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Synthesis of dithiolate gold(III) complexes by dithiolate transfer reactions. X-ray structure of $[Au(C_6F_5)(S_2C_6H_4)(PPh_3)]$

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Abstract

The reaction of ethanolic solutions of $Na_2(S{-}S)$ $\{S{-}S = 1,2\text{-}S_2C_6H_4$ or $3,4\text{-}S_2C_6H_3(CH_3)\}$ with $[Sn(CH_3)_2Cl_2]$ or $(PPN)_2[ZnCl_4]$ gives $[Sn(CH_3)_2(S{-}S)]$ and $(PPN)_2[Zn(S{-}S)_2]$, respectively. The tin derivative with 1,3-dithiol-2-thione-4,5-dithiolate (dmit), $[Sn(CH_3)_2(dmit)]$, is obtained by reaction of $[Sn(CH_3)_2Cl_2]$ with $(NEt_4)_2[Zn(dmit)_2]$. The tin and zinc complexes further react with the gold(III) derivatives *cis*-$[Au(C_6F_5)Cl_2L]$ giving rise to dithiolate gold(III) complexes $[Au(C_6F_5)(S{-}S)L]$. The structure of $[Au(C_6F_5)(S_2C_6H_4)(PPh_3)]$ has been established by an X-ray diffraction study, and shows a square-planar coordination of the gold with the dithiolate chelating.

Keywords: Gold; Tin; Zinc; Dithiolate complexes; Synthesis; X-ray structure

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1. Introduction

There has been a resurgence of interest in metal thiolate chemistry, because of the occurrence of metal–thiolate complexes in biological systems [1–3] and their important applications in fields such as fungicides [3,4], electrical conductors [5,6] and inorganic pharmaceuticals, [4,7–9] and several reviews on the subject have been published [1–3,10,11].

One of the major routes to metal dithiolate complexes involves the nucleophilic displacement of metal-bond halide groups by dithiolate and a range of complexes have been prepared in this way. With gold(III) complexes, this leads to homoleptic anions, and a great variety of them has been prepared $[Au(S{-}S)_2]^-$ $\{S{-}S^{2-} = S(CN)C{=}C(CN)S$ (maleonitriledithiolate) [12]; $S_2C{=}C(CN)_2$ (isomaleonitriledithiolate) [13]; $1,2\text{-}S_2C_6H_4$ (1,2-benzenedithiolate) [14]; $3,4\text{-}S_2C_6H_3CH_3$ (dimercaptotoluene) [15–18]; C_3S_5 (1,3-dithiol-2-thione-4,5-dithiolate) [19]; $C_4H_4S_4$ (5,6-dihidro-1,4-ditiino-2,3-dithiolate) [20]$\}$.

Heteroleptic dithiolate gold(III) complexes are far less well known, and $[Au(mnt)(S_2CNR_2)]$ [12,21] (mnt = maleonitriledithiolate), $[Au_2(\mu_2\text{-}CH_2PPh_2CH_2)_2(S_2C_6H_4)_2]$ [22] have been obtained by nucleophilic displacement of halide or benzoate group by dithiolate.

More promising is the use of other metal complexes, such as tin derivatives [23,24], as thiolate transfer groups. Using this idea, Vicente et al. [25] obtained a number of gold(III) complexes, $Q[Au(mnt)X_2]$ (X = Br, Cl, $Q = NMe_4$), $[Au(mnt)ClL]$ (L = tetrahydrothiophene, PPh_3 or py) and $[Au(mnt)(L{-}L)][Au(mnt)Cl_2]$ (L–L = bipy or phen), using $[Sn(CH_3)_2(mnt)]$. It has been shown recently that zinc derivatives such as $(NR_4)_2[Zn(dmit)_2]$ (dmit = 1,3-dithiol-2-thione-4,5-dithiolate) can transfer the dithiolate group to other metal derivatives, including gold(I) complexes [26,27].

In this paper we show how the tin and zinc complexes, $[SnMe_2(S{-}S)]$ or $(NR_4)_2[Zn(S{-}S)_2]$, can transfer the dithiolate group S–S under very mild conditions to gold(III) derivatives. The transfer properties of zinc complexes are particularly interesting because the displacement of Zn(II) from metallothionein containing zinc plays an important role in the metabolism of gold drugs and the cytotoxicity of some gold complexes as anticancer agents [28]. We describe the preparation of

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several complexes $[Au(C_6F_5)(S{-}S)L]$ $\{S{-}S = 1,2\text{-}S_2C_6H_4$, $3,4\text{-}S_2C_6H_3CH_3$ or C_3S_5 (dmit)$\}$; L = $AsPh_3$, PPh_3 or PPh_2Me). The X-ray structure of $[Au(C_6F_5)(S_2C_6H_4)(PPh_3)]$ shows a square-planar coordination of gold, and the benzenedithiolate acting as a bidentate chelate ligand.

2. Results and discussion

The addition of ethanolic or methanolic solutions of $Na_2(S{-}S)$ $\{S{-}S = 1,2\text{-}S_2C_6H_4$, $3,4\text{-}S_2C_6H_3CH_3$ or C_3S_5 (dmit)$\}$ to *cis*-$[Au(C_6F_5)Cl_2L]$ (L = PPh_3, PPh_2Me, or $AsPh_3$) gives red or green solutions from which no pure compound can be crystallized. As the direct synthesis failed, we tried to prepare complexes with other metals in order to transfer these groups to a gold. We chose tin derivatives initially because it has been shown that they can easily transfer maleonitriledithiolate to gold(I) or gold(III) [25].

Tin complexes can be obtained by addition of a water solution of $[Sn(CH_3)_2Cl_2]$ to a freshly prepared ethanolic solution of $Na_2(S{-}S)$ ($S{-}S = 1,2\text{-}S_2C_6H_4$ or $3,4\text{-}S_2C_6H_3CH_3$) (Eq. 1). The same reaction with $C_3S_5^{2-}$ gives oily products.

$$[Sn(CH_3)_2Cl_2] + Na_2(S{-}S) \longrightarrow [Sn(CH_3)_2(S{-}S)] + 2NaCl \qquad (1)$$

$S{-}S = 1,2\text{-}S_2C_6H_4$ (**1a**), $3,4\text{-}S_2C_6H_3CH_3$ (**1b**)

The dmit analogue $[Sn(CH_3)_2(dmit)]$ can be achieved by the reaction of $[Sn(CH_3)_2Cl_2]$ with the zinc derivative $(NEt_4)_2[Zn(dmit)_2]$ (Eq. 2). The zinc compound is a dmit transfer agent as we recently showed in gold(I) chemistry [26]. The tin and the zinc complexes can be separated easily because of their different solubilities in diethyl ether.

$$2[Sn(CH_3)_2Cl_2] + (NEt_4)_2[Zn(dmit)_2] \rightarrow 2[Sn(CH_3)_2(dmit)](\mathbf{1c}) + (NEt_4)_2[ZnCl_4] \qquad (2)$$

Complexes **1a** and **1b** are white, and **1c** is orange. They are all solids, stable to air and moisture at room temperature. They are soluble in common organic solvents. Their C, H and S analyses and conductivities (see Table 1) confirm the nature of these compounds. Their ^1H NMR spectra show a singlet for methyl

Table 1
Analytical data for the complexes

Complex	Analysis (%) [a]				Λ_M [b]	mp [c]	m/z [e] $[M^+]$
	C	H	N	S			
1a $[Sn(CH_3)_2(1,2\text{-}S_2C_6H_4)]$	33.75	3.4	–	22.35	1	132	290(100)
	(33.25)	(3.5)	–	(22.2)			
1b $[Sn(CH_3)_2(3,4\text{-}S_2C_6H_3CH_3)]$	35.75	3.85	–	20.65	1	132	304(100)
	(35.65)	(4.0)	–	(21.15)			
1c $[Sn(CH_3)_2(dmit)]$	18.05	1.85	–	46.0	19	200 [d]	346(34)
	(17.4)	(1.75)	–	(46.45)			
2a $(PPN)_2[Zn(1,2\text{-}S_2C_6H_4)_2]$	70.6	4.65	1.9	8.55	181	208	–
	(70.9)	(4.8)	(1.95)	(9.0)			
2b $(PPN)_2[Zn(3,4\text{-}S_2C_6H_3CH_3)_2]$	70.8	4.75	1.75	8.25	204	85	–
	(71.2)	(5.0)	(1.95)	(8.85)			
3a $[Au(C_6F_5)(1,2\text{-}S_2C_6H_4)(PPh_3)]$	46.7	2.55	–	8.4	5	222	766(100)
	(47.0)	(2.7)	–	(8.35)			
3b $[Au(C_6F_5)(3,4\text{-}S_2C_6H_3CH_3)(PPh_3)]$	47.55	2.7	–	8.25	9	108	780(100)
	(47.7)	(2.7)	–	(8.2)			
3c $[Au(C_6F_5)(dmit)(PPh_3)]$	38.95	1.9	–	18.85	10	195	823(100)
	(39.4)	(1.85)	–	(19.5)			
4a $[Au(C_6F_5)(1,2\text{-}S_2C_6H_4)(PPh_2Me)]$	42.7	2.45	–	9.6	3	76 [d]	704(100)
	(42.6)	(2.45)	–	(9.1)			
4b $[Au(C_6F_5)(3,4\text{-}S_2C_6H_3CH_3)(PPh_2Me)]$	42.7	2.55	–	8.45	8	80 [d]	718(72)
	(43.45)	(2.65)	–	(8.95)			
4c $[Au(C_6F_5)(dmit)(PPh_2Me)]$	34.75	1.8	–	21.1	1	135 [d]	761(70)
	(34.75)	(1.7)	–	(21.1)			
5a $[Au(C_6F_5)(1,2\text{-}S_2C_6H_4)(AsPh_3)]$	44.25	2.4	–	7.55	6	218	810(100)
	(44.45)	(2.35)	–	(8.05)			
5b $[Au(C_6F_5)(3,4\text{-}S_2C_6H_3CH_3)(AsPh_3)]$	45.15	2.7	–	7.75	6	151 [d]	824(100)
	(45.15)	(2.55)	–	(7.8)			
5c $[Au(C_6F_5)(dmit)(AsPh_3)]$	37.1	1.7	–	18.65	22	190 [d]	867(100)
	(37.4)	(1.75)	–	(18.5)			

[a] Calculated values are given in parentheses. [b] In acetone, values in Ω^{-1} cm^2 mol^{-1}. [c] Melting point,°C. [d] Decomposed without melting. [e] Intensities in %.

groups bonded to tin flanked by two pairs of satellites because of the two active tin isotopes. Besides the phenyl protons (see Experimental details), **1b** shows a resonance for the methyl group. The FAB mass spectra show the parent peak as the base peak in complexes **1a** and **1b**; complex **1c** shows a weaker parent peak.

The dithiolate zinc complexes can be obtained by direct synthesis with ethanolic $Na_2(S{-}S)$ solutions and $(PPN)_2[ZnCl_4]$ (Eq. 3)

$$(PPN)_2[ZnCl_4] + 2\ Na_2(S{-}S) \longrightarrow (PPN)_2[Zn(S{-}S)_2] + 4\ NaCl \qquad (3)$$

$S{-}S = 1{,}2\text{-}S_2C_6H_4$ (**2a**), $3{,}4\text{-}S_2C_6H_3CH_3$ (**2b**)

Complexes **2a** and **2b** are yellow solids, stable to air and moisture at room temperature. They show conductivities of ca. 200 Ω^{-1} cm^2 mol^{-1}, characteristic of 1:2 electrolytes, consistent with their formulation.

The tin and zinc complexes **1a**–**1c**, **2a** and **2b** are suitable reagents for transferring dithiolate to gold(III) under very mild conditions (Eqs. 4 and 5)

$$cis\text{-}[Au(C_6F_5)Cl_2L] + [Sn(CH_3)_2(S{-}S)] \longrightarrow [Au(C_6F_5)(S{-}S)L] + [Sn(CH_3)_2Cl_2] \qquad (4)$$

$L = PPh_3$ (**3a**–**3c**), PPh_2Me (**4a**–**4c**), $AsPh_3$ (**5a**–**5c**)

$$cis\text{-}[Au(C_6F_5)Cl_2L] + \underset{Q = NEt_4 \text{ or } PPN}{Q_2[Zn(S{-}S)_2]} \rightarrow [Au(C_6F_5)(S{-}S)L] + Q_2[ZnCl_4] \qquad (5)$$

The dithiolatepentafluorophenyl complexes are red (**3a**, **3b**), pink (**4a**, **4b**), green (**3c**), garnet (**4c**, **5a**, **5b**) or brown (**5c**) solids, stable to air and moisture at room temperature. They are soluble in common organic solvents and are non-conducting in acetone. Their ^{19}F, ^{31}P and ^{1}H NMR spectra (see Experimental details) are consistent with the proposed formulation, showing three different sorts of signals in the ^{19}F NMR spectra characteristic of only one C_6F_5 group bonded to gold(III). Complexes **3** and **4** show only one singlet in the ^{31}P NMR spectrum assignable to only one type of phosphorus. The ^{1}H NMR spectra are more complicated, but in accordance with the expected multiplicities and intensities ratio (see Experimental details). Their mass spectra show the parent peak as the base peaks, with the exception of complexes **4b** and **4c**, which show weaker parent peaks (approximately 70%)

The structure of complex **3a** has been determinated 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. The gold exhibits a very regular square-planar geometry with angles S(1)–Au–S(2) 89.9(1)°, S(1)–Au–P 90.6(1)°, S(2)–Au–C(1) 87.0(1)° and P–Au–C(11) 92.5(1)° close to the ideal value. The gold atom lies 0.063 Å out of the plane formed by the four donor atoms. The Au–S bond lengths are Au–S(1) 2.314(1) Å and 2.299(1) Å, the longest being *trans* to the C_6F_5, that reflects a higher *trans* influence of the pentafluorophenyl group compared to PPh_3 [29]. These distances are very similar to those observed in other bis(dithiolate)gold(III) complexes, such as $[Au\{S_2C_2(CN)_2\}_2]^-$ (2.309 Å) [30], $[Au(1{,}2\text{-}S_2C_6H_4)_2]^-$ [15] (2.305 Å) and $[Au(3{,}4\text{-}S_2C_6H_3Me)_2]^-$ [18] [2.287(3) Å and 2.329(4) Å], and shorter than in related gold(I) derivatives: e.g. $[Au_2(1{,}2\text{-}S_2C_6H_4)(PPh_3)_2]$ [2.325(3) Å and 2.316(3) Å] [18].

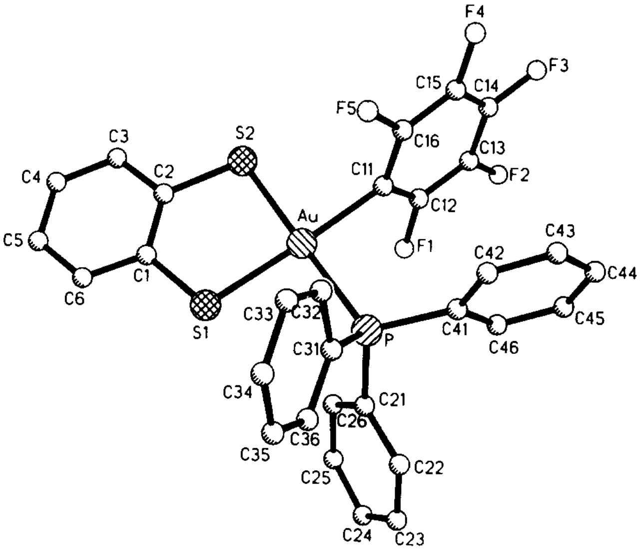

Fig. 1. The molecule of complex **4a** in the crystal, showing the atom numbering scheme. Hydrogen atoms are omitted for clarity atom radii are arbitrary.

The Au–P distance is 2.340(1) Å and, although there are not many data for Au^{III}–P bond lengths, this value lies in between those for $[AuCl_3(PPh_3)]$ [31] [2.335(4) Å] and $[AuMe_3(PPh_3)]$ [32] [2.350(6) Å and 2.347(6) Å, two independent molecules]. The Au–C bond is 2.061(4) Å which is similar to those in the complex $[Au(C_6F_5)_2\{S_2CN(CH_2Ph)_2\}]$ [2.047(6) Å and 2.049(6) Å] [33]. The dithiolate is slightly twisted with respect to the gold atom, the latter being 0.1542 Å out of the plane formed for that ligand.

The arsine in the triphenylarsine complexes can be removed easily by the addition of equimolecular amounts of triphenylphosphine or diphenylmethylphosphine, affording complexes **3** and **4** in a very good yield.

3. Experimental details

The starting materials $[Au(C_6F_5)Cl_2L]$ [34] were prepared as described previously. All others reagents were commercially available.

The C, H, N, 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 Gallenkamp apparatus. The IR spectra were recorded (4000–200 cm^{-1}) on Perkin-Elmer 599 and Perkin-Elmer 3400 spectrophotometers, using Nujol mulls between polyethylene sheets. The NMR spectra were recorded on Varian XL 300 and Bruker ARX 300 spectrometers, in $CDCl_3$. Chemical shifts are cited relative to $SiMe_4$ (external ^1H), 85% H_3PO_4 (external ^{31}P) and $CFCl_3$ (external ^{19}F). Mass spectra were recorded on a VG Autospec, FAB technique, using 3-nitrobenzylalcohol as matrix. The elemental analyses, conductivities, yields and melting point data of the new complexes are listed in Table 1.

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) for the complex **3a**

Atom	x	y	z	U_{eq} [a]
Au	2427(1)	2322(1)	302(1)	19(1)
S(1)	1303(1)	1707(1)	871(1)	27(1)
S(2)	2948(1)	3663(1)	1348(1)	25(1)
P	1918(1)	930(1)	−760(1)	20(1)
C(1)	1458(2)	2727(3)	1717(2)	23(1)
C(2)	2171(2)	3557(4)	1918(2)	22(1)
C(3)	2269(2)	4354(4)	2599(2)	32(1)
C(4)	1667(3)	4312(4)	3054(2)	37(1)
C(5)	972(2)	3485(5)	2858(2)	36(1)
C(6)	869(3)	2690(4)	2198(2)	31(1)
C(11)	3448(2)	2944(4)	−156(2)	24(1)
C(12)	3417(2)	4085(4)	−654(2)	27(1)
C(13)	4097(2)	4574(5)	−950(2)	36(1)
C(14)	4836(2)	3878(5)	−742(2)	35(1)
C(15)	4891(2)	2727(4)	−243(3)	34(1)
C(16)	4198(2)	2277(4)	40(2)	29(1)
F(1)	2701(1)	4771(3)	−887(1)	42(1)
F(2)	4043(2)	5717(3)	−1432(1)	56(1)
F(3)	5503(1)	4361(3)	−1017(1)	52(1)
F(4)	5612(1)	2075(3)	−40(2)	57(1)
F(5)	4281(1)	1138(3)	531(2)	48(1)
C(21)	972(2)	1648(4)	−1265(2)	23(1)
C(22)	584(2)	872(4)	−1891(2)	30(1)
C(23)	−147(2)	1399(5)	−2277(2)	34(1)
C(24)	−479(2)	2699(5)	−2056(2)	35(1)
C(25)	−80(2)	3480(5)	−1467(2)	37(1)
C(26)	648(2)	2961(4)	−1062(2)	29(1)
C(31)	1743(2)	−894(4)	−422(2)	23(1)
C(32)	2377(2)	−1568(4)	48(2)	30(1)
C(33)	2272(3)	−2929(5)	362(2)	37(1)
C(34)	1525(2)	−3631(4)	210(2)	38(1)
C(35)	887(3)	−2962(5)	−235(3)	38(1)
C(36)	983(2)	−1586(4)	−558(2)	30(1)
C(41)	2610(2)	795(4)	−1460(2)	25(1)
C(42)	3230(2)	−253(5)	−1417(2)	35(1)
C(43)	3774(3)	−250(5)	−1928(3)	45(1)
C(44)	3699(2)	762(5)	−2508(2)	43(1)
C(45)	3087(3)	1793(5)	−2563(2)	42(1)
C(46)	2546(2)	1828(5)	−2041(2)	35(1)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3
Selected bond lengths (Å) and angles (°) for complex **3a**

Au–S(1)	2.314(1)	Au–S(2)	2.299(1)
Au–P	2.340(1)	Au–C(11)	2.061(4)
S(1)–C(1)	1.766(4)	S(2)–C(2)	1.756(4)
P–C(21)	1.811(3)	P–C(31)	1.806(4)
P–C(41)	1.820(4)		
S(1)–Au–S(2)	89.9(1)	S(1)–Au–P	90.6(1)
S(2)–Au–P	179.0(1)	S(1)–Au–C(11)	176.9(1)
S(2)–Au–C(11)	87.0(1)	P–Au–C(11)	92.5(1)
Au–S(1)–C(1)	103.0(1)	Au–S(2)–C(2)	103.1(1)
Au–P–C(21)	113.2(1)	Au–P–C(31)	106.4(1)
C(21)–P–C(31)	109.3(2)	Au–P–C(41)	114.2(1)
C(21)–P–C(41)	105.3(2)	C(31)–P–C(41)	108.4(2)
S(1)–C(1)–C(2)	121.1(3)	S(1)–C(1)–C(6)	119.5(3)
S(2)–C(2)–C(3)	118.3(3)	S(2)–C(2)–C(1)	122.6(3)
Au–C(11)–C(12)	120.9(3)	Au–C(11)–C(16)	122.3(3)
P–C(21)–C(22)	118.7(3)	P–C(21)–C(26)	121.4(3)
P–C(31)–C(32)	117.8(3)	P–C(31)–C(36)	122.7(3)
P–C(41)–C(42)	122.6(3)	P–C(41)–C(46)	118.8(3)

*3.1. Synthesis of [Sn(CH$_3$)$_2$(S–S)]: S–S = 1,2-S$_2$C$_6$H$_4$ **1a**, S–S = 3,4-S$_2$C$_6$H$_3$CH$_3$ **1b***

To an ethanolic solutions (5 cm^3) of the dithiol (1 mmol) was added 10 cm^3 of an ethanolic solution of KOH (0.1 M). After 15 min, a water solution (50 cm^3) of $[Sn(CH_3)_2Cl_2]$ (0.220 g, 1 mmol) was added. After stirring for 30 min a white precipitate of complexes were filtered off. **1a** (Yield: 80%) ^1H NMR (in ppm): δ 7.45 (m, 2H, 3,6-$S_2C_6H_4$), 6.90 (m, 2H, 4,5-$S_2C_6H_4$), 1.00 (s, $^2J_{^{117}Sn-H} = 60.3$ Hz, $^2J_{^{119}Sn-H} = 63.4$ Hz, 6H, CH_3) **1b** (Yield: 96%) ^1H NMR: δ 7.32 (d, $^3J_{H5H6} = 8.1$ Hz, 1H, 5-$S_2C_6H_3CH_3$), 7.28 (d, $^4J_{H2H6} = 1.2$ Hz, 1H, 2-$S_2C_6H_3CH_3$), 6.72 (dd, 1H, 6-$S_2C_6H_3CH_3$), 2.22 (s, 3H, $S_2C_6H_3CH_3$), 0.99 (s, $J_{^{117}Sn-H} = 59.5$ Hz, $J_{^{119}Sn-H} = 62.6$ Hz, 6H, CH_3).

*3.2. [Sn(CH$_3$)$_2$(S–S)]: S–S = C$_3$S$_5$ (dmit) **1c***

To an acetone solution (15 cm^3) of $(NEt_4)_2[Zn(dmit)_2]$ (0.107 g, 0.15 mmol) under dinitrogen, was added $[Sn(CH_3)_2Cl_2]$ (0.065 g, 0.3 mmol). After stirring for 4 h, the solution was concentrated to 1 cm^3, and diethyl ether (15 cm^3) was added. A white solid of the zinc salt precipitated immediately, which was filtered off. The remaining solution was concentrated to 5 cm^3. Addition of hexane (10 cm^3) gave an orange solid **1c** (Yield: 65%) ^1H NMR (in ppm): δ 1.17 (s, $^2J_{^{117}Sn-H} = 62.5$ Hz, $^2J_{^{119}Sn-H} = 65.2$ Hz, 6H, CH_3).

*3.3. (PPN)$_2$[Zn(S–S)$_2$]: S–S = 1,2-S$_2$C$_6$H$_4$ **2a**, 3,4-S$_2$C$_6$H$_3$CH$_3$ **2b***

To an ethanolic solution (25 cm^3) of the dithiol (1 mmol) was added 10 cm^3 of an ethanolic solution of

KOH (0.1 M). After stirring for 15 min $(PPN)_2[ZnCl_4]$ (0.685 g, 0.5 mmol) was added. After stirring for 12 h the solutions were concentrated to 5 cm^3. Addition of hexane (25 cm^3) led the precipitation of the yellow complexes. **2a** (Yield: 91%) ^{1}H NMR: δ 7.59–7.40 (m, 60H, PPN), 6.57 (m, 4H, 3,6-$S_2C_6H_4$), 6.38 (m, 4H, 4,5-$S_2C_6H_4$). **2b** (Yield: 60%) ^{1}H NMR: δ 7.60–7.29 (m, 60H, PPN), 6.20 (d, J = 7.6 Hz, 2H, $S_2C_6H_3CH_3$), 1.97 (s, 6H, $S_2C_6H_3CH_3$).

*3.4. $[Au(C_6F_5)(S\text{–}S)L]$: S–S = 1,2-$S_2C_6H_4$ L = PPh_3 **3a**, PPh_2Me **4a**, $AsPh_3$ **5a**, S–S = 3,4-$S_2C_6H_3CH_3$ L = PPh_3 **3b**, PPh_2Me **4b**, $AsPh_3$ **5b***

(a) To a dichlorometane (30 cm^3) solution of **1a** (0.029 g, 0.1 mmol) or **1b** (0.030 g, 0.1 mmol) was added $[Au(C_6F_5)Cl_2L]$ L = PPh_3 (0.067 g, 0.1 mmol), PPh_2Me (0.063 g, 0.1 mmol), $AsPh_3$ (0.074 g, 0.1 mmol), and the resulting solutions were stirring for 1 h. Evaporation of the solvent to 5 cm^3, and addition of hexane (20 cm^3) afforded pink **3a** (yield: 77%), **3b** (yield: 52%), **4a** (yield: 53%), **4b** (yield: 60%) or red **5a** (yield: 92%), **5b** (yield: 71%).

(b) To a dichloromethane (30 cm^3) solution of **2a** (0.076 g, 0.05 mmol) or **2b** (0.077 g, 0.05 mmol) was added $[Au(C_6F_5)Cl_2L]$ L = PPh_3 (0.067 g, 0.1 mmol), PPh_2Me (0.063 g, 0.1 mmol), or $AsPh_3$ (0.074 g, 0.1 mmol). After stirring for 3 h, the solutions were concentrated to 5 cm^3. Addition of diethyl ether (15 cm^3) gave a white precipitate of $(PPN)_2[ZnCl_4]$. The solutions were filtered through 1 cm of diatomaceous earth. The solvent was removed to 5 cm^3 and addition of hexane (20 cm^3) led to the precipitation of pink **3a** (yield: 55%), **3b** (yield: 52%), **4a** (yield: 58%), **4b** (yield: 60%) or red **5a** (yield: 69%), **5b** (yield: 61%) solids.

(c) To a dichloromethane (30 cm^3) solution of **5a** (0.081 g, 0.1 mmol) or **5b** (0.082 g, 0.1 mmol) was added PPh_3 (0.030 g, 0.1 mmol) or PPh_2Me (0.002 cm^3, 0.1 mmol). After stirring 3 h, the solvents were evaporated to 5 cm^3. Addition of hexane (20 cm^3) gave pink **3a** (yield: 84%), **4a** (yield: 85%) solids. **3a** $^{31}P\{^1H\}$ NMR (in ppm): δ 30.6 (s); ^{1}H NMR: δ 7.64–7.43 (m, 15H, PPh_3), 7.31 and 6.90 (m, 4H, $S_2C_6H_4$); ^{19}F NMR: δ −120.6 (m, 2F, Fo), −157.7 (t, $^3J_{FpFm}$ = 18.5 Hz, 1F, Fp), −161.2 (m, 2F, Fm). **3b** $^{31}P\{^1H\}$ NMR: δ 30.7 (s); ^{1}H NMR: δ 7.63–7.43 (m, 15H, PPh_3), 7.11 and 6.72 (m, 3H, $S_2C_6H_3CH_3$), 2.22 (s, 3H, $S_2C_6H_3CH_3$); ^{19}F NMR: δ −120.6 (m, 2F, Fo), −157.8 (t, $^3J_{FpFm}$ = 19.3 Hz, 1F, Fp), −161.3 (m, 2F, Fm). **4a** $^{31}P\{^1H\}$ NMR: δ 17.0 (s); ^{1}H NMR: δ 7.58–7.43 (m, 10H, PPh_2Me), 7.30 and 6.89 (m, 4H, $S_2C_6H_4$), 2.44 (d, $^2J_{P-H}$ = 12.0 Hz, 3H, PPh_2Me); ^{19}F NMR: δ −120.0 (m, 2F, Fo), −157.0 (t, $^3J_{FpFm}$ = 19.4 Hz, 1F, Fp), −161.0 (m, 2F, Fm). **4b** $^{31}P\{^1H\}$ NMR: δ 17.5 (s); ^{1}H NMR: δ 7.60–7.40 (m, 10H, PPh_2Me), 7.14 and 6.72 (m, 3H, $S_2C_6H_3CH_3$), 2.43 (d, $^2J_{P-H}$ = 12.0 Hz, 3H, PPh_2Me), 2.24 (s, 3H, $S_2C_6H_3CH_3$); ^{19}F NMR: δ −120.0 (m, 2F, Fo), −157.1 (t, $^3J_{FpFm}$ = 20.0 Hz, 1F, Fp), −161.1 (m, 2F, Fm). **5a** ^{1}H NMR: δ 7.55–7.42 (m, 15H, $AsPh_3$), 7.33 and 6.93 (m, 4H, $S_2C_6H_4$); ^{19}F NMR: δ −119.9 (m, 2F, Fo), −157.4 (t, $^3J_{FpFm}$ = 19.3 Hz, 1F, Fp), −161.1 (m, 2F, Fm). **5b** ^{1}H NMR: δ 7.56–7.42 (m, 15H, $AsPh_3$), 7.17 and 6.76 (m, 3H, $S_2C_6H_3CH_3$), 2.25 (s, 3H, $S_2C_6H_3CH_3$); ^{19}F NMR: δ −119.6 (m, 2F, Fo), −157.3 (t, $^3J_{FpFm}$ = 19.7 Hz, 1F, Fp), −160.9 (m, 2F, Fm).

*3.5. $[Au(C_6F_5)(dmit)L]$: L = PPh_3 **3c**, PPh_2Me **4c**, $AsPh_3$ **5c***

(a) To an acetone solution (15 cm^3) of $[Sn(CH_3)_2(dmit)]$ (0.034, 0.1 mmol) was added $[Au(C_6F_5)Cl_2L]$ L = PPh_3 (0.067 g, 0.1 mmol), PPh_2Me (0.063 g, 0.1 mmol), or $AsPh_3$ (0.074 g, 0.1 mmol) and the resulting solutions were stirring for 1 h. Evaporation of the solvent to 5 cm^3 and addition of hexane (20 cm^3) gave green **3c** (Yield: 75%), garnet **4c** (Yield: 87%) or brown **5c** (Yield: 68%) solids.

(b) To an acetone solution (20 cm^3) of $(NEt_4)_2[Zn(dmit)_2]$ was added $[Au(C_6F_5)Cl_2L]$ L = PPh_3 (0.067 g, 0.1 mmol), PPh_2Me (0.063 g, 0.1 mmol), or $AsPh_3$ (0.074 g, 0.1 mmol). After stirring for 4 h, the solutions were concentrated to 5 cm^3. Addition of hexane (15 cm^3) gave the corresponding green **3c** (yield: 78%), garnet **4c** (yield: 80%) or brown **5c** (yield: 61%) solids, which were washed with distilled water and dried in vacuo. **3c** $^{31}P\{^1H\}$ NMR (in ppm): δ 30.95 (s); ^{19}F NMR: δ −121.3 (m, 2F, Fo), −156.0 (t, $^3J_{FpFm}$ = 18.5 Hz, 1F, Fp), −160.2 (m, 2F, Fm). **4c** $^{31}P\{^1H\}$ NMR: δ 33.8 (s, br); ^{1}H NMR: δ 7.58–7.43 (m, 10H, PPh_2Me), 2.07 (d, $^2J_{P-H}$ = 13.2 Hz, 3H, PPh_2Me); ^{19}F NMR: δ −120.65 (m, 2F, Fo), −155.1 (t, $^3J_{FpFm}$ = 19.4 Hz, 1F, Fp), −159.9 (m, 2F, Fm). **5c** ^{19}F NMR: δ −120.5 (m, 2F, Fo), −155.65 (t, $^3J_{FpFm}$ = 19.3 Hz, 1F, Fp), −160.1 (m, 2F, Fm).

*3.6. X-ray structure determination of complex **3a***

3.6.1. Crystal data

$C_{30}H_{19}AuF_5PS_2$, M = 766.5, monoclinic, space group $P2_1/n$, a = 16.528(6) Å, b = 9.108(2) Å, c = 17.927(5) Å, β = 98.34(5)°, V = 2670.1(14) Å^3, Z = 4, D_c = 1.907 Mg m^{-3}, $F(000)$ = 1480, λ(Mo Kα) = 0.71073 Å, μ = 5.78 mm^{-1}, T = −100°C.

3.6.2. Data collection and reduction

A red prism of 0.68 × 0.41 × 0.20 mm was mounted in inert oil (RS 3000, Riedel de Haën) on a glass fibre and transferred to the cold gas stream of a Stoe-Siemens four-circle diffractometer, ω/θ scan with ω scan width = 0.90°, variable ω scan speed 8.16–27.20° min^{-1}, graphite-monochromated Mo-kα radiation, 5213 reflections measured to $2\theta_{\max} 50°$. Averaging equivalents gave 4701 independent reflections ($R_{\text{int}} = 0.038$), of which 4294 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens SHELXTL PLUS) [35]. Cell constants were refined from setting $\pm\omega$ angles of 28 reflections in the range 2θ 20.46–26.03. Absorption correction was applied on the basis of Ψ-scans, transmission factors 0.51–0.99, three standard reflections, no decay.

3.6.3. Structure solution and refinement

Heavy-atom method, full-matrix least-squares refinement on F to $R = 0.022$, $wR = 0.029$. All non-H atoms anisotropic; riding H atom. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0004\, F^2$; 352 parameters. $S = 1.08$; maximum $\Delta\rho = 0.86$ e Å^{-3}.

Tables of thermal parameters and observed and calculated structure factors are available from the authors and full lists of data have also been deposited at the Cambridge Crystallographic Data Centre.

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