ELSEVIER

Journal of Organometallic Chemistry 574 (1999) 207–212

Journal of Organometallic Chemistry

Phosphinethiolate tin(IV)-11 group-metal derivatives. X-ray structure of $[Au_2Sn(^tBu)_2(C_6F_5)_2(SC_6H_4PPh_2)_2]$[1]

Eduardo J. Fernández [a], Michael B. Hursthouse [b], Mariano Laguna [c,]*, Raquel Terroba [a,b]

[a] *Departamento de Química, Universidad de la Rioja, 26001 Logroño, Spain*
[b] *Department of Chemistry, University of Wales Cardiff, PO Box 912, Cardiff CF1 3TB, UK*
[c] *Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-C.S.I.C., 50009 Zaragoza, Spain*

Received 6 August 1997; received in revised form 13 February 1998

Abstract

$[SnR_2Cl_2]$ reacts with $(SC_6H_4PPh_2)^-$ giving $[SnR_2(SC_6H_4PPh_2)_2]$ (R = Me, ^{t}Bu, Ph) (**1a**–**c**). These compounds can displace tetrahydrothiophene from $[Au(C_6F_5)(tht)]$ or $[Au(tht)_2]ClO_4$ or reacts with $AgClO_4$. Complexes $[SnR_2\{(SC_6H_4PPh_2)Au(C_6F_5)\}_2]$ (**2a**–**c**) and $[SnR_2(SC_6H_4PPh_2)_2M]ClO_4$ (M = Au **3a**–**c**; M = Ag **4a**–**c**) are obtained. The crystal structure of $[Sn(^tBu)_2\{(SC_6H_4\text{-}PPh_2)Au(C_6F_5)\}_2]$ (**2b**) has been established by X-ray diffraction. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Tin; Gold; Silver; Phosphinethiolate; Heteronuclear complexes

---

1. Introduction

Transition metal complexes containing thiolates and thioethers have received a great deal of attention because they are involved in both enzymatic [1] and catalytic [2] processes, besides having some important applications in medicine, as in the case of gold complexes for the treatment of rheumatoid arthritis [3] with thiomalategold(I) (*Myocrysin*) or the triethylphosphine gold(I) thioglucose derivative *Auranofin* ([2,3,4,6-tetra-*O*-acetyl-1-thio-α-D-glucopyranosal-S) (triethylphosphine)gold(I)]. In addition *Auranofin* has proved to be an effective cytotoxic agent against melanoma and P388 leukaemia cells [4] and, which is more important, aurothioglucosa and aurothiomalate have anti-HIV-1 activity in vitro [5]. On the other hand, the presence of phosphines in these complexes enlarge their properties and phosphine-complex chemistry is the basis for a variety of catalytic reactions [6]. The development of these two fields of research led to the recent interest in mixed-donor phosphorus–sulphur ligands not only for the possible addition of the above mentioned properties, but also for the potential preparation of new heteronuclear complexes due to the different coordination properties of the P and S ends [7]. These type of derivatives with transition and main group metal centers and no metal–metal bond are very important for their new reactivity patterns [8].

Phosphorus–thioether chelates have been studied by the research groups of Meek [9], Clark [10], Roundhill [11], Sanger [12] among others [13] but the chemistry of phosphinethiol ligands has received less attention. In this paper we report the preparation of tin complexes with $(SC_6H_4PPh_2)^-$, and the new compounds $[SnR_2(SC_6H_4PPh_2)_2]$ were used for the synthesis of heteropolynuclear complexes with 11 group metals. The structure of $[Sn(^tBu)_2\{(SC_6H_4PPh_2)Au(C_6F_5)\}_2]$ has been established by X-ray diffraction.

---

* Corresponding author. Tel.: +34 976 761181; fax: +34 976 761187; e-mail: mlaguna@posta.unizar.es

[1] Dedicated to Professor P. Royo on the occasion of his 60th birthday.

PII S0022-328X(98)00508-7

Table 1
Data for the new compounds

Complex	Yield (%)	Analyses (%)[a]					$^{31}P\{^1H\}^e$
		C	H	S	Λ_M^b	M.p. (°C)	(*J*)
1a $[SnMe_2(SC_6H_4PPh_2)_2]$	82	61.7	4.9	8.35	f	138	−12.5(s)
		(62.05)	(4.65)	(8.7)			(75.7)
1b $[Sn^tBu_2(SC_6H_4PPh_2)_2]$	63	64.05	5.25	7.8	2	172	−12.5(s)
		(64.5)	(5.65)	(7.8)			
1c $[SnPh_2(SC_6H_4PPh_2)_2]$	94	66.7	4.15	6.85	3	147	−13.8(s)
		(67.05)	(4.45)	(7.45)			(101.9)
2a $[SnMe_2\{(SC_6H_4PPh_2)Au(C_6F_5)\}_2]$	61	40.75	2.3	4.1	3	117	37.0(s)
		(41.05)	(2.35)	(4.4)			
2b $[Sn^tBu_2\{(SC_6H_4PPh_2)Au(C_6F_5)\}_2]$	59	43.75	2.65	4.45	6	112	35.6(s)
		(43.45)	(3.0)	(4.15)			
2c $[SnPh_2\{(SC_6H_4PPh_2)Au(C_6F_5)\}_2]$	68	45.85	2.3	4.1	15	99	36.2(s)
		(45.4)	(2.4)	(4.05)			
3a $[SnMe_2(SC_6H_4PPh_2)_2Au]ClO_4$	82	43.8	2.75	5.75	88	133[d]	35.4(s)
		(44.25)	(3.3)	(6.2)			
3b $[Sn^tBu_2(SC_6H_4PPh_2)_2Au]ClO_4$	76	46.95	3.75	5.85	99	162[d]	35.9(s)
		(47.35)	(4.15)	(5.75)			
3c $[SnPh_2(SC_6H_4PPh_2)_2Au]ClO_4$	45	49.45	2.95	5.25	85	158[d]	36.9(s)
		(49.8)	(3.3)	(5.55)			
4a $[SnMe_2(SC_6H_4PPh_2)_2Ag]ClO_4$	70	47.75	3.7	6.15	36[c]	154[d]	4.6(dd)
		(48.4)	(3.65)	(6.8)			(443.3) (511.6)
4b $[Sn^tBu_2(SC_6H_4PPh_2)_2Ag]ClO_4$	61	51.1	4.65	6.45	33[c]	116[d]	5.7(dd)
		(51.45)	(4.5)	(6.25)			(441.8) (508.3)
4c $[SnPh_2(SC_6H_4PPh_2)_2Ag]ClO_4$	50	53.65	3.4	5.9	41[c]	158[d]	5.2(dd)
		(54.05)	(3.6)	(6.0)			(471.1) (543.7)

[a] Calculated values are given in parentheses.

[b] In acetone, values in $\Omega^{-1}cm^2\ mol^{-1}$.

[c] In dichloromethane.

[d] Decompose without melting.

[e] In $CDCl_3$ δ in ppm., *J* in Hz.

2. Results and discussion

Recently [14] we have described the preparation of dithiolate tin complexes by metathetical reaction of $[SnR_2Cl_2]$ with the dithiolate disodium salt. Likewise the reaction of $[SnR_2Cl_2]$ with $NaSC_6H_4PPh_2$ in a 1:2 ratio, affords compounds **1a–c** in good yields (Eq. (1)).

$$[SnCl_2R_2] + 2HSC_6H_4PPh_2 \xrightarrow[NaOEt]{EtOH} 2HCl + [SnR_2(SC_6H_4PPh_2)_2]$$

$$R = Me\ \mathbf{1a},\ {}^tBu\ \mathbf{1b},\ Ph\ \mathbf{1c} \qquad (1)$$

The ^1H-NMR spectra of compounds **1a–b** show singlets due to the methyl and *tert*-butyl radicals bonded to the metal showing tin satellites. In the $^{31}P\{^1H\}$-NMR a singlet in negative values of δ is observed in all the cases, with a similar δ to the starting phosphine ($\delta = -13.1$ ppm) [15] (Table 1). In the methyl and phenyl derivatives, these singlets appear with the satellites from the tin active nuclei (^{117}Sn and ^{119}Sn), but the constant values 75.7 and 42.3 Hz are not in accordance with a Sn–P bond (ca. 1350 Hz [16]), and must be a $^4J_{Sn-P}$. The mass spectra (LSIMS +) of these compounds show no peaks of their parent ion but $[M\text{-}SC_6H_4PPh_2]^+$ and $[M\text{-}2R\text{-}SC_6H_4PPh_2]^+$ are present in accordance with the formulation.

With these data we propose a tetracoordinated SnC_2S_2 core for the tin compounds, the phosphorus atoms being uncoordinated. The presence of these free donor-atoms gives the possibility of using the complexes **1a–c** as starting materials in the synthesis of heterometallic derivatives. The reaction of the tin compounds **1a–c** with $[Au(C_6F_5)(tht)]$ in a 1:2 ratio gives trinuclear complexes (Eq. (2)).

$$[SnR_2(SC_6H_4PPh_2)_2] + 2[Au(C_6F_5)(tht)]$$

$$\rightarrow [SnR_2\{(SC_6H_4PPh_2)Au(C_6F_5)\}_2] + 2tht$$

$$R = Me\ (\mathbf{2a}),\ {}^tBu\ (\mathbf{2b}),\ Ph\ (\mathbf{2c}) \qquad (2)$$

After coordination, the $^{31}P\{^1H\}$-NMR spectra show a broad singlet (probably because the coupling with the fluorine atoms) for all these new compounds with δ values typical of Au–P complexes (Table 1, $\Delta\delta \approx 50$ ppm) and the ^1H-NMR spectra show singlets for the methyl groups of complexes **2a–b** higher field displaced from the mononuclear tin derivatives. Whereas the proton-NMR spectra show tin satellites, they are absent in the phosphorus NMR. The three resonances in

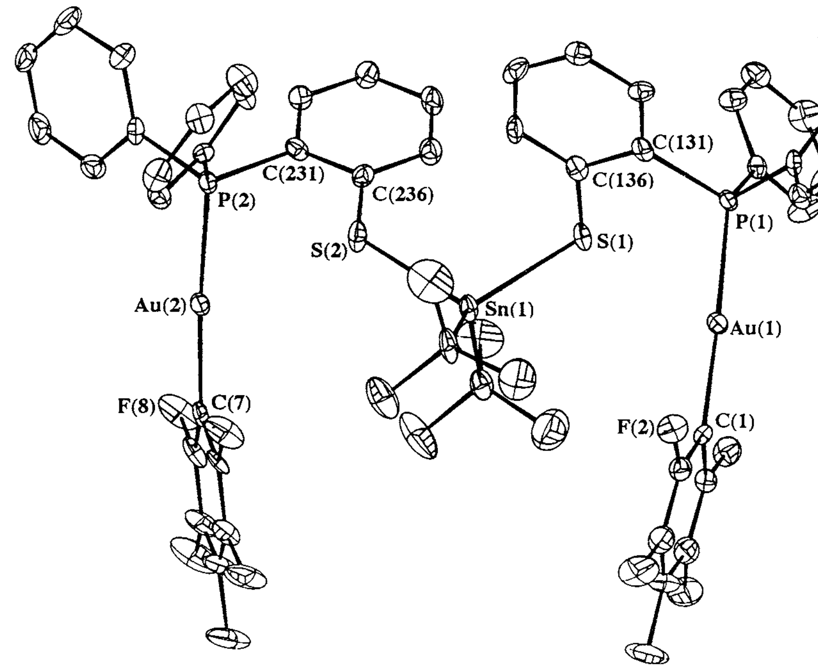

Fig. 1. Molecule of compound **2b** in the crystal. Displacement parameter ellipsoids represent 50% probability surfaces. H atoms are omitted for clarity.

^{19}F-NMR spectra in 2:1:2 ratio are in agreement with equivalent pentafluorophenyl groups bonded to a gold(I) center. Although complexes **2a**–**c** behave as non conducting in acetone solution their LSIMS mass spectra do not show peaks corresponding to heteronuclear species except for **2b** which show peaks at *m*/*z* 1380 (6%) $[M\text{-}C_6F_5]^+$ and 1038 (7%) $[M\text{-}SC_6H_4PPh_2\text{-}C_6F_5]^+$.

The molecular structure of the complex $[Au_2Sn(C_6F_5)_2{}^tBu_2(SC_6H_4PPh_2)_2]$ **2b**, has been established by X-ray diffraction and is shown in Fig. 1. Atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3. Every phosphinethiolate ligand is bridging the tin center and one of the gold atoms. The tin(IV) is bonded to the sulphur atoms of the P,S-donor ligands with distances Sn–S(1) = 2.444(3) and Sn–S(2) = 2.434(3) Å and to the *tert*-butyl groups with bond lengths Sn–C(20) = 2.194(11) and Sn–C(30) = 2.197(12) Å similar to other Sn(IV)–C compounds [17] and is in a distorted tetrahedral arrangement with angles C(20)–Sn–C(30) = 122.3(5), C(20)–Sn–S(2) = 98.1(3), C(30)–Sn–S(2) = 110.7(3), C(20)–Sn–S(1) = 112.3(3), C(30)–Sn–S(1) = 101.0(3) and S(2)–Sn–S(1) = 113.01(11)°. The '$Sn^tBu_2(SC_6H_4PPh_2)_2$' unit acts as a bridging ligand between two '$Au(C_6F_5)$' fragments. The gold(I) atoms are in a linear coordination, C(1)–Au(1)–P(1) = 177.5(3)° and C(7)–Au(2)–P(2) = 176.0(3)°. The gold–phosphorus bond lengths are Au(1)–P(1) = 2.269(3) and Au(2)–P(2) = 2.270(3) Å and are similar to those found in $[Au(C_6F_5)(PPh_2CH(PPh_2Me)]$ 2.287(2) Å and $[Au(C_6F_5)\{PPh_2CH(PPh_2Me)Au(C_6F_5)\}]$ 2.286(4)Å [18]. The gold–carbon distances are Au(1)–C(1) = 2.052(10) and Au(2)–C(7) = 2.013(11) Å, and are in the range of the latter compounds 2.057 and 2.053 Å. The tin–gold distances are Sn–Au(1) = 5.08 and Sn–Au(2) = 5.48 Å, so there are no significant interactions between the metallic centers.

The formation of heteronuclear tin complexes can be extended reacting complexes **1a**–**c** with $[Au(tht)_2]ClO_4$ and $AgClO_4$ in a 1:1 molar ratio (Eqs. (3) and (4)).

$$[SnR_2(SC_6H_4PPh_2)_2] + [Au(tht)_2]ClO_4$$

$$\rightarrow [SnR_2(SC_6H_4PPh_2)_2Au]ClO_4 + 2tht$$

$$R = Me\ (\mathbf{3a}),\ {}^tBu\ (\mathbf{3b}),\ Ph\ (\mathbf{3c}) \tag{3}$$

$$[SnR_2(SC_6H_4PPh_2)_2] + AgClO_4$$

$$\rightarrow [SnR_2(SC_6H_4PPh_2)_2Ag]ClO_4$$

$$R = Me\ (\mathbf{4a}),\ {}^tBu\ (\mathbf{4b}),\ Ph\ (\mathbf{4c}) \tag{4}$$

The acetone solutions of the gold complexes **3a**–**c** show conductivity values in agreement with a formulation as 1:1 electrolytes [19]; Complexes **4a**–**c** are not enough soluble in acetone and their conductivities has been measured in dichloromethane solutions, showing values characteristic of 1:1 electrolytes (Table 1) [20]. The IR spectra of these new derivatives show bands at 1100 (vs, br) and 620 (m) cm^{-1} indicating ionic ClO_4 [21]. The ^{1}H-NMR of complexes **3** and **4** show singlets for the methyl groups at lower field than in the starting materials. The $^{31}P\{^1H\}$-NMR show a sharp singlet for the complexes **3a**–**c** and a doublet of doublets for **4a**–**c** because of the two active silver nuclei (Table 1). The coupling constants are in the range of 508.3–543.7 Hz for $^1J_{^{109}Ag-P}$ and 441.8–471.1 Hz for $^1J_{^{107}Ag-P}$ which

Table 2
Atomic coordinates ($\times 10^{-4}$) and equivalent isotropic displacement parameters ($\text{Å}^2 \times 10^3$) for **2b**

	x	y	z	U_{eq}
Sn(1)	3784(1)	5898(1)	2713(1)	27(1)
Au(1)	1978(1)	4471(1)	4759(1)	27(1)
Au(2)	5592(1)	7597(1)	484(1)	26(1)
S(1)	3523(2)	4174(2)	3245(2)	31(1)
S(2)	5428(3)	5618(3)	2046(2)	37(1)
P(1)	3149(2)	2703(2)	4807(2)	23(1)
P(2)	6900(2)	5842(2)	695(2)	24(1)
C(1)	961(8)	6095(9)	4684(6)	25(2)
C(2)	1135(9)	6695(9)	5106(6)	30(3)
C(3)	572(10)	7798(11)	5003(7)	42(3)
C(4)	−232(11)	8400(10)	4457(8)	48(3)
C(5)	−442(9)	7823(10)	4015(7)	40(3)
C(6)	132(9)	6727(9)	4150(6)	26(3)
F(2)	1968(5)	6175(6)	5646(3)	40(2)
F(3)	784(6)	8356(7)	5434(5)	66(2)
F(4)	−825(7)	9496(6)	4355(6)	78(3)
F(5)	−1195(6)	8422(6)	3439(4)	59(2)
F(6)	−96(5)	6211(6)	3704(4)	43(2)
C(7)	4377(9)	9110(9)	353(6)	26(2)
C(8)	3660(11)	9691(10)	−300(6)	38(3)
C(9)	2802(11)	10637(10)	−367(8)	47(4)
C(10)	2544(11)	11090(10)	215(9)	52(4)
C(11)	3192(11)	10577(10)	864(7)	40(3)
C(12)	4032(9)	9642(9)	907(6)	26(3)
F(8)	3885(7)	9258(6)	−894(4)	59(2)
F(9)	2159(8)	11149(7)	−1015(5)	84(3)
F(10)	1643(7)	12056(7)	143(6)	90(3)
F(11)	2877(7)	11045(6)	1452(4)	65(2)
F(12)	4661(7)	9166(6)	1552(4)	57(2)
C(111)	3333(9)	1750(9)	5733(6)	27(3)
C(112)	3306(9)	2145(10)	6352(6)	31(3)
C(113)	3506(10)	1423(11)	7076(7)	42(3)
C(114)	3697(9)	336(10)	7201(6)	37(3)
C(115)	3705(9)	−811(0)	6598(7)	38(3)
C(116)	3529(9)	624(9)	5862(6)	31(3)
C(121)	2770(8)	2091(9)	4186(5)	23(2)
C(122)	1707(9)	2361(11)	4057(7)	45(3)
C(123)	1435(11)	1829(15)	3610(9)	68(5)
C(124)	2177(11)	1115(11)	3276(7)	49(4)
C(125)	3245(10)	868(10)	3387(6)	39(3)
C(126)	3541(9)	1329(9)	3857(6)	34(3)
C(131)	4515(9)	2549(9)	4550(6)	27(3)
C(132)	5405(9)	1751(9)	5003(6)	28(3)
C(133)	6412(9)	1634(9)	4800(6)	32(3)
C(134)	6564(9)	2278(10)	4152(7)	39(3)
C(135)	5683(9)	3104(10)	3679(6)	33(3)
C(136)	4672(9)	3242(9)	3866(6)	28(3)
C(211)	7784(9)	5609(9)	−69(6)	28(3)
C(212)	7486(10)	6383(10)	−765(6)	34(3)
C(213)	8152(12)	6213(11)	−1350(7)	47(3)
C(214)	9106(11)	5327(11)	−1257(7)	44(3)
C(215)	9407(10)	4534(12)	−570(7)	47(3)
C(216)	8765(9)	4668(10)	31(6)	34(3)
C(221)	7747(8)	5451(19)	1511(6)	26(2)
C(222)	8177(10)	4382(10)	1998(6)	38(3)
C(223)	8748(11)	4176(11)	2646(7)	45(3)
C(224)	8951(10)	4953(10)	2823(7)	37(3)
C(225)	8580(10)	5998(12)	2363(7)	44(3)
C(226)	7937(10)	6297(10)	1702(6)	34(3)
C(231)	6315(9)	4831(9)	870(6)	26(2)
C(232)	6525(9)	4120(9)	417(6)	31(3)
C(233)	6033(9)	3394(10)	514(7)	37(3)
C(234)	5358(9)	3325(10)	1096(6)	36(3)
C(235)	5131(9)	4010(10)	1544(6)	34(3)
C(236)	5616(9)	4770(9)	1447(6)	27(2)
C(20)	4164(12)	6510(11)	3578(6)	41(3)
C(21)	4172(14)	7654(12)	3190(8)	66(5)
C(22)	5267(15)	5726(15)	3948(9)	82(6)
C(23)	3372(14)	6521(15)	4161(9)	78(5)
C(30)	2365(10)	6896(10)	1930(6)	36(3)
C(31)	2490(13)	6297(14)	1338(8)	74(5)
C(32)	2358(16)	8005(13)	1557(10)	90(6)
C(33)	1355(14)	7072(17)	2332(10)	93(6)

are very close to those reported for a P_2S_2 tetracoordination of silver complexes [22].

The mass spectra of complexes **3a–c** and **4a–b** show in all complexes the peak corresponding with the cation formulation $[\text{M-ClO}_4]^+$, furthermore others corresponding with the lack of one or two organic groups bonded to tin are also present.

Based on all these data and the well known preference of silver(I) for tetracoordination, a structure with the silver atom with P,P,S,S-coordination likewise to the reported $\text{TiCp}_2(\text{S–P})_2$ unit [7] could be possible for complexes **4a–c**. Because of the preferred two-coordination of gold(I), it could be proposed for complexes **3a–c**, a polymer chain or an heterodinuclear structure, with the gold centers in a linear arrangement.

3. Experimental section

The C, H, S analyses were carried out on a Perkin–Elmer 2400 Microanalyser. Conductivities were measured in approximately 5×10^{-4} mol dm^{-3} acetone solutions, with a Jenway 4010 Conductimeter. The melting points were measured in a Gallekamp apparatus and are uncorrected. The infrared spectra were recorded (4000–200 cm^{-1}) on Perkin–Elmer 883 Spectrophotometer, using Nujol mulls between polyethylene sheets. The NMR spectra were recorded on Bruker ARX 300 Spectrometer, in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (^{1}H), 85% H_3PO_4 (external ^{31}P) and $CFCl_3$ (^{19}F). Mass spectra were recorded on VG Autospec with LSIMS (Liquid Secondary Ion Mass Spectrometry) technique using 3-nitrobenzylalcohol as matrix and a caesium gun. The elemental analyses, conductivities, yield, melting point and ^{31}P{^{1}H} data of the new complexes are listed in Table 1.

Table 3
Selected bond lengths (Å) and angles (°) for **2b**

Sn(1)–C(20)	2.194(11)	Sn(1)–C(30)	2.197(12)
Sn(1)–S(2)	2.434(3)	Sn(1)–S(1)	2.4443)
Au(1)–C(1)	2.052(10)	Au(1)–P(1)	2.2693)
Au(2)–C(7)	2.013(11)	Au(2)–P(2)	2.2703)
S(1)–C(136)	1.787(12)	S(2)–C(236)	1.765(10)
C(20)–Sn(1)–C(30)	122.3(5)	C(20)–Sn(1)–S(2)	98.1(3)
C(30)–Sn(1)–S(2)	110.7(3)	C(20)–Sn(1)–S(1)	112.3(3)
C(30)–Sn(1)–S(1)	101.0(3)	S(2)–Sn(1)–S(1)	113.0(1)
C(1)–Au(1)–P(1)	177.5(3)	C(7)–Au(2)–P(2)	179.0(3)
C(136)–S(1)–Sn(1)	106.0(4)	C(236)–S(2)–Sn(1)	112.5(4)
C(111)–P(1)–Au(1)	112.6(4)	C(121)–P(1)–Au(1)	114.5(4)
C(131)–P(1)–Au(1)	114.9(3)	C(221)–P(2)–Au(2)	112.2(3)
C(231)–P(2)–Au(2)	110.4(4)	C(211)–P(2)–Au(2)	115.0(4)
C(6)–C(1)–Au(1)	123.3(7)	C(2)–C(1)–Au(1)	122.6(8)
C(12)–C(7)–Au(2)	125.2(8)	C(8)–C(7)–Au(2)	123.2(8)
C(23)–C(20)–Sn(1)	108.4(9)	C(22)–C(20)–Sn(1)	110.1(9)
C(21)–C(20)–Sn(1)	107.5(8)	C(32)–C(30)–Sn(1)	109.5(9)
C(33)–C(30)–Sn(1)	111.1(9)	C(31)–C(30)–Sn(1)	106.5(9)

3.1. Syntheses

The starting materials ($HSC_6H_4PPh_2$) [15], [Au(C_6F_5)(tht)] [23] (tht = tetrahydrothiophen), and [Au(tht)$_2$]ClO_4 [24] were prepared as described previously. All other reagents were commercially available.

3.1.1. [SnR$_2$(SC$_6$H$_4$PPh$_2$)$_2$] [R = Me (1a), ^{t}Bu (1b), Ph (1c)]

To a solution of ($HSC_6H_4PPh_2$) (0.294 g, 1 mmol) in EtOH and EtONa (20 cm^3, 0.1M) is added [$SnCl_2R_2$] [R = Me (0.110 g, 0.5 mmol), ^{t}Bu (0.152 g, 0.5 mmol), Ph (0.172 g, 0.5 mmol)]. After stirring 5 h the new compounds are filtered as white solids. ^{1}H-NMR: **1a** $\delta = 7.57$, 7.06 and 6.69 (m, 8H, C_6H_4), 7.33–7.16 (m, 20H, Ph), 0.66 (s, $^2J_{Sn-H} = 62.2$Hz, 6H, Me). **1b** $\delta =$ 7.74, 7.05 and 6.70 (m, 8H, C_6H_4), 7.30–7.11 (m, 20H, Ph), 1.20 (s, $^3J_{Sn-H} = 42.3$Hz, 18H, ^{t}Bu). **1c** $\delta = 7.66$, 6.99 and 6.49 (m, 8H, C_6H_4) 7.44–7.11 (m, 30H, Ph). Mass spectra *m/z* (%) [M-$SC_6H_4PPh_2$]$^+$ and [M-2R-$SC_6H_4PPh_2$]$^+$: **1a** 441 (100) and 411 (15). **1b** 527 (60) and 411 (100). **1c** 565 (41) and 411 (15).

*3.1.2. [Au$_2$Sn(C$_6$F$_5$)$_2$R$_2$(SC$_6$H$_4$PPh$_2$)$_2$] [R = Me (**2a**), ^{t}Bu (**2b**), Ph (**2c**)]*

To a dichloromethane solution (20 cm^3) of **1a** (0.074 g, 0.1 mmol), **1b** (0.082 g, 0.1 mmol) or **1c** (0.086 g, 0.1 mmol) was added [Au(C_6F_5)(tht)] (0.090 g, 0.2 mmol). After 2 h stirring the solutions were concentrated in vacuum and the addition of hexane affords the precipitation of the new compounds as white solids. **2a** ^{1}H-NMR: $\delta = 7.91$, 7.17 and 6.73 (m, 8H, C_6H_4), 7.59–7.31 (m, 20H, Ph), 0.27 (s, $^2J_{Sn-H} = 61.2$Hz, 6H, Me); ^{19}F-NMR: $\delta = -115.5$ (m, 4F, F*o*), -158.4 (t, $^3J_{FpFm} = 19.6$ Hz, 2F, F*p*), -162.3 (m, 4F, F*m*). **2b** $\delta = 8.18$, 7.12 and 6.79 (m, 8H, C_6H_4), 7.66 − 7.28 (m 20H, Ph), 0.95 (s, $^3J_{Sn-H} = 36.2$ Hz, 18H, ^{t}Bu); ^{19}F-NMR: $\delta = -115.3$ (m, 4F, F*o*), -159.0 (t, $^3J_{FpFm} =$ 20.0 Hz, 2F, F*p*), -162.8 (m, 4F, F*m*). **2c** $\delta = 7.78$–7.03 and 6.59 (m, 38H, C_6H_4); ^{19}F-NMR: $\delta = -115.0$ (m, 4F, F*o*), -159.4 (t, $^3J_{FpFm} = 20.2$ Hz, 2F, F*p*), -162.6 (m, 4F, F*m*).

*3.1.3. [MSnR$_2$(SC$_6$H$_4$PPh$_2$)$_2$]ClO$_4$ [M = Au R = Me (**3a**), ^{t}Bu (**3b**), Ph (**3c**), M = Ag R = Me (**4a**), ^{t}Bu (4b), Ph (**4c**)]*

To a dichloromethane (M = Au) or acetone (M = Ag) solution (20 cm^3) of **1a** (0.074 g, 0.1 mmol), **1b** (0.082 g, 0.1 mmol) or **1c** (0.086 g 0.1 mmol) was added [Au(tht)$_2$]ClO_4 (0.047 g, 0.1 mmol) or $AgClO_4$ (0.021 g, 0.1 mmol). After 2 h stirring the solutions were concentrated in vacuum and the addition of hexane affords the precipitation of the new compounds as white solids. ^{1}H-NMR: **3a** $\delta = 7.88$–7.04 and 6.85 (m, 28H, Ph), 0.91 (s, $^2J_{Sn-H} = 62.2$Hz, 6H, Me). **3b** $\delta = 7.76$, 7.26 and 6.94 (m, 8H, C_6H_4), 7.61–7.42 (m, 20H, Ph), 1.30 (s, $^3J_{Sn-H} = 40.2$Hz, 18H, ^{t}Bu). **3c** $\delta = 7.65$–7.05 and 6.78 (m, 28H, Ph). **4a** ^{1}H-NMR: $\delta = 7.76$ and 7.63–7.09 (m, 28H), 0.82 (s, 6H, Me). **4b** $\delta = 7.83$ and 6.96 (m, 8H, C_6H_4), 7.52–7.30 (m, 20H, Ph), 1.24 (s, 18H, ^{t}Bu). **4c** $\delta = 7.65$–7.05, 6.94 and 6.78 (m, 28H, Ph). Mass spectra *m/z* (%) [M-ClO_4]$^+$, [M-ClO_4-R]$^+$ and [M-ClO_4-2R]$^+$ **3a** 933 (100), no peak and 903 (11); **3b** 1017 (41), no peak and 903 (23); **3c** 1057 (80), 980 (42) and 903 (45); **4a** 841 (11), 826 (4) and 811 (4); **4b** 927 (53), 870 (30) and 811 (32).

*3.2. Crystal structure determination of compound **2b***

Single crystals were grown by diffusing hexane into a dichloromethane solution of complex [Au$_2$Sn(C_6F_5)$_2$-^{t}Bu$_2$($SC_6H_4PPh_2$)$_2$] **2b** at r.t., and mounted in inert oil.

3.2.1. Crystal data and data collection parameters

2b $C_{56}H_{46}Au_2F_{10}P_2S_2Sn$, $M = 1547.61$, triclinic, $a =$ 13.654(5), $b = 13.679(7)$, $c = 18.645(7)$ Å, $\alpha = 73.37(3)$, $\beta = 86.12(3)$, $\gamma = 65.86(3)$°, $U = 3040(2)$ Å^3, $T = 150$ K, space group $P\bar{1}$, graphite monochromated Mo–K$_\alpha$ radiation $\lambda = 0.71069$ Å, $Z = 2$, $D_{calc} = 1.691$ mg m^{-3}, $F(000) = 1484$, colourless prism with dimensions $0.24 \times 0.22 \times 0.18$ mm, $\mu = 5.407$ mm^{-1}; Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator, following procedures described elsewhere [25], θ range for data collection 1.76 to 25.12°, $-16 \le h \le 16$, $-15 \le k \le 16$, $-21 \le l \le 14$; 12849 reflections collected, 8332 independent ($R_{int} = 0.063$).

3.2.2. Structure solution and refinement

The structure was determined using the PATT instruction of SHELXS 86 [26], the structure were refined by full-matrix least squares on F_o^2, using the program SHELXL93 [27]. All data used were corrected for Lorentz-polarization factors, and subsequently for absorption using the program DIFABS [28]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in idealised positions. Refinement proceeded to $R = 0.0499$, $wR = 0.1475$ and goodness of fit on F^2 1.080 for 664 parameters and 12 restraints, and $R = 0.0565$, $wR = 0.1494$ for all data. In the final Fourier synthesis the electron density fluctuates in the range 3.342 to -1.350 e Å^{-3}.

Tables of thermal parameters and observed and calculated structure factors have been deposited at the Cambridge Crystallographic Data Centre.

Acknowledgements

The Spanish authors thank the Dirección General de Investigación Científica y Técnica (PB95- 0140) for financial support and Ministerio de Educación y Cultura for a grant (to R.T.), and M.B.H. thanks the Engineering and Physical Sciences Research Council for support of the X-ray facilities.

References

[1] H. Holm, J.A. Ibers, Science 209 (1980) 223.

[2] (a) Ph. Kalck, Organometallic in Organic Synthesis in: A. de Meijere, H.T. Dieck (Ed.), Springer Verlag, Heidelberg, 1987, p. 297. (b) S Cladiali, J.C. Bayón, C. Claver, Tetrahedron Asymm. 6 (1995) 1453. (c) J.R. Dilworth, Coord. Chem. Rev. 154 (1996) 163

[3] (a) K. Landé, Münchener Med. Wochenschr. 74 (1927) 1132. (b) J. Forestier, Bull. Mém. Soc. Méd. Hop (París) 53 (1929) 323. (c) D.R. Haynes, M.N. Whitehouse, in: K.D. Rainsforth, G.P. Velo (Eds.), Anti-Rheumatic Therapy, Kluwer, Dordrecht, 1989, p. 207. (d) C.F. Shaw III, A.A. Isab, J.D. Hoeschele, M. Starich, J. Jocke, P. Schulteis, J. Xiao, J. Am. Chem. Soc. 116 (1994) 2254. (e) G.C. Graham, G.D. Champion, J.B. Ziegher, Inflammorpharmacology 1 (1991) 99.

[4] (a) O.M.N. Dhubhghaill, P.J. Sadler, Metal complexes, in: B.K. Keppler (Ed.), Cancer Chemotherapy, VCH, Weinhein, 1993. (b) C.K. Mirabelli, R.K. Johnson, D.T. Hill, L.F. Faucette, G.R. Girard, G.Y. Kuo, C.M. Sung, S.T. Crooke, J. Med. Chem. 29 (1986) 218.

[5] (a) T. Okada, B.K. Patterdon, O.S. Ye, M.E. Gurney, Virology 192 (1993) 631. (b) H.A. Blough, M. Richetti, B.H. Montagnier, Chem. Abstr. 115 (1991) 174630p.

[6] (a) L.H. Pignolet (Ed.), Homogeneous Catalysis with Metal Phosphine Complexes, Plenum Press, New York, 1983. (b) M.C. Simpson, D.J. Colehamilton, Coord. Chem. Rev. 155 (1955) 163.

[7] (a) G.S. White, D.W. Stephan, Organometallics 6 (1987) 2169. (b) G.S. White, D.W. Stephan, Inorg. Chem. 24 (1985) 1499. (c) G.S. White, D.W. Stephan, Organometallics 7 (1988) 903.

[8] D.E. Stephan, Coord. Chem. Rev. 95 (1989) 41.

[9] (a) P.G. Eller, J.M. Ricker, D.W. Meek, J. Am. Chem. Soc. 95 (1973) 3540. (b) D.W. Meek, Inorg. Nucl. Chem. Lett. 5 (1969) 235.

[10] J.D. Orbell, G.R. Clark, J. Organomet. Chem. 215 (1981) 121.

[11] D.M. Roundhill, S.G.N. Roundhill, W.B. Breaulieu, U. Bagchi, Inorg. Chem. 19 (1980) 3365.

[12] A. Sanger, Can. J. Chem. (1983) 2214.

[13] (a) N. Froelich, P.B. Hitchcock, J. Hu, M.F. Lappert, J. R. Dilworth, J. Chem. Soc. Daton Trans. (1966) 1941. (b) F. Morandini, P. Rigo, M. Bressau, J. Organomet. Chem. 247 (1983) C8. (c) M. Bressan, G. Polzonetti, C. Furlani, Polyhedron 2 (1983) 523. (d) T. Gerdan, R. Kramolowsky, Z. Naturforsch B, Anorg. Chem. Org. Chem. (1982) 332. (e) T.N. Lockyer, Aust. J. Chem. 27 (1974) 259.

[14] E. Cerrada, E.J. Fernández, M.C. Gimeno, A. Laguna, M. Laguna, M.D. Villacampa, J. Organomet. Chem. 492 (1995) 105.

[15] E. Block, G. Ofori-Okai, J. Zubieta, J. Am. Chem. Soc. 111 (1989) 2327.

[16] J. Mason, Multinuclear NMR, Plenum Press, New York and London, 1987, pp 318–22.

[17] (a) A.G. Davies, in: G. Wilkinson, F.G.A. Stone, E.W. Abel (Eds.), Comprehensive Organometallic Chemistry II, vol 2, Pergamon, Oxford, 1995. (b) R. Rulkens, A.J. Lough, I. Manners, Angew. Chem. Int. Ed. Engl. 35 (1996) 1805. (c) R.J. Batchelor, F.W.B. Einstein, C.H.W. Jones, R.D. Sharma, Inorg. Chem. 27 (1988) 4636. (d) M. Weidenbruch, J. Schlaetke, K. Peters, H.G. von Schnering, J. Organomet. Chem. 414 (1991) 319.

[18] R. Usón, A. Laguna, M. Laguna, I. Lázaro, A. Morata, P.G. Jones, G.M. Sheldrick, J. Chem. Soc. Dalton Trans. (1986) 669.

[19] W.J. Geary, Coord. Chem. Rev. 7 (1971) 81.

[20] M. Contel, PhD Pamplona, 1996.

[21] M.N. Gowda, S.B. Naikan, G.K.N. Reddy, Adv. Inorg. Chem. Radiochem. 28 (1984) 255.

[22] A.R.J. Gence, A.M. Gibson, N.K. Guymer, G. Reid, J. Chem. Soc. Dalton Trans. (1996) 4099.

[23] R. Usón, A. Laguna, J. Vicente, J. Chem. Soc. Chem. Commun. (1976) 353.

[24] R. Usón, A. Laguna, M. Laguna, J. Jiménez, M.P. Gómez, A. Sainz, P.G. Jones, J. Chem. Soc. Dalton Trans. (1990) 3457.

[25] A.A. Danopoulos, G. Wilkinson, B. Hussain-Bates, M.B. Hursthouse, J. Chem. Soc. Dalton Trans. (1991) 1855.

[26] G.M. Sheldrick, SHELXS 86, Acta Crystallogr. Sect. A, 46 (1990) 467.

[27] G.M. Sheldrick, SHELXL 93, Programm for Crystal Structure Refinement. University of Götingen, Germany, 1993.

[28] N.P.C. Walker, D. Stuart, Acta Crystallogr. Sect. A. 39 (1983) 158. (adapted for FAST geometry by A. Karaulov, University of Wales, Cardiff, 1991).