

Heteronuclear tin(IV)–silver(I) complexes with phosphinothiolate ligands. X-ray structure of [AgSn(μ -SC₆H₄PPh₂)₂Me₂(PPh₂Me)]CF₃SO₃·CH₂Cl₂

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Received 25 September 2000; accepted 6 December 2000

Abstract

[SnR₂(SC₆H₄PPh₂)₂] (R = Me or Ph) react with silver complexes such as [Ag(CF₃SO₃)(PR₃)] (PR₃ = PPh₃ and PPh₂Me) to give [AgSn(μ -SC₆H₄PPh₂)₂R₂(PR₃)]CF₃SO₃ (**1–4**) where silver atom are coordinated to the PPh₂ group of the phosphinothiolate ligand as confirmed in the X-ray crystal structure of [AgSn(μ -SC₆H₄PPh₂)₂Me₂(PPh₂Me)]CF₃SO₃·CH₂Cl₂ (**2**). Similar tin derivatives [SnR₂{(SC₆H₄)₂PPh}] (R = Me, **5**; R = Ph, **6**) were synthesised and reacted with [Ag(CF₃SO₃)(PR₃)] and [Ag(CF₃SO₃)] to give in both cases [AgSn{ μ -(C₆H₄)₂PPh}R₂]CF₃SO₃ (R = Me, **7**; R = Ph, **8**) © 2001 Elsevier Science B.V. All rights reserved.

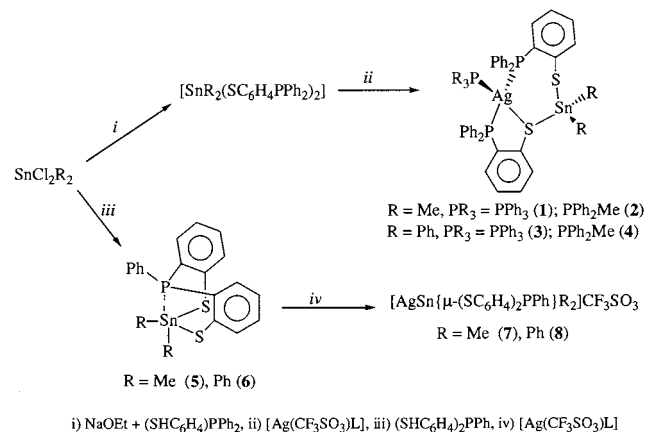
Keywords: Tin; Silver; Phosphinothiolate; Heteronuclear derivatives

1. Introduction

Much of the current interest in metallic thiolate complexes stems from the discovery that some metallic derivatives with sulphur atoms in the co-ordination sphere form the active centres of enzymes [1] such as hydrogenases and CO-dehydrogenases [2].

In the same way, the chemistry of asymmetric multi-dentate ligands have attracted a great deal of attention, in particular towards the phenomenon of hemilability [3]. Thiolate phosphine ligands are a good example of asymmetric multi-dentate ligands. Both phosphorus and sulphur are excellent ligand donor atoms for a wide range of metals, while the low ionisation energy of sulphur and the presence of several lone pairs of electrons offer the possibility of a rich sulphur-based chemistry of the complexes. The best known are

R₂PCH₂CH₂S⁻ and R₂PC₆H₄S⁻ ligands [4–6], but in recent years there has been an increasing interest in the ligands RP(C₆H₄S⁻)₂ and P(C₆H₄S⁻)₃ [4,6–8], which are considered as potentially tri- and tetra-dentate ligands.



Scheme 1. Synthesis of complexes **1–8**.

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Table 1
Selected bond lengths (Å) and bond angles (°) for **2**

Bond lengths			
Ag(1)–P(3)	2.4377(11)	Sn(1)–C(14)	2.125(4)
Ag(1)–P(2)	2.4673(10)	Sn(1)–C(15)	2.128(4)
Ag(1)–P(1)	2.4979(12)	Sn(1)–S(3)	2.4215(10)
Ag(1)–S(1)	2.6728(11)	Sn(1)–S(1)	2.5513(11)
Bond angles			
P(3)–Ag(1)–P(2)	119.38(4)	C(6)–S(1)–Ag(1)	104.97(12)
P(3)–Ag(1)–P(1)	118.14(4)	Sn(1)–S(1)–Ag(1)	109.51(4)
P(2)–Ag(1)–P(1)	109.64(4)	C(7)–S(3)–Sn(1)	100.15(13)
P(3)–Ag(1)–S(1)	121.26(4)	C(1)–P(1)–Ag(1)	109.65(14)
P(2)–Ag(1)–S(1)	100.99(4)	C(31)–P(1)–Ag(1)	108.59(13)
P(1)–Ag(1)–S(1)	80.21(4)	C(21)–P(1)–Ag(1)	123.53(13)
C(14)–Sn(2)–C(15)	125.84(18)	C(13)–P(2)–Ag(1)	110.47(13)
C(14)–Sn(1)–S(3)	111.23(13)	C(71)–P(2)–Ag(1)	117.49(13)
C(15)–Sn(1)–S(3)	116.57(12)	C(61)–P(2)–Ag(1)	114.19(13)
C(14)–Sn(1)–S(1)	99.53(13)	C(12)–P(3)–Ag(1)	111.50(12)
C(15)–Sn(1)–S(1)	100.92(13)	C(41)–P(3)–Ag(1)	123.54(13)
S(3)–Sn(1)–S(1)	94.15(4)	C(51)–P(3)–Ag(1)	108.11(13)
C(6)–S(1)–Sn(1)	99.70(12)		

In a recent paper [9] we described the synthesis of tin (IV) complexes with phosphinethiolate ligands with the general formula $[\text{SnR}_2(\text{SC}_6\text{H}_4\text{PPh}_2)_2]$ as well as their reactivity towards gold (I) and silver (I) derivatives, mainly with the former. With continued interest in the formation of heteronuclear tin–silver complexes, we report the reaction between $[\text{Ag}(\text{CF}_3\text{SO}_3)(\text{PR}_3)]$ ($\text{PR}_3 = \text{PPh}_3$ and PPh_2Me) and $[\text{SnR}_2(\text{SC}_6\text{H}_4\text{PPh}_2)_2]$. In addition, we have prepared similar tin derivatives with the phosphine $\text{PPh}(\text{C}_6\text{H}_4\text{SH})_2$, $[\text{SnR}_2\{\text{SC}_6\text{H}_4\text{PPh}\}]$, and performed the subsequent formation of the heterometallic complexes. The X-ray structure of $[\text{AgSn}(\mu\text{-SC}_6\text{H}_4\text{PPh}_2)_2\text{Me}_2(\text{PPh}_2\text{Me})]\text{CF}_3\text{SO}_3$ confirms the heteronuclear nature of these complexes and the role of phosphinothiolate as bridging ligand.

2. Results and discussion

The reaction of $[\text{SnR}_2(\text{SC}_6\text{H}_4\text{PPh}_2)_2]$ ($\text{R} = \text{Me}$ and Ph) with $[\text{AgCF}_3\text{SO}_3(\text{PR}_3)]$ ($\text{PR}_3 = \text{PPh}_3$ and PPh_2Me) affords complexes **1–4** with the general formula $[\text{AgSn}(\mu\text{-SC}_6\text{H}_4\text{PPh}_2)_2\text{R}_2(\text{PR}_3)]\text{CF}_3\text{SO}_3$ ($\text{R} = \text{Me}$, $\text{PR}_3 = \text{PPh}_3$ (**1**); PPh_2Me (**2**); $\text{R} = \text{Ph}$, $\text{PR}_3 = \text{PPh}_3$ (**3**); PPh_2Me (**4**)) in good yields as a result of the co-ordination of $[\text{AgPR}_3]^+$ units to the starting material (Scheme 1, i, ii).

The $^1\text{H-NMR}$ spectra at room temperature of methyl compounds **1–2** show, among other resonances, a singlet for methyl protons. At -80°C each singlet splits into two singlets flanked by the tin satellites, displaced up- and downfield respectively from the starting tin derivatives. The presence of two methyl resonances suggests that the two Me groups are inequivalents at

low temperature. This difference can be attributed to an unsymmetrical co-ordination of the silver centre. The $^{31}\text{P}\{^1\text{H}\}\text{-NMR}$ spectra (-80°C) of compounds **1–4** show two AM_2X system. A and M are the phosphorus atoms and X is the ^{107}Ag nucleus (51.8% isotopic abundance), in one case, and the ^{109}Ag nucleus (48.2% isotopes abundance) in the other. Thus, a doublet of doublets of doublets is observed for the M_2 part (PPh_2 groups of the phosphinethiolate) and a doublet of doublets of triplets for A part (PR_3 ligand co-ordinated to the silver atom). It is noticeable that the relative position of the signals is interchanged for the PPh_2Me complexes, because of the more basic behaviour of such ligand. Table 1 shows the $^{31}\text{P}\text{-}^{109}\text{Ag}$ and $^{31}\text{P}\text{-}^{107}\text{Ag}$ coupling values for complexes **1–4**. The $^{13}\text{C-NMR}$ spectra at room temperature of **1** and **2** show only one signal in the region of the methyl groups at δ 4.6 and 4.1 ppm, respectively. In **2** the methyl group of the monodentate phosphine is also observed and centred at 12.4 ppm as a doublet ($J_{\text{P-C}} = 8$ Hz). The $^{119}\text{Sn-NMR}$ spectra at -40°C show a doublet at about -93 ppm for derivatives **1, 2** with a small Sn–P coupling constant of ca. 50 Hz. In the case of the phenyl tin complexes **3, 4** the signals are upfield displaced and appear as broad singlets.

The acetone solutions of complexes **1–4** show a 1:1 electrolyte behaviour [10]. The IR spectra show bands in the region of 1270, 1225 and 1160 cm^{-1} which are characteristic of an ionic triflate [11]. The complexes do not show the molecular peak in the LSIMS⁺ mass spectra. Instead, the peak corresponding to the loss of the monodentate phosphine is present in all cases with the appropriate isotope distribution pattern: m/z (%) = 843 (70) ($[\text{AgSn}(\text{SC}_6\text{H}_4\text{PPh}_2)_2\text{Me}_2]^+$) and 967 (54) ($[\text{AgSn}(\text{SC}_6\text{H}_4\text{PPh}_2)_2\text{Ph}_2]^+$).

The molecular structure of complex $[\text{AgSn}(\mu\text{-SC}_6\text{H}_4\text{PPh}_2)_2\text{Me}_2(\text{PPh}_2\text{Me})]\text{CF}_3\text{SO}_3$ (**2**) has been established by X-ray diffraction of its dichloromethane solvate and the cation is shown in Fig. 1. Selected bond lengths and angles are given in Table 1.

The structure consists of two phosphinothiolate ligands co-ordinated to the Sn center through the S atom. An additional Ag– PPh_2Me unit is bonded to two PPh_2 groups and to one S end of the phosphinothiolate ligands. The tin(IV) is bonded to the sulphur atoms of the P,S-donor ligand with distances Sn–S(3) = 2.4215(10) Å, similar to those found in complex $[\text{Au}_2\text{Sn}(\mu\text{-S}_2\text{C}_6\text{H}_4\text{PPh}_2)_2(\text{C}_6\text{F}_5)_2\text{Bu}_2]$ [9] and Sn–S(1) = 2.5513(11) Å. The latter is slightly longer as a consequence of the additional co-ordination of S(1) to the silver atom. Sn(IV) shows a distorted tetrahedral geometry with angles C(14)–Sn–C(15) = 125.84(18), S(3)–Sn–C(15) = 116.57(12), S(1)–Sn–S(3) = 94.15(4) and S(1)–Sn–C(14) = 99.53(13)°. The $\text{SnMe}_2\text{-}(\text{S}_2\text{C}_6\text{H}_4\text{PPh}_2)$ unit acts as a P,P,S-donor ligand for the Ag– PPh_2Me fragment through both P atoms and

one of the S atom, giving again a distorted tetrahedral arrangement around the silver atom with angles P(2)–Ag–P(3) = 119.38(4), P(1)–Ag–P(2) = 109.64(4), S(1)–Ag–P(3) = 121.26(4) and P(1)–Ag–S(1) = 80.21(4)°. The Ag–P and Ag–S distances Ag–P(1) = 2.4979(12), Ag–P(2) = 2.4673(19), Ag–P(3) = 2.4377(11) and Ag–S = 2.6728(11) Å are in the range of previously reported compounds [(ⁿBu)₃PAg(SPPPh₂)₃C]; [Ag₂(pz-CS₂)-(PPh₃)₂]; [Ag(PPh₃)₂(pytH)₂]NO₃; [Ag(L)(PPh₃)₂](BF₄)₂, L = 2,5,8,17,20,23 - hexathia[9](1,2)[9](4,5)cyclophane [12].

The synthesis of similar heterometallic Ag–Sn derivatives was performed starting from [SnR₂{(SC₆H₄)₂PPh}] (R = Me, **5** and R = Ph, **6**). The synthesis of the latter is similar to that of [SnR₂(SC₆H₄PPh₂)₂] [9], using the P,S₂-donor ligand PPh(C₆H₄S)₂ and SnCl₂R₂ in a 1:1 molar ratio. Thus, complexes **5** and **6** were isolated as air-stable solids at room temperature when [SnR₂Cl₂] was added to a solution of PPh(C₆H₄SH)₂ in sodium ethoxide (Scheme 1, iii).

The ¹H-NMR spectrum of **5** at room temperature shows two different signals in the methyl region at 0.94 and 0.74 ppm showing the inequivalence of the Me groups. It is not possible to distinguish the inequivalence of the phenyl groups in **6** because these protons appear as multiplets. The ³¹P-NMR spectra of **5** and **6** show a singlet at –32.1 (**5**) and –24.8 ppm (**6**), i.e. highfield displaced from the free phosphine (–19.2 ppm). These signals are flanked by tin satellites, *J*_{Sn–P} = 190 Hz (**5**) and 114 Hz (**6**) and, in accordance with that, the ¹¹⁹Sn-NMR spectra show doublets at –91.1 ppm (**5**) and –155 ppm (**6**). These coupling constant

values are higher than those reported for [SnR₂(SC₆H₄PPh₂)₂] (R = Me and Ph) [9] (*J*_{Sn–P} = 75.7 and 42.3 Hz, respectively) and far smaller than those reported for Sn–P bonds (ca. 1350 Hz) [13]. More illustrative is the ¹³C-NMR spectrum of **5** which shows again two different signals in the methyl region. One of them appears at 8.5 ppm as a singlet and the other as a doublet centred at 3.1 ppm (*J*_{P–C} = 20 Hz), due to an additional coupling with the P atom.

The mass spectra (LSISM⁺, nba as matrix) show the parent peaks in both derivatives with *m/z* (%) = 475 (65) ([SnMe₂(SC₆H₄)₂PPh]⁺) and 597 (15) ([SnPh₂(SC₆H₄)₂PPh]⁺). Other fragmentation peaks corresponding to [M – R]⁺ are also observed at *m/z* (%) = 459 (92) (**5**) and 521 (55) (**6**). These data point to the probable mononuclear nature of **5** and **6**.

The inequivalence of the methyl groups in complex **5**, as shown by ¹³C-NMR and ¹H-NMR point to a pseudo-pentacoordination for [SnMe₂{(SC₆H₄)₂PPh}] (Scheme 1) as suggested for [Sn(Ph)(Cl){(SCH₂–CH₂)₂EPh}] (R = Me and Ph; E = P, O, S) [14]. The values of ²*J*(Sn–C) and ²*J*(Sn–H) have been used as confirmation of trigonal-bipyramidal structure and apical or equatorial disposition of the methyl groups in several complexes ([RR'Sn(CH₂CH₂CH₂)₂E] (E = NME, O, S and R, R' = halogen, alkyl or aryl)) [15]. In our case, we do not have the values of ¹*J*(Sn–C) because of the poor solubility of complex **5** and the ²*J*(Sn–H) values are not very different (60 and 63 Hz, respectively). Only the ²*J*(P–C) coupling constant with one of the methyl groups and the ²*J*(Sn–P) are the evidence of the contact between the tin and the phosphorus centres. Therefore, the structure of **5** and **6** should be among a tetrahedral disposition with a SnC₂S₂ core and the trigonal-bipyramidal structure with a P–Sn contact shown in Scheme 1.

In order to obtain the corresponding heterometallic Sn–Ag derivatives, we carried out the reaction starting from either **5** or **6** and [AgCF₃SO₃(PR₃)] (PR₃ = PPh₃ and PPh₂Me) as described above for the synthesis of complexes **1–4**. In this case the reaction led a mixture of products that could not be separated, but [AgSn{μ-(SC₆H₄)₂PPh}R₂]CF₃SO₃ complexes were identified as major products in both cases, as a result of the dissociation of the monodentate phosphine. In order to isolate these products in a pure form, we carried out the same reaction in the presence of [AgCF₃SO₃] without phosphine ligand. Thus, complexes [AgSn{μ-(SC₆H₄)₂PPh}R₂]CF₃SO₃ (R = Me, **7**; R = Ph, **8**) were isolated as colourless air-stable solids (Scheme 1, iv).

The acetone solutions of **7** and **8** show an 1:1 electrolyte behaviour and the IR spectra show the characteristic bands of the triflate as counter ion [11]. Only **7** shows the molecular peak in the LSISM⁺ (nba as matrix) mass spectra with the loss of the anion at *m/z* = 579 (**7**).

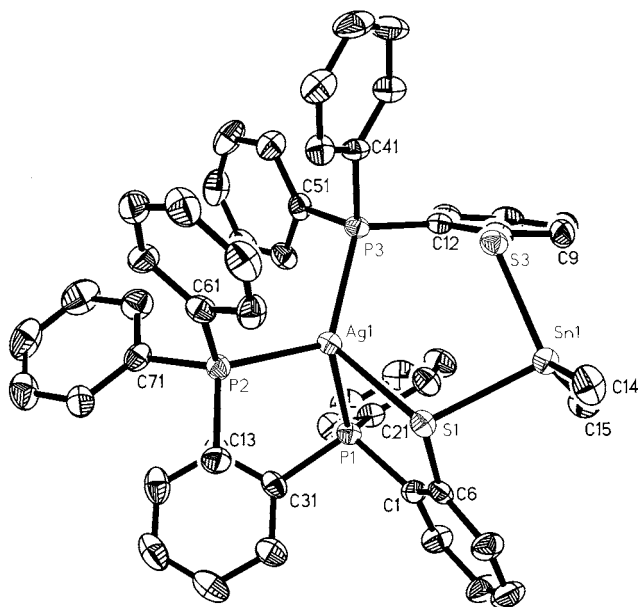


Fig. 1. Cation of compound **2** in the crystal. Displacement parameter ellipsoids represent 50% probability. H atoms are omitted for clarity.

The ^{31}P -NMR spectra of **7** and **8** show a doublet of doublets at negative displacements, as a consequence of a coupling of the phosphorus atom with either ^{109}Ag or ^{107}Ag of the two isotopomers. The ^1H -NMR spectrum of **7** shows two different broad singlets corresponding to Me groups and its ^{13}C -NMR spectrum shows two singlets in the methyl region. Both data point to the inequivalence of methyl groups. The ^{119}Sn -NMR spectra at -40°C show broad singlets in both cases at 131.7 ppm (**7**) and -8.1 ppm (**8**), as a consequence of the proximity of the silver atom, as occurred in ^1H -NMR. We were not able to grow crystals for X-ray studies but a structure similar to that reported for complex **2**, with an extra Ag–S bond in place of the PPh_2Me ligand, should be predictable.

3. Conclusion

In conclusion we describe some heteronuclear Sn–Ag complexes with the phosphino–thiolate ligands $\text{SC}_6\text{H}_4\text{PPh}_2$ and $(\text{SC}_6\text{H}_4)_2\text{PPh}$. Although the coordination of the ligands in the starting tin derivatives $[\text{SnR}_2(\text{SC}_6\text{H}_4\text{PPh}_2)_2]$ and $[\text{SnR}_2\{(\text{SC}_6\text{H}_4)_2\text{PPh}\}]$ ($\text{R} = \text{Me}$ and Ph) are mainly through the sulphur atoms, the formation of heteronuclear complexes involves the coordination of the phosphorus atoms to the silver centre. In addition, the silver centre is bonded to some of the thiolate end of the ligands; therefore, the X-ray structure of $[\text{AgSn}(\mu\text{-SC}_6\text{H}_4\text{PPh}_2)_2\text{Me}_2(\text{PPh}_2\text{Me})]\text{CF}_3\text{SO}_3\cdot\text{CH}_2\text{Cl}_2$ shows two different co-ordination modes of the bridging ligand.

4. Experimental

4.1. General procedures

IR spectra were recorded on a Perkin Elmer 883 spectrophotometer, over the range $4000\text{--}200\text{ cm}^{-1}$, by using Nujol mulls between polyethylene sheets. ^1H - and ^{31}P -NMR spectra were recorded on a Varian UNITY 300 or BRUKER 300 in CDCl_3 or CD_2Cl_2 solutions; chemical shifts are quoted relative to SiMe_4 (^1H) and H_3PO_4 (external ^{31}P). The C, H, N and S analyses were performed with a Perkin–Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec, by liquid secondary ion mass spectrometry (LSIMS +) using nitrobenzylalcohol as matrix and a caesium gun. $[\text{Ag}(\text{CF}_3\text{SO}_3)]$ and $[\text{Ag}(\text{CF}_3\text{SO}_3)(\text{PR}_3)]$ were prepared by established procedures [16]. All other reagents were used as supplied. The syntheses of $\text{Ph}_2\text{P}(\text{C}_6\text{H}_4\text{SH})$ and $\text{PhP}(\text{C}_6\text{H}_4\text{SH})_2$ were carried out using the standard literature method [17].

4.2. Synthesis

4.2.1. Synthesis of $[\text{AgSnR}_2(\text{SC}_6\text{H}_4\text{PPh}_2)_2(\text{L})]\text{TfO}$ ($\text{R} = \text{Me}$, $\text{L} = \text{PPh}_3$ (**1**); $\text{L} = \text{PPh}_2\text{Me}$ (**2**); $\text{R} = \text{Ph}$, $\text{L} = \text{PPh}_3$ (**3**); $\text{L} = \text{PPh}_2\text{Me}$ (**4**))

To a solution of $[\text{SnR}_2(\text{SC}_6\text{H}_4\text{PPh}_2)_2]$ ($\text{R} = \text{Me}$, 0.110 g, 0.15 mmol; $\text{R} = \text{Ph}$, 0.129 g, 0.15 mmol) in dichloromethane (20 ml) was added $[\text{Ag}(\text{CF}_3\text{SO}_3)(\text{PR}_3)]$ ($\text{PR}_3 = \text{PPh}_3$, 0.078 g, 0.15 mmol; $\text{PR}_3 = \text{PPh}_2\text{Me}$, 0.068 g, 0.15 mmol). After 4 h the solutions were concentrated in vacuum to 5 ml and the addition of diethyl ether (30 ml) led to the precipitation of the new complexes as colourless solids, which were filtered off, washed with ether and dried in vacuum. Yield (%): **7** (**1**), **80** (**2**), **60** (**3**), **70** (**4**). ^1H -NMR: **1** ($(\text{CD}_3)_2\text{CO}$, -80°C) δ 7.80–6.86 (m, 43H, Ph), 0.95 (s, 3H, $J_{\text{Sn-H}} = 55$ Hz, Me), 0.36 (s, 3H, $J_{\text{Sn-H}} = 70$ Hz, Me); **2** ($(\text{CD}_3)_2\text{CO}$, -90°C) δ 7.85–7.05 (m, 38H, Ph), 1.15 (s, br, 3H, Me), 1.08 (s, 3H, $J_{\text{Sn-H}} = 63$ Hz, Me), 0.15 (s, 3H, Me); **3** (CD_2Cl_2 , -90°C) δ 7.59–6.59 (m, Ph); **4** (CD_2Cl_2 , -90°C): δ 7.61–7.57 (m, 48H, Ph), 1.07 (s, 3H, $J_{\text{P-H}} = 15$ Hz, Me). ^{119}Sn -NMR (CDCl_3 , -40°C): **1**: δ -93.3 (d, $J_{\text{Sn-P}} = 52$ Hz); **2**: δ -93.36 (d, $J_{\text{Sn-P}} = 51$ Hz); **3**: δ -4.2 (s, br); **4**: δ 3.3 (s, br). ^{13}C -NMR (CDCl_3): **1**: δ 137.4–127.1 (m, Ph), 4.6 (s, br); **2**: 137.4–127.3 (m, Ph), 12.4 (d, $J_{\text{C-P}} = 8$ Hz), 4.1 (s, br). MS: m/z (rel.%): **1** 843 (71), 443 (50); **2** 843 (70); **3** 967 (54); **4** 967 (35). A_M ($\Omega^{-1}\text{ cm}^2\text{ mol}^{-1}$): 106 (**1**), 99 (**2**), 103 (**3**), 94 (**4**). Anal. Calc. for $\text{C}_{57}\text{H}_{49}\text{O}_3\text{P}_3\text{S}_3\text{F}_3\text{SnAg}$: C, 54.58; H, 3.91; S, 7.65. Found for **1**: C, 54.09; H, 3.62; S, 7.50%. Anal. Calc. for $\text{C}_{52}\text{H}_{47}\text{O}_3\text{P}_3\text{S}_3\text{F}_3\text{SnAg}$: C, 52.38; H, 3.95; S, 8.05. Found for **2**: C, 51.82; H, 3.71; S, 7.85%. Anal. Calc. for $\text{C}_{67}\text{H}_{53}\text{O}_3\text{P}_3\text{S}_3\text{F}_3\text{SnAg}$: C, 58.37; H, 3.84; S, 6.98. Found for **3**: C, 57.75; H, 3.60; S, 6.85%. Anal. Calc. for $\text{C}_{62}\text{H}_{51}\text{O}_3\text{P}_3\text{S}_3\text{F}_3\text{SnAg}$: C, 56.36; H, 3.87; S, 7.30. Found for **4**: C, 55.91; H, 3.62; S, 7.01%.

4.2.2. Synthesis of $[\text{SnR}_2(\text{SC}_6\text{H}_4)_2\text{PPh}]$ ($\text{R} = \text{Me}$ (**5**); $\text{R} = \text{Ph}$ (**6**))

To a suspension of $\text{PPh}(\text{C}_6\text{H}_4\text{SH})_2$ (0.049 g, 0.15 mmol) in EtOH (10 ml) was added a NaOEt (3 ml, 0.1 M). After 15 min of stirring SnCl_2R_2 ($\text{R} = \text{Me}$, 0.030 g; $\text{R} = \text{Ph}$, 0.052 g, 0.15 mmol) was added. Colourless solids appeared immediately. After 4 h of stirring the solids were filtered off, washed with ethanol and dried in vacuum. Yield (%): **92** (**5**), **70** (**6**). ^1H -NMR (CDCl_3): **5**: δ 7.65(m, 2H), 7.06(m, 2H), 7.41–6.21 (m, 9H, Ph), 0.94 (s, 3H, $J_{\text{Sn-H}} = 60$ Hz, Me), 0.74 (s, 3H, $J_{\text{Sn-H}} = 63$ Hz, Me); **6**: δ 7.79–7.05 (m, Ph). ^{31}P -NMR(CDCl_3): **5**: δ -32.2 (s); **6**: δ -24.8 (s). ^{119}Sn -NMR (CDCl_3 , -40°C): **5**: δ -91.1 (d, $J_{\text{Sn-P}} = 190$ Hz); **6**: δ -155.5 (d, $J_{\text{Sn-P}} = 114$ Hz). ^{13}C -NMR (CDCl_3): **5**: δ 133.3–124.4 (m, Ph), 8.5 (s), 3.1 (d, $J_{\text{C-P}} = 20$ Hz). MS: m/z (rel.%): **5** 459 (91), 475(60, $[\text{M}^+]$); **6** 521 (100), 599 (25, $[\text{M}^+]$). Anal. Calc. for $\text{C}_{20}\text{H}_{19}\text{PS}_2\text{Sn}$: C, 51.09; H, 4.05;

S, 13.63. Found for **5**: C, 50.6; H, 3.71; S, 12.5%. Anal. Calc. for $C_{30}H_{23}PS_2Sn$: C, 60.32; H, 3.88; S, 10.73. Found for **6**: C, 59.8; H, 3.41; S, 10.6%.

4.2.3. Synthesis of $[AgSnR_2(SC_6H_4)_2PPh]CF_3SO_3$ ($R = Me$ (**7**); $R = Ph$ (**8**))

To a solution of $SnR_2(SC_6H_4)_2PPh$ ($R = Me$, 0.071 g, 0.15 mmol; $R = Ph$, 0.091 g, 0.15 mmol) in dichloromethane (20 ml) was added $[AgCF_3SO_3]$ (0.038 g, 0.15 mmol) or $[Ag(CF_3SO_3)(PR_3)]$ ($PR_3 = PPh_3$, 0.078 g, 0.15 mmol; $PR_3 = PPh_2Me$, 0.068 g, 0.15 mmol). After 4 h the solutions were concentrated to 5 ml and the addition of hexane (30 ml) led the precipitation of the new complexes as colourless solids, which were filtered off, washed with hexane and dried in vacuum. Yield (%): 75 (**7**), 70 (**8**), 1H -NMR ($CDCl_3$): **7**: δ 7.63(m, 2H), 7.46–6.21 (m, 9H, Ph), 6.93(m, 2H), 1.09 (s, br, 3H, Me), 0.21 (s, br, 3H, Me); **8**: δ 7.75–6.78 (m, Ph). ^{31}P -NMR ($CDCl_3$): **7**: δ -4.4 (dd, $J_{107Ag-p} = 418$ Hz, $J_{109Ag-p} = 483$ Hz); **8**: δ -3.4 (dd, $J_{107Ag-p} = 448$ Hz, $J_{109Ag-p} = 508$ Hz). ^{119}Sn -NMR ($CDCl_3$, -40°C): **7**: δ 131.7 (s, br); **8**: δ -8.1 (s, br). ^{13}C -NMR ($CDCl_3$): **7**: δ 137.8–122.7 (m, Ph), 1.7 (s, Me), 1 (s, Me). MS: m/z (rel.%): **7** 459 (65), 475(25, $[M^+]$) 579 (25, $[M^+]$), 431 (30). Anal. Calc. for $C_{21}H_{19}O_3PS_3F_3SnAg$: C, 34.54; H, 2.62; S, 13.17. Found for **7**: C, 33.9; H, 2.3; S, 12.6%. Anal. Calc. for $C_{31}H_{23}O_3PS_3F_3SnAg$: C, 43.58; H, 2.71; S, 11.25. Found for **8**: C, 44.2; H, 2.8; S, 10.6%.

4.3. Crystal structure determination of compound **2**

Single crystal were grown by diffusing hexane into a dichloromethane solution of complex $[AgSn(PPh_2Me)_2Me_2(SC_6H_4PPh_2)_2]CF_3SO_3$ (**2**) and mounted in inert oil.

4.3.1. Crystal data and data collection parameters

$C_{55}H_{55}AgCl_2F_3O_3P_3S_3Sn$ (**2**), $M = 1283.52$, Monoclinic, $a = 18.95(4)$, $b = 10.124(2)$, $c = 28.558(6)$ Å, $\beta = 99.70(3)^\circ$. $V = 5401.7(19)$ Å³, $T = 150$ K, space group $P2_1/c$, graphite monochromated Mo-K α radiation, $\lambda = 0.71069$ Å, $Z = 4$, $D_{calc} = 1.578$ mg m⁻³, $F(000) = 2592$, colourless prism with dimensions $0.15 \times 0.1 \times 0.1$ mm³, $\mu = 1.181$ mm⁻¹; Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator, following procedures described previously [18], θ range for data collection 2.14 – 25.99° , $-23 \leq h \leq 23$, $-12 \leq k \leq 12$, $-35 \leq l \leq 35$; 38272 reflections collected, 10471 independent ($R_{int} = 0.0684$).

4.3.2. Structure solution and refinement

The structure was solved by direct methods (SHELXS-97) [19] and refined by full-matrix least-squares on F^2 , using the program SHELXL-97 [20]. All data were corrected using the program SORTAV [21]. The non-hydro-

gen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in idealised positions. Refinement proceeded to $R = 0.041$ $wR = 0.1095$ for 625 parameters, and $R = 0.0622$ $wR = 0.1248$ for all data. In the final Fourier synthesis the electron density fluctuates in the range 0.789 and -0.893 e Å⁻³.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 149862. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1233-336033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

Acknowledgements

The Spanish authors thank the Dirección General de Enseñanza Superior (PB98-0542) for financial support and M.B.H. thanks the Engineering and Physical Sciences Research Committee for support of the X-ray facilities.

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