds of the types II and III contain pentacoordinated tin atoms, whereas for the derivatives of type I only those with X = O reach this coordination number by dimerisation involving oxygen bridges. Our studies on  $\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{PPh}$  and its pentacarbonylchromium complex revealed that the two compounds exhibit very different, strongly solvent dependent, <sup>31</sup>P and <sup>119</sup>Sn NMR chemical shifts [2]. In order to gain more insight into the nature of coordination sphere of the tin atom in this particular stannylene complex we have determined the molecular structure of  $(\text{CO})_5\text{Cr}-\text{Sn}(\text{SCH}_2\text{CH}_2)_2-$

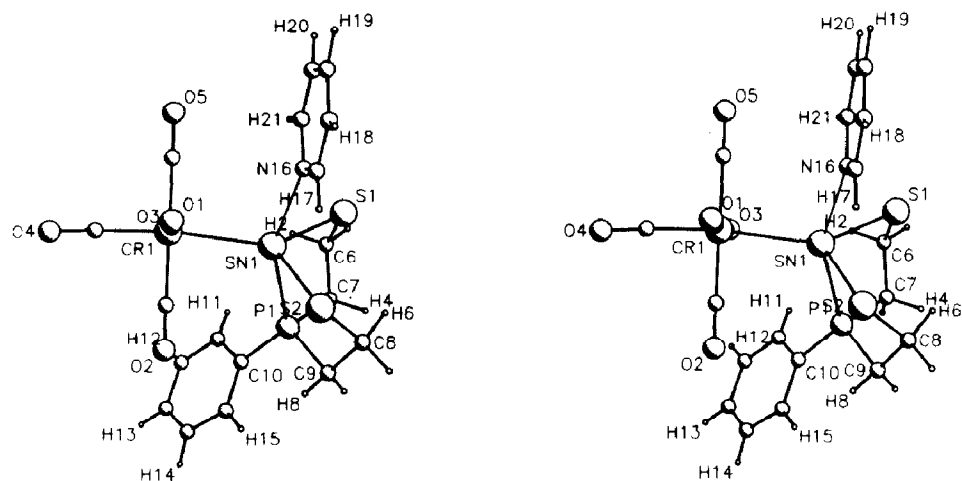


Fig. 1. Stereoscopic view of compound 1 showing the numbering of the atoms (PLUTO, Motherwell and Clegg, 1978).

PPh · Py (1). It will be shown below that this compound is the first pentacoordinated stannylene complex stabilized by two different donor atoms, viz. N and P.

## Results and discussion

The structure of compound 1 is shown in Fig. 1. Bond lengths bond angles and torsion angles are summarized in Tables 1 to 3. The tin atom has a distorted trigonal bipyramidal configuration, with the donor atoms nitrogen and phosphorus occupying the axial positions and the two sulphur atoms and the chromium located equatorially. It is interesting to note that the N–Sn–P angle of  $153.9^\circ$  in 1 is close

Table 1

Selected bond lengths (Å) with e.s.d. in parentheses

Cr(1)–Sn(1)	2.618(1)	S(1)–Sn(1)	2.472(1)
S(2)–Sn(1)	2.462(1)	P(1)–Sn(1)	2.756(1)
N(16)–Sn(1)	2.514(4)	C(1)–Cr(1)	1.883(4)
C(2)–Cr(1)	1.888(5)	C(3)–Cr(1)	1.893(4)
C(4)–Cr(1)	1.843(4)	C(5)–Cr(1)	1.888(4)
C(6)–S(1)	1.828(5)	C(8)–S(2)	1.828(4)
C(7)–P(1)	1.830(4)	C(9)–P(1)	1.816(4)
C(10)–P(1)	1.811(4)	C(1)–O(1)	1.133(6)
C(2)–O(2)	1.138(7)	C(3)–O(3)	1.141(5)
C(4)–O(4)	1.147(5)	C(5)–O(5)	1.135(6)
C(7)–C(6)	1.528(7)	C(9)–C(8)	1.537(6)
C(11)–C(10)	1.381(5)	C(15)–C(10)	1.388(6)
C(12)–C(11)	1.382(7)	C(13)–C(12)	1.347(8)
C(14)–C(13)	1.355(6)	C(15)–C(14)	1.395(8)
C(17)–N(16)	1.333(5)	C(21)–N(16)	1.339(5)
C(18)–C(17)	1.389(9)	C(19)–C(18)	1.373(9)
C(20)–C(19)	1.376(7)	C(21)–C(20)	1.372(8)

Table 2

Selected bond angles ( $^{\circ}$ ) with e.s.d. in parentheses

S(1)–Sn(1)–Cr(1)	135.8(1)	S(2)–Sn(1)–Cr(1)	121.3(1)
S(2)–Sn(1)–S(1)	103.0(1)	P(1)–Sn(1)–Cr(1)	106.7(1)
P(1)–Sn(1)–S(1)	78.9(1)	P(1)–Sn(1)–S(2)	80.0(1)
N(16)–Sn(1)–Cr(1)	99.4(1)	N(16)–Sn(1)–S(1)	81.5(1)
N(16)–Sn(1)–S(2)	87.8(1)	N(16)–Sn(1)–P(1)	153.9(1)
C(1)–Cr(1)–Sn(1)	87.8(1)	C(2)–Cr(1)–Sn(1)	83.9(1)
C(2)–Cr(1)–C(1)	92.0(2)	C(3)–Cr(1)–Sn(1)	89.7(1)
C(3)–Cr(1)–C(1)	175.6(2)	C(3)–Cr(1)–C(2)	91.3(2)
C(4)–Cr(1)–Sn(1)	172.5(2)	C(4)–Cr(1)–C(1)	90.8(2)
C(4)–Cr(1)–C(2)	88.8(2)	C(4)–Cr(1)–C(3)	92.2(2)
C(5)–Cr(1)–Sn(1)	94.7(1)	C(5)–Cr(1)–C(1)	87.5(2)
C(5)–Cr(1)–C(2)	178.6(2)	C(5)–Cr(1)–C(3)	89.1(2)
C(5)–Cr(1)–C(4)	92.5(2)	C(6)–S(1)–Sn(1)	101.2(1)
C(8)–S(2)–Sn(1)	100.2(1)	C(7)–P(1)–Sn(1)	103.1(2)
C(9)–P(1)–Sn(1)	102.4(2)	C(9)–P(1)–C(7)	106.5(2)
C(10)–P(1)–Sn(1)	127.8(1)	C(10)–P(1)–C(7)	107.2(2)
C(10)–P(1)–C(9)	108.1(2)	O(1)–C(1)–Cr(1)	176.6(4)
O(2)–C(2)–Cr(1)	179.0(3)	O(3)–C(3)–Cr(1)	178.2(3)
O(4)–C(4)–Cr(1)	177.4(5)	O(5)–C(5)–Cr(1)	178.0(3)
C(7)–C(6)–S(1)	112.5(3)	C(6)–C(7)–P(1)	111.3(3)
C(9)–C(8)–S(2)	112.6(2)	C(8)–C(9)–P(1)	109.4(3)
C(11)–C(10)–P(1)	119.4(3)	C(15)–C(10)–P(1)	122.2(3)
C(15)–C(10)–C(11)	118.3(4)	C(12)–C(11)–C(10)	120.3(4)
C(13)–C(12)–C(11)	121.6(4)	C(14)–C(13)–C(12)	118.9(5)
C(15)–C(14)–C(13)	121.6(5)	C(14)–C(15)–C(10)	119.3(4)
C(17)–N(16)–Sn(1)	124.1(3)	C(21)–N(16)–Sn(1)	117.0(3)
C(21)–N(16)–C(17)	118.4(4)	C(18)–C(17)–N(16)	122.1(5)
C(19)–C(18)–C(17)	118.7(5)	C(20)–C(19)–C(18)	119.5(6)
C(21)–C(20)–C(19)	118.5(5)	C(20)–C(21)–N(16)	122.9(4)

to the S(1)–Sn(1) ... S(1') angle of  $153.6^{\circ}$  in the  $\psi$ -trigonal bipyramidal coordinated free ligand Sn(SCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh in its dimeric structure [2].

The Sn–P interaction in **1** is lower than that in the stannylenes Sn(SCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>PPh as a consequence of both the additional pyridine complexation and the increased “hardness” of the tin atom in the complex **1**. Nevertheless, the intramolecular Sn–P bond with a formal bond order of 0.74 is still stronger than the intermolecular Sn–N contact, with a formal bond order of about 0.59 if the tin atom in compound **1** is assumed to be a four-coordinate with a covalent radius of 1.40 Å [5].

Table 3

Torsion angles of the eight-membered ring

S(1)–Sn(1)–S(2)–C(8)	–45.6
Sn(1)–S(2)–C(8)–C(9)	–64.3
S(2)–C(8)–C(9)–P(1)	63.8
C(8)–C(9)–P(1)–C(7)	79.7
C(9)–P(1)–C(7)–C(6)	–129.5
P(1)–C(7)–C(6)–S(1)	58.2
C(7)–C(6)–S(1)–Sn(1)	–63.9
C(6)–S(1)–Sn(1)–S(2)	110.4

The Cr–Sn distance of 2.618 Å is very similar to that of 2.623 Å in  $(\text{CO})_5\text{CrSn}(\text{SCH}_2\text{CH}_2)_2\text{NBu}^+$  [1], which shows that the strength of the  $\pi$  interaction between the transition metal and the tin atom is not influenced by additional donor acceptor interactions [6]. The Sn–S bond lengths are shorter than in the free stannylene  $\text{Sn}(\text{SCH}_2\text{CH}_2)_2\text{PPh}$  [2] but somewhat longer than those in the tetracoordinated complex  $(\text{CO})_5\text{CrSn}(\text{SCH}_2\text{CH}_2)_2\text{NBu}^+$  [1].

The torsion angles summarized in Table 3 show that the complexation of the stannylene results in a conformational change of the eight-membered ring. In compound **1** the ring adopts a boat-chair conformation.

The pentacarbonyl chromium fragment shows no unusual features.

## Experimental

Single crystals of compound **1** were obtained by crystallization of  $(\text{CO})_5\text{CrSn}(\text{SCH}_2\text{CH}_2)_2\text{PPh}$  [2] from pyridine. A parallelepiped crystal of dimensions 0.2 ×

Table 4

Atomic coordinates ( $\times 10^4$ ,  $\times 10^5$  for Sn and Cr) and equivalent temperature factors ( $\text{Å}^2$ )

	$x/a$	$y/b$	$z/c$	$B_{\text{eq}}^a$
Sn(1)	21021(2)	16245(2)	23962(1)	2.81(1)
Cr(1)	43510(5)	−6688(5)	26971(4)	3.11(1)
S(1)	1053(1)	2940(1)	799(1)	3.81(1)
S(2)	438(1)	3041(1)	3949(1)	4.28(1)
P(1)	2800(1)	3968(1)	2277(1)	3.18(1)
O(1)	2584(4)	−1610(5)	4495(3)	8.07(9)
O(2)	4757(5)	1279(4)	4193(3)	7.69(9)
O(3)	6021(4)	188(4)	746(3)	6.26(6)
O(4)	6932(4)	−3046(4)	3315(5)	9.16(10)
O(5)	3898(4)	−2615(4)	1236(3)	6.18(6)
C(1)	3234(4)	−1216(4)	3835(3)	4.63(6)
C(2)	4594(5)	558(4)	3627(3)	4.72(7)
C(3)	5378(4)	−112(4)	1481(3)	4.19(6)
C(4)	5942(4)	−2155(4)	3060(4)	5.39(8)
C(5)	4061(4)	−1864(4)	1771(3)	4.08(6)
C(6)	2295(4)	3720(4)	206(3)	4.28(6)
C(7)	2340(4)	4805(4)	964(3)	4.34(6)
C(8)	162(3)	4875(4)	3463(3)	4.52(6)
C(9)	1497(4)	5150(4)	3326(4)	4.45(6)
C(10)	4474(3)	3969(3)	2380(3)	3.39(5)
C(11)	5562(4)	3460(5)	1520(3)	4.61(7)
C(12)	6877(4)	3343(5)	1615(4)	5.68(8)
C(13)	7139(5)	3719(5)	2536(4)	5.62(9)
C(14)	6080(6)	4235(6)	3384(4)	6.41(11)
C(15)	4734(5)	4377(5)	3326(3)	5.14(8)
N(16)	472(3)	427(3)	2325(2)	3.89(5)
C(17)	−418(4)	289(5)	3181(4)	5.15(8)
C(18)	−1171(5)	−538(6)	3141(5)	6.71(11)
C(19)	−993(5)	−1228(5)	2185(5)	6.14(10)
C(20)	−65(5)	−1100(5)	1302(4)	5.35(8)
C(21)	648(4)	−272(4)	1406(3)	4.48(7)

<sup>a</sup>  $B_{\text{eq}} = (8/3)\pi^2 \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$

0.15 × 0.3 mm was sealed in a capillary. The space group ( $P\bar{1}$ ) was established by Weissenberg photographs. The unit-cell parameters were obtained by least-squares refinement from the setting angles using 15 reflections in the range  $5^\circ \leq 2\theta \leq 15^\circ$ :  $a$  10.654(2),  $b$  10.146(3),  $c$  12.448(3) Å,  $\alpha$  85.31(2),  $\beta$  79.66(2),  $\gamma$  65.53(2)°,  $V$  1204.8 Å<sup>3</sup>,  $Z = 2$ , (C<sub>20</sub>H<sub>18</sub>NO<sub>5</sub>PS<sub>2</sub>CrSn),  $D_{\text{calc}}$  1.70 g · cm<sup>-3</sup>. The intensities were collected in the  $\omega$ -scan mode with a Syntex P2<sub>1</sub> diffractometer, using monochromatic Mo- $K_\alpha$  radiation. 4990 independent reflections with  $\sin \theta/\lambda \leq 0.627 \text{ \AA}^{-1}$  were measured of which 4456 were considered as observed using the criterion  $I \geq 2.5\sigma(I)$ . A standard reflection (-3, 1, 2) checked every 50 reflections showed no significant variation. The structure was solved by the Patterson function using SHELX 76 [7]. H atoms were located by differing Fourier synthesis. Anisotropic least squares refinement using  $F$  was carried out for all non-hydrogen atoms [8]. The hydrogen atoms were refined isotropically with a common isotropic temperature factor ( $B = 5.8 \text{ \AA}^2$ ) (Table 4). The weighting scheme used was  $\omega = 1/(\sigma^2 F_o + 0.0025 F^2)$ , ( $S = 0.84$ ). The final  $R$  value was 0.034 ( $R_w = 0.037$ ) for 4456 observed reflections with a final maximum shift to error 0.71. Maximum and minimum heights in final difference Fourier synthesis were 1.58 and  $-1.04 \text{ e} \cdot \text{\AA}^{-3}$  around the tin atom, respectively. Atomic scattering factors were taken from International Tables for X-ray Crystallography Vol. IV (1974).

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