Pergamon

PII: S0277–5387(98)00066–7

Polyhedron Vol. 17, No. 15, pp. 2433–2439, 1998

0277–5387/98 $19.00+0.00

Dithiolate diphosphine polynuclear gold complexes. X-ray structure of $[Au_2(\mu\text{-dppm})(C_6F_5)_2(S_2C_6H_4)]$

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

[a]Departamento de Química, Universidad de la Rioja, 26001 Logroño, Spain

[b]Department of Chemistry, University of Wales Cardiff, P.O. Box 912, Cardiff CF1 3TB, U.K.

[c]Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza, C.S.I.C., 50009 Zaragoza, Spain

(Received 21 November 1997; accepted 4 February 1998)

Abstract—The gold(I) complexes $[Au_2(S–S)(AsPh_3)]n$ (S–S = $S_2C_6H_4$, $S_2C_6H_3CH_3$) react with $(Ph_2P(CH_2)nPPh_2)$ (n = 1, dppm; 2, dppe) affording $[Au_2(S–S)(dppe)]$ (**1**–**2**) or $[Au_4(S–S)_2(dppm)_2]$ (**3**, **4**). The gold(III) derivative $[Au(C_6F_5)(S–S)(AsPh_3)]$ reacts with dppe giving rise to $[\{Au(C_6F_5)(S–S)\}_2(\mu\text{-dppe})]$ (**5**, **6**) or with dppm affording $[Au(C_6F_5)(S–S)dppm]$ (**7**, **8**). Complexes **7**, **8** further react with the gold(I) compounds [AuX(tht)] (X = Cl, C_6F_5) giving after substitution of the tetrahydrothiophene group, $[Au_2(\mu\text{-dppm})(C_6F_5)X(S–S)]$ (**9**, **10**). The crystal structure of $[Au_2(\mu\text{-dppm})(C_6F_5)_2(S_2C_6H_4)]$ (**10**) has been established by X-ray diffraction and shows a linear Au(I) atom, bonded to a C_6F_5 group and a phosphorus of the dppm, which then bridges via the other phosphorus to a square planar Au(III) atom, which also carries a C_6F_5 group and a chelating dithiolate. © 1998 Elsevier Science Ltd. All rights reserved

Keywords: gold; dithiolate; diphosphine; pentafluorophenyl; X-ray structure

1. INTRODUCTION

The use of bidentate phosphines as building blocks for polymetallic complexes has developed enormously over the last 20 years and a number of reviews of this area have appeared [1–5]. Other bidentate ligands such as di- or polythiolates or thioether have been used less extensively although good examples in the chemistry of gold have been reported covering all the oxidation states of this metal: $[Au_4(S–S)_2(PEt_3)_2]$ [S–S = 1,2-benzenedithiolate ($S_2C_6H_4$), 3,4-toluenedithiolate ($S_2C_6H_3CH_3$)] [6, 7], $[Au_3(S–S)(PPh_3)_3](ClO_4)$ [8] or the benzenehexathiol derivative "golden wheel" $[\{CSAu(PPh_3)\}_6]$ [9] as gold(I) derivatives, [Au([9]aneS$_3$)$_2$](BF$_4$)$_2$ as gold(II) species [10], $[Au_2(CH_2PPh_2CH_2)_2(S_2C_6H_4)_2]$ [11] and $[\{Au(C_6F_5)(S–S)\}_3]$ [12] as gold(III) examples.

The combination of the two fields in gold chemistry is of additional interest because some of the Au–S drugs increase their effects when a phosphine ligand is present [13, 14] not only as antiarthritics but in their anticancer activity [15] or in the inhibitory effects on HIV-1 [16, 17]. In this paper we describe the synthesis of mainly polynuclear gold(I) or/and gold(III) complexes containing dppm ($Ph_2PCH_2PPh_2$) or dppe ($Ph_2P(CH_2)_2PPh_2$), by reaction of $[Au_2(S–S)(AsPh_3)]n$ [8] and $[Au(C_6F_5)(S–S)(AsPh_3)]$ [18] (S–S = bezenedithiolate or toluenedithiolate) with the diphosphines. The crystal structure of the digold(I, III) complex $[Au_2(\mu\text{-dppm})(C_6F_5)_2(S_2C_6H_4)]$ has been established by X-ray diffraction.

*Author to whom correspondence should be addressed.

2. EXPERIMENTAL

2.1. *General procedures*

The C, H and 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 using a Gallenkamp apparatus and are uncorrected. The infrared spectra were recorded (4000–200 cm^{-1}) on a Perkin-Elmer 883 spectrophotometer, using Nujol mulls between polyethylene sheets. The NMR spectra were recorded on a 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 LSIMS Technique using 3-nitrobenzylalcohol as a matrix and a cesium gun. The elemental analyses, conductivities, yield, melting point and $^{31}P\{^1H\}$ data of the new complexes are listed in Table 1.

2.2. *Starting materials*

The starting materials $[Au_2(S–S)(AsPh_3)]n$ [8], $[Au(C_6F_5)(S–S)(AsPh_3)]$ [18] (S–S = 1,2-$S_2C_6H_4$, 3,4-$S_2C_6H_3CH_3$), [AuCl(tht)] [19] and $[Au(C_6F_5)(tht)]$ [20] (tht = tetrahydrothiophene), were prepared as described previously. All other reagents were commercially available.

2.3. *Preparation of* [*Au*$_2$(S–S)(dppe)] [S–S = 1,2-$S_2C_6H_4$ (**1**), 3,4-$S_2C_6H_3CH_3$ (**2**)]

To a dichloromethane (30 cm^3) suspension of $[Au_2(S–S)(AsPh_3)]n$ [S–S = 1,2-$S_2C_6H_4$ (0.084 g, 0.1 mmol), $S_2C_6H_3CH_3$ (0.085 g, 0.1 mmol)], was added dppe (0.040 g, 0.1 mmol). After 3 h the solution was concentrated in vacuum, addition of diethylether led the precipitation of the new complexes as white solids (**1**–**2**). ^{1}H NMR: **1**: $\delta = 8.01$ and 6.71 (m, 4H, $S_2C_6H_4$); 7.80–7.06 (m, 20H, Ph); 2.70 (m, 4H, -CH_2-). **2**: $\delta = 7.89$ (d, $^3J_{H_5H_6} = 8.1$ Hz, 1H, H5–$S_2C_6H_3CH_3$); 7.86 (m, 1H, H2–$S_2C_6H_3CH_3$); 7.55–7.35 (m, 20H, Ph); 6.88 (dd, $^3J_{H_5H_6} = 8.1$ Hz, $^3J_{H_2H_6} = 0.7$ Hz, 1H, H6–$S_2C_6H_3CH_3$); 2.65 (m, 4H, -CH_2-); 2.60 (s, 3H, -CH_3). Mass spectra, *m*/*z*(%): **1**: 932(12) (M^+), 581(4) ([M−(S–S)]$^+$), 1129(7) ([M+Au]$^+$), 1330(5) ([M+(P–P)]$^+$). **2**: 946(72) (M^+), 581(70) ([M−(S–S)]$^+$), 749(5) ([M−Au]$^+$), 1143(70) ([M+Au]$^+$), 1344(1) ([M+(P–P)]$^+$).

Table 1. Data for the new complexes **1**–**10**

Complex	Yield (%)	Analysis (%)[a] C	H	S	Λ_M[b]	^{31}P[c] mp (°C)	$P_{coord.}$	P_{free}
1 [Au_2(1,2-$S_2C_6H_4$)dppe]	69	41.4 (41.15)	2.8 (3.0)	6.85 (6.9)	[d]	280	32.4(s)	–
2 [Au_2(3,4-$S_2C_6H_3CH_3$)dppe]	77	41.5 (41.85)	3.1 (3.2)	6.6 (6.75)	[d]	208[e]	31.7(s)	–
3 [Au_4(1,2-$S_2C_6H_4$)$_2$(dppm)$_2$]	60	40.55 (40.5)	2.9 (2.85)	7.6 (7.0)	11	126[e]	[f]	
4 [Au_4(3,4-$S_2C_6H_3CH_3$)$_2$(dppm)$_2$]	79	40.85 (41.2)	2.8 (3.05)	6.95 (6.9)	5	188	[f]	
5 [$Au_2(C_6F_5)_2$(1,2-$S_2C_6H_4$)$_2$dppe]	66	43.25 (42.7)	2.55 (2.3)	8.5 (9.1)	9	120[e]	32.9(s)	–
6 [$Au_2(C_6F_5)_2$(3,4-$S_2C_6H_3CH_3$)$_2$dppe]	68	44.0 (43.5)	3.05 (2.55)	8.4 (8.95)	15	142[e]	32.9(s)	–
7 [$Au(C_6F_5)$(1,2-$S_2C_6H_4$)dppm]	65	50.25 (50.0)	3.0 (2.95)	6.8 (7.2)	20	65	24.2(d) (59.1)	−27.2(d)
8 [$Au(C_6F_5)$(3,4-$S_2C_6H_3CH_3$)dppm]	56	50.35 (50.55)	2.95 (3.15)	6.6 (7.1)	17	75	24.1(d) (54.0)	−27.2(d)
9 [$Au_2(C_6F_5)$Cl(1,2-$S_2C_6H_4$)dppm]	75	40.1 (39.65)	2.45 (2.35)	5.25 (5.7)	5	123[e]	19.6(s) 18.7(s)	–
10 [$Au_2(C_6F_5)_2$(1,2-$S_2C_6H_4$)dppm]	67	41.5 (41.25)	1.95 (2.1)	5.45 (5.1)	9	150	28.4(s) 19.7(s)	

[a]Calculated values are given in parentheses.
[b]In acetone, values in Ω^{-1} cm^2 mol^{-1}.
[c]In $CDCl_3$ δ in ppm, J in Hz.
[d]Low solubility.
[e]Decompose without melting.
[f]See text.

2.4. *Preparation of* [Au_4(S–S)$_2$(dppm)$_2$] [S–S = 1,2-$S_2C_6H_4$ (**3**), 3,4-$S_2C_6H_3CH_3$ (**4**)]

To a dichloromethane (30 cm^3) suspension of [Au_2(S–S)($AsPh_3$)]n [S–S = 1,2-$S_2C_6H_4$ (0.084 g, 0.1 mmol), $S_2C_6H_3CH_3$ (0.085 g, 0.1 mmol)], was added dppm (0.038 g, 0.1 mmol). After 3 h the solution was concentrated in vacuum, addition of diethylether led the precipitation of the new complexes as yellow solids. ^{1}H NMR: **3**: δ = 8.00 and 6.85 (m, 8H, $S_2C_6H_4$); 7.03–6.85 (m, 40H, Ph); 4.66 (m, 2H, -CH_2-) and 4.12 (t, J = 12.8 Hz, 2H, -CH_2-). **4**: δ = 7.98–6.70 (m, 46H, aromatic); 4.66 (m, 2H, -CH_2-) and 4.13 (t, J = 12.5 Hz, 2H, -CH_2-); 2.33 (s, 6H, -CH_3). Mass spectra, m/z(%): **3**: 1696(70) ([M−(S–S)]$^+$), 918(37) ([M/2]$^+$), 2033(12) ([M+Au]$^+$). **2**: 1684(7) (M$^+$), 1710(100) ([M−(S–S)]$^+$), 932(36) ([M/2]$^+$), 2061(28) ([M+Au]$^+$).

2.5. *Preparation of* [{$Au(C_6F_5)$(S–S)}$_2$(μ-dppe)] [S–S = 1,2-$S_2C_6H_4$ (**5**), 3,4-$S_2C_6H_3CH_3$ (**6**)]

To a dichloromethane solution (20 cm^3) of dppe (0.020 g, 0.05 mmol) was added [Au(C_6F_5) (S–S)($AsPh_3$)] [1,2-$S_2C_6H_4$ (0.081 g, 0.1 mmol) or 3,4-$S_2C_6H_3CH_3$ (0.082 g, 0.1 mmol)]. After 1 h stirring the solution was concentrated in vacuum and the addition of hexane affords the precipitation of the new complexes as a pink solid **5** or a violet one **6**. **5** ^{1}H NMR: δ = 7.74–7.16 and 6.90 (m, 24H, aromatic), 3.28 (m, 4H, -CH_2-); ^{19}F NMR: δ = −119.3 (m, 4F, Fo), −156.9 (t, $^3J_{F_pF_m}$ = 20.3 Hz, 2F, Fp), −161.1 (m, 4F, Fm). **6** ^{1}H NMR: δ = 7.60–7.40 and 6.79 (m, 23H, aromatic), 3.27 (m, 4H, -CH_2-), 2.28 (s, 3H, -CH_3); ^{19}F NMR: δ = −119.6 (m, 4F, Fo), −157.2 (t, $^3J_{F_pF_m}$ = 19.9 Hz, 2F, Fp), −160.8 (m, 4F, Fm). Mass spectra, m/z (%): **5**: 1406(13) (M$^+$), 1266(6) ([M−(S–S)]$^+$), 1099(100) ([M−(S–S)−(C_6F_5)]$^+$), 1603(5) ([M+Au]$^+$). **6**: 1434(5) (M$^+$),1280(3) ([M−(S–S)]$^+$), 1113(25) ([M−(S–S)−(C_6F_5)]$^+$), 1631(3) ([M+Au]$^+$).

2.6. *Preparation of* [$Au(C_6F_5)$(S–S)(dppm)] [S–S = 1,2-$S_2C_6H_4$ (**7**), 3,4-$S_2C_6H_3CH_3$ (**8**)]

To a dichloromethane solution (20 cm^3) of dppm (0.038 g, 0.1 mmol) was added [Au(C_6F_5)(S–S)($AsPh_3$)] [1,2-$S_2C_6H_4$ (0.081 g, 0.1 mmol) or 3,4-$S_2C_6H_3CH_3$ (0.082 g, 0.1 mmol)]. After 1 h stirring the solution was concentrated in vacuum and the addition of hexane affords the precipitation of the new complexes as pink solids. **7** ^{1}H NMR: δ = 7.68–7.16 and 6.91 (m, 24H, aromatic), 3.60 (d, $^2J_{P-H}$ = 10.6 Hz, 2H, -CH_2-); ^{19}F NMR: δ = −119.5 (m, 2F, Fo), −156.8 (t, $^3J_{F_pF_m}$ = 19.9 Hz, 1F, Fp), −160.8 (m, 2F, Fm). **8** ^{1}H NMR: δ = 7.74–7.09 and 6.80 (m, 23H, aromatic), 3.58 (d, $^2J_{P-H}$ = 10.3 Hz, 2H, -CH_2-), 2.26 (s, 3H, -CH_3); ^{19}F NMR: δ = −119.5 (m, 2F, Fo), −156.9 (t, $^3J_{F_pF_m}$ = 20.7 Hz, 1F, Fp), −160.9 (m, 2F, Fm). Mass spectra, m/z(%): **7**: 888(63) (M$^+$), 721(34) ([M−(C_6F_5)]$^+$), 748(85) ([M−(S–S)]$^+$), 1085(19) ([M+Au]$^+$). **8**: 902(98) (M$^+$), 735(31) ([M−(C_6F_5)]$^+$), 748(62) ([M−(S–S)]$^+$), 1099(24) ([M+Au]$^+$).

2.7. *Preparation of* [$Au_2(C_6F_5)X(S_2C_6H_4)$(μ-dppm)] [X = Cl (**9**), C_6F_5 (**10**)]

To a dichloromethane solution (20 cm^3) of **7** (0.089 g, 0.1 mmol) was added [AuX(tht)] [Cl (0.032 g, 0.1 mmol) or C_6F_5 (0.045 g, 0.1 mmol)]. After 1 h stirring the solution was concentrated in vacuum and the addition of hexane affords the precipitation of the new complexes as pink solids. **9** ^{1}H NMR: δ = 7.73–7.31 (m, 20H, Ph), 6.98 (m, 4H, $S_2C_6H_4$), 4.15 ("t", $^2J_{PH}$ = 9.9 Hz, 2H, -CH_2-); ^{19}F NMR: δ = −120.0 (m, 2F, Fo), −156.2 (t, $^3J_{F_pF_m}$ = 19.9 Hz, 1F, Fp), −160.4 (m, 2F, Fm). **10** ^{1}H NMR: δ = 7.74–7.29 (m, 20H, Ph), 6.97 (m, 4H, $S_2C_6H_4$), 4.16 ("t", $^2J_{P-H}$ = 9.8 Hz, 2H, -CH_2-); ^{19}F NMR: δ = −116.1 (m, 2F, Fo), −119.9 (m, 2F, Fo), −156.3 (t, $^3J_{F_pF_m}$ = 19.6 Hz, 1F, Fp), −158.1 (t, $^3J_{F_pF_m}$ = 20.0 Hz, 1F, Fp), −160.5 (m, 2F, Fm) −162.5 (m, 2F, Fm). Mass spectra, m/z(%): **9**: 1085(100) ([M−Cl]$^+$), 945(42) ([M−Cl−(S–S)]$^+$). **7**: 1251(57) (M$^+$), 1085(100) ([M−(C_6F_5)]$^+$), 945(96) ([M−(C_6F_5)−(S–S)]$^+$).

2.8. *X-ray determination of compound* **10**

Single crystals were grown by diffusing hexane into a dichlorometane solution of complex [$Au_2(C_6F_5)_2$ ($S_2C_6H_4$)(μ-dppm)] (**10**) at room temperature and mounted in inert oil.

2.9. *Crystal data and data collection parameters*

$C_{44}H_{28}Au_2Cl_2F_{10}P_2S_2$, M = 1337.56, triclinic, space group P-1, a = 12.381(3) Å, b = 13.517(3) Å, c = 14.5500(7) Å. α = 89.450(1)°, β = 112.450(8)°, γ = 102.75(2)°, V = 2187.4(7) Å^3, Z = 2, D_c = 2.031 Mg m^{-3}, F(000) = 1272, λ(Mo–Kα) = 0.71069 Å, μ = 7.066 mm^{-1}, T = 150 K. A red prism of 0.20 × 0.18 × 0.14 mm was used, unit cell dimensions and intensity data were measured using a Delft Instruments FAST TV area detector diffractometer positioned at the window of a rotating-anode generator and using Mo–Kα radiation, as previously described [21]. θ range for data collection 1.83 to 24.96°, $-14 \leqslant h \leqslant 0$, $0 \leqslant h \leqslant 14$, $-15 \leqslant k \leqslant 0$, $0 \leqslant k \leqslant 10$, $-16 \leqslant l \leqslant 0$; $0 \leqslant l \leqslant 16$; 8920 reflections collected, 6040 independent (R_{int} = 0.070).

2.10. *Structure solution and refinement*

The structure was determined using the PATT instruction of SHELXS 86 [22], the structure was refined by full-matrix least squares on F_0^2, using the

program SHELXL 93 [23]. All data used were corrected for Lorentz-polarization factors and subsequently for absorption using the program DIFABS [24]. The non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were included in idealised positions. Refinement on F^2 proceeded to $R = 0.0404$, wR = 0.1027 and goodness of fit 0.941 for 559 parameters and 48 restrains and $R = 0.0515$, wR = 0.1045 for all data. In the final Fourier synthesis the electron density fluctuated in the range 1.850 to -1.482 e Å^{-3}.

3. RESULTS AND DISCUSSION

The substitution of triphenylarsine in $[Au_2(S–S)(AsPh_3)]n$ derivatives by diphosphines takes place in mild conditions as recently reported for monodentate phosphines [8, 18]. The nuclearity of the new complexes are dependent on the diphosphine used, $Ph_2P(CH_2)nPPh_2$ ($n = 1$, dppm; 2, dppe) (eqns (1) and (2)).

$$1/n[Au_2(S–S)(AsPh_3)]_n + \text{dppe} \rightarrow [Au_2(S–S)\text{dppe}] + AsPh_3 \quad (1)$$

(S–S) = 1,2-$S_2C_6H_4$ (**1**); 3,4-$S_2C_6H_3CH_3$ (**2**)

$$2/n[Au_2(S–S)(AsPh_3)]_n + 2\text{dppm} \rightarrow [Au_4(S–S)_2(\text{dppm})_2] + 2AsPh_3 \quad (2)$$

(S-S) = 1,2-$S_2C_6H_4$ (**3**); 3,4-$S_2C_6H_3CH_3$ (**4**)

The proposed nuclearity of the complexes is made on the basis of NMR data, mainly $^{31}P\{^1H\}$ and in the mass spectra of the complexes. So the $^{31}P\{^1H\}$ NMR of **1** and **2** show singlets showing two equivalent phosphorus atoms in accordance with a dinuclear ten-membered ring structure (Table 1). The mass spectra (LSIMS+) show the parent peaks $[\{Au_2(S–S)(\text{dppe})\}^+]$ at m/z (%): 932(12) for **1** and 946(72) for **2**, although higher nuclearity peaks, such as $[M+Au]^+$ or $[M+(\text{dppe})]^+$, are present in lower intensities than the parent ion, probably due to some ion–molecule association as in other thiolate gold complexes [8, 25]. Compound **2** has been described previously [26] and a dinuclear structure has been suggested.

The $^{31}P\{^1H\}$ NMR of the dppm complexes (**3**, **4**) presents an AA′BB′ system, which by iteration procedures show: $\delta_A = 35.4$, $\delta_B = 25.3$ ppm; $J_{AA'} = 177$, $J_{AB} = J_{A\acute{B}} = 82.2$, $J_{AB'} \approx 0$ and $J_{BB'} \approx 0$ Hz for **3** and $\delta_A = 35.7$, $\delta_B = 25.7$ ppm; $J_{AA'} = 179$, $J_{AB} = J_{A\acute{B}} = 83.1$, $J_{AB'} \approx 0$ and $J_{BB'} \approx 0$ Hz for **4** showing that in these case a dinuclear structure is ruled out. The patterns of these spectra and the corresponding ^1H NMR (see below) are very close to those reported for $[Au_4(C_3S_5)_2(\text{dppm})_2]$ [25] which present an asymmetric tetranuclear structure. The mass spectra (LSIMS+) show the parent peak $[\{Au_4(S–S)_2(\text{dppm})_2\}^+]$ at m/z (%): 1864(7) for **4** and $[\{Au_4(S–S)(\text{dppm})_2\}^+]$ or $[M–(S–S)]^+$ at 1696(70) for **3** and 1710(100) for **4** in accordance with a tetranuclear formulation.

The ^1H NMR shows among other resonances, two groups of signals for the methylene groups from the dppm [Fig. 1(a)]. There are two possibilities for explaining these two resonances for the methylene groups: either these signals belong to inequivalent methylenes or the CH_2 groups are equivalent and the protons from every -CH_2- are inequivalent. The $^1H\{^{31}P\}$ shows an AB pattern [Fig. 1(b)], so the methylene groups are equivalent and both signals come from two inequivalent protons of a CH_2 group, that are coupled one to another ($^2J_{HH} = 12{,}8$ Hz), in accordance with the ^1H–^1H correlation. The selective irradiation of ^{31}P (26 and 36 ppm) [Fig. 1(c)], shows that one proton signal is only coupled with the 26 ppm-phosphorus-atoms (the higher field signal), while the other one is coupled with both [Fig. 1(c) and (d)]. The complex signal that persists in the 26 ppm-^{31}P-irradiation [Fig. 1(c)] shows that this signal is coupled with two 36 ppm-phosphorus-atoms. All these NMR data and the mass spectra are consistent with a tetranuclear structure for complexes **3** and **4** similar to the one reported for the dmit derivative [25] (Fig. 2), although other polynuclear structures are not ruled out.

When the processes 1 and 2 are undertaken starting from the gold(III) complex $[Au(C_6F_5)(S–S)(AsPh_3)]$, the nuclearity of new complexes are again dependent on the diphosphine used. So with dppe the complexes are dinuclear (eqn (3)) whereas with dppm are mononuclear, with the ligand acting in a monodentate fashion (eqn (4)). It is noteworthy that the new products (**5**–**8**) are obtained independently of the molar ratio used in the reactions, although the best yield (Table 1) are obtained when the ratio shown in the equations are used.

$$2[Au(C_6F_5)(S–S)(AsPh_3)] + \text{dppe} \rightarrow [\{Au(C_6F_5)(S–S)\}_2(\mu\text{-dppe})] + 2AsPh_3 \quad (3)$$

S–S = $S_2C_6H_4$ (**5**); $S_2C_6H_3CH_3$ (**6**)

$$[Au(C_6F_5)(S-S)(AsPh_3)] + \text{dppm} \rightarrow [Au(C_6F_5)(S-S)\text{dppm}] + AsPh_3 \quad (4)$$

S−S = $S_2C_6H_4$(**7**);$S_2C_6H_3CH_3$(**8**)

The ^{19}F NMR of the new complexes consists of three groups of resonances in a 2:1:2 ratio for the *ortho*, *para* and *meta* ^{19}F nuclei of the C_6F_5 group (see Section 2). The $^{31}P\{^1H\}$ NMR of the complexes **7** and **8** shows two doublets at ≈ 24 and -27 ppm, that are in agreement with one phosphorus atom coordinated and the other one free. By contrast, the compounds **5** and **6** show a singlet that is in accordance with the equivalence of both phosphorus atoms (Table 1). Besides other resonances the ^1H NMR show the signals corresponding to the methylene groups from the diphosphine. The mass spectra (LSIMS+) show the peak corresponding to the molecular ion at m/z (%)

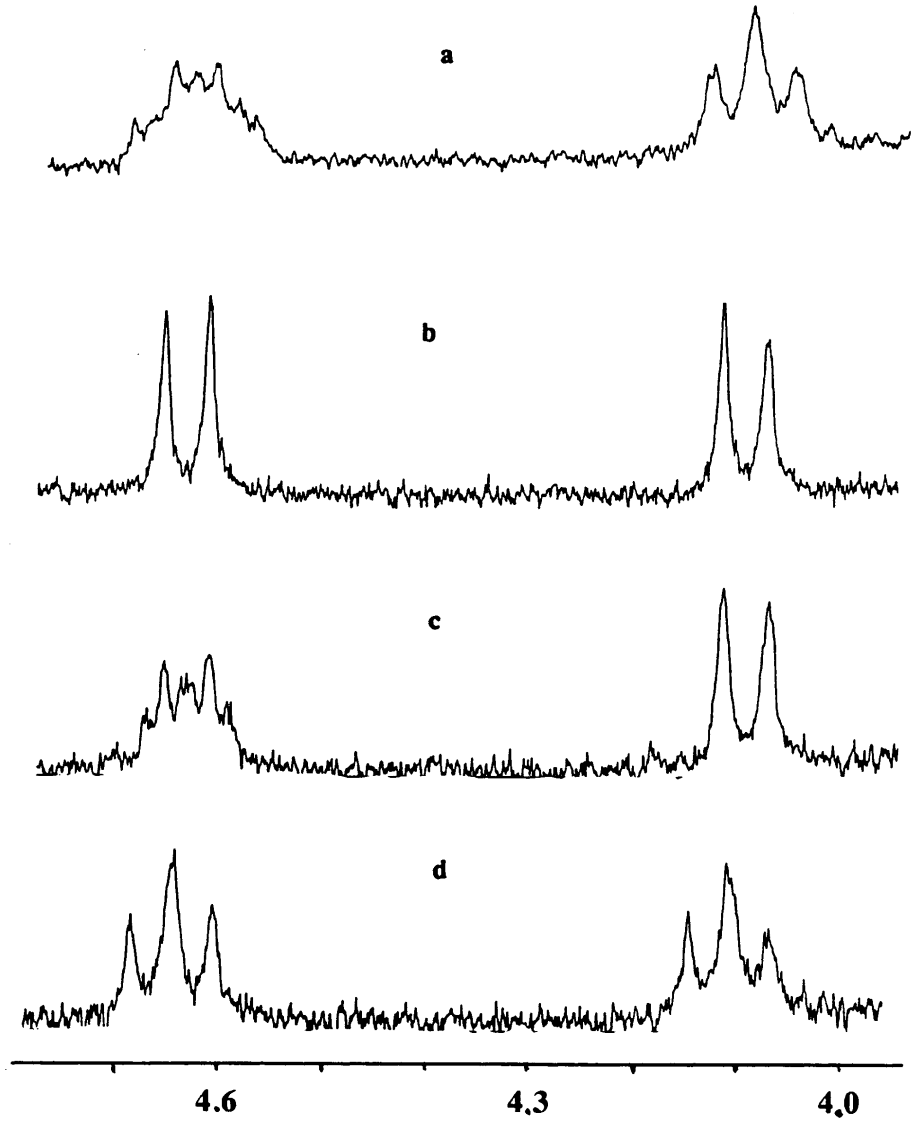

Fig. 1. ^{1}H NMR of complex **3**: (a) without decoupling, (b) $^{1}H\{^{31}P\}$ NMR, (c) 26 ppm-^{31}P decoupled and (d) 36 ppm-^{31}P decoupled.

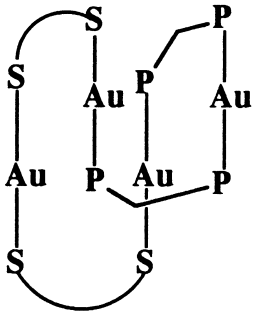

Fig. 2. Schematic view of structure for $[Au_4(C_3S_5)_2(dppm)_2]$ and proposed for complex **3** and **4**.

1406(13) **5**, 1434(5) **6**, 888(63) **7** and 902(98) **8**, in accordance with the proposed formulation.

The lack of dinuclear derivatives of gold(III) dppm complexes even when 2:1 ratios are used in processes 4 could be due to space requirement. So we tried the reaction with gold(I) complexes which are less space demanding. In these cases and starting from tetrahydrothiophene (tht) derivatives [AuX(tht)] (X = Cl; C_6F_5) unsymmetrical digold(I, III) complexes are obtained (eqn (5)).

$$[Au(C_6F_5)(S_2C_6H_4)(dppm)] + [AuX(tht)] \rightarrow [Au_2(C_6F_5)X(S_2C_6H_4)(\mu\text{-dppm})] + tht \quad (5)$$

X = Cl (**9**); C_6F_5 (**10**)

The ^{19}F NMR shows the same pattern as that in the previous compounds and in complex **10** other three groups of signals appear, in a typical position for a new C_6F_5 group bonded to gold(I) (see Section 2). In the mass spectra (LSIMS+) the base peak (100%) of both compounds correspond with the species $[\{M–X\}^+]$ at m/z 1085 and in complex **10** the molecular peak $[M^+]$ appears at m/z 1251 (57%). The resonance corresponding to the $-CH_2-$ group in the ^1H NMR (**9**, **10**) is a *pseudo*-triplet, due to similar coupling constant with both phosphorus.

The molecular structure of complex **10** was resolved by single crystal X-ray diffraction study of its dichloromethane solvate (Fig. 3). Selected bond lengths and angles are given in Table 2. The complex is dinuclear with a gold(I) and a gold(III) atoms bridged by the dppm ligand. The gold(III) centre is bonded to one pentafluorophenyl group, to one of the phosphorus of the dppm and to the dithiolate ligand acting as a chelating anion, in a square-planar geometry with angles C(21)–Au(2)–S(2) 85.6(3)°, S(2)–Au(2)–S(1) 90.07(11)°, C(21)–Au(2)–P(2) 90.0(3)°, S(1)–Au(2)–P(2) 94.48(10)°; this Au(2) atom lies 0.099 Å out of the plane formed by the four donor atoms. The "$Au(C_6F_5)(S_2C_6H_4)$" fragment is similar to the recently reported $[Au(C_6F_5)(S_2C_6H_4)(PPh_3)]$ [18] and $[Au(C_6F_5)(S_2C_6H_4)(SC_6H_4SPPh_3)]$ [12]. The Au(2)–S bond lengths are Au(2)–S(1) 2.308(3) and Au(2)–S(2) 2.296(3) Å which 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) [27], $[Au(1,2\text{-}S_2C_6H_4)_2]^-$ (2.305 Å)[28], $[Au(3,4\text{-}S_2C_6H_3CH_3)_2]^-$ (2.287(3) and 2.319(4) Å) [8], $[Au(C_6F_5)(S_2C_6H_4)PPh_3]$ (2.314(1) and 2.299(1) Å) [18], $[Au(C_6F_5)(S_2C_6H_4)(SC_6H_4S–Ph_3)]$ (2.314(4) and 2.299(4) Å) [12]. The Au(2)–P(2) distance is 2.336(3) Å and is similar to $[Au(C_6F_5)(S_2C_6H_4)(PPh_3)]$ (2.340(1) Å) [18]. The other phosphorus atom is bonded to the gold(I) centre Au(1)–P(1) 2.264(3) Å and are similar to those found in $\{Au(C_6F_5)"P"\}$ arrangement $[Au(C_6F_5)(PPh_2–CH–PPh_2Me)]$ (2.287(2) Å) [29], $[Au(C_6F_5)(PPh_2–CH\{Au(C_6F_5)\}–PPh_2Me)]$ (2.286(4) Å) [29]. The other gold center is in a linear geometry typical of gold(I) complexes C(1)–Au(1)–P(1) 174.2(3)°. The gold(I)–carbon bond length is Au(1)–C(1) 2.039(12) Å and is in the range of the latter complexes, 2.057(6), 2.053 and 2.052(10) Å.

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

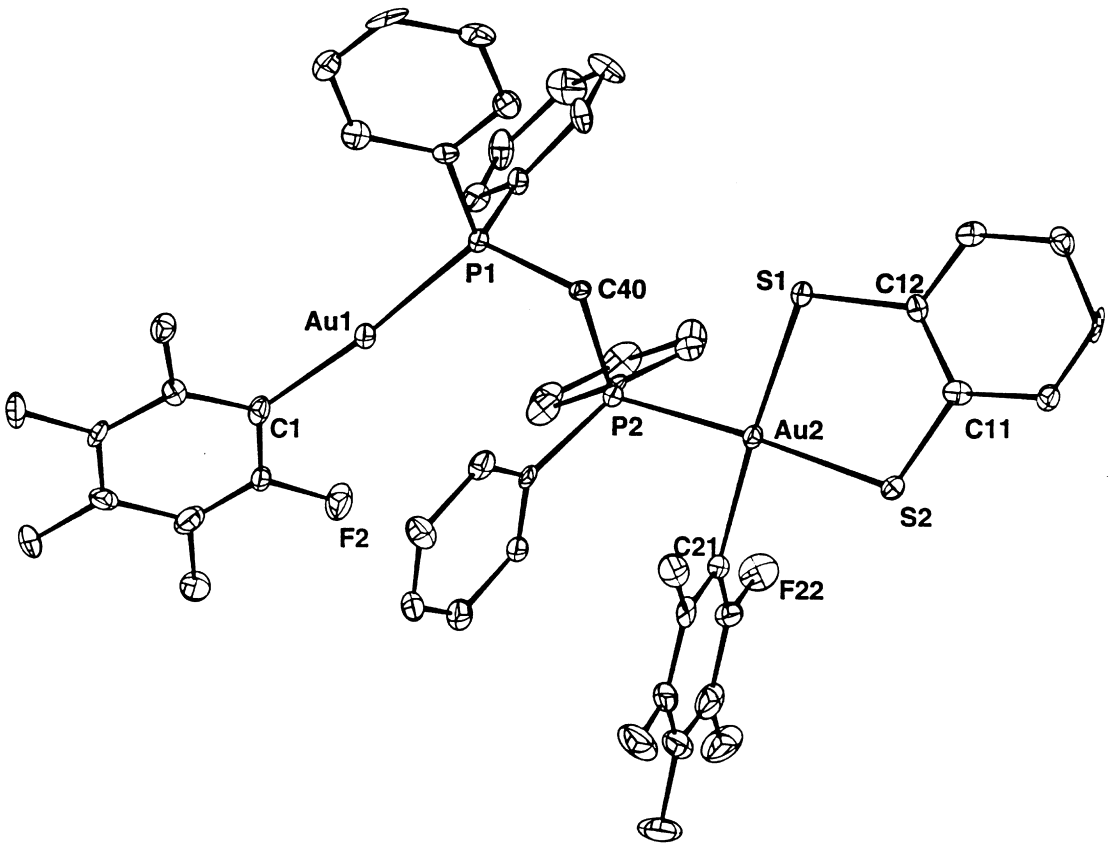

Fig. 3. The molecule of complex **10** in the crystal. Hydrogen atoms and dicholorometane are omitted for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for **10**

Au(1)–C(1)	2.039(12)	Au(1)–P(1)	2.264(3)
Au(2)–C(21)	2.060(11)	Au(2)–S(2)	2.296(3)
Au(2)–S(1)	2.308(3)	Au(2)–P(2)	2.336(3)
S(1)–C(12)	1.758(11)	S(2)–C(11)	1.743(11)
P(1)–C(40)	1.847(10)	P(2)–C(40)	1.810(11)

C(1)–Au(1)–P(1)	174.2(3)	C(21)–Au(2)–S(2)	85.6(3)
C(21)–Au(2)–S(1)	175.3(3)	S(2)–Au(2)–S(1)	90.07(11)
C(21)–Au(2)–P(2)	90.0(3)	S(2)–Au(2)–P(2)	172.25(11)
S(1)–Au(2)–P(2)	94.48(10)	C(12)–S(1)–Au(2)	102.7(4)
C(11)–S(2)–Au(2)	104.0(4)	C(6)–C(1)–Au(1)	123.2(9)
C(2)–C(1)–Au(1)	123.6(8)	C(22)–C(21)–Au(2)	123.0(9)
C(26)–C(21)–Au(2)	121.4(9)	C(111)–P(1)–C(40)	104.7(5)
C(121)–P(1)–C(40)	105.0(5)	C(111)–P(1)–Au(1)	112.4(4)
C(121)–P(1)–Au(1)	113.3(4)	C(40)–P(1)–Au(1)	115.9(3)
C(211)–P(2)–C(40)	105.9(5)	C(40)–P(2)–C(221)	108.8(5)
C(211)–P(2)–Au(2)	108.1(4)	C(40)–P(2)–Au(2)	112.2(4)
C(221)–P(2)–Au(2)	112.1(3)	P(2)–C(40)–P(1)	116.2(6)

Engineering and Physical Sciences Research Committee for support of the X-ray facilities.

REFERENCES

1. Puddephatt, R., *J. Chem. Soc. Rev*., 1983, **12,** 99.
2. Balch, A. L., *Homogeneous Catalysis with Metal Phosphine Complexes*, ed. L. H. Pignolet. Plenum, New York, 1983, p. 167.
3. Balch, A. L., *Comm. Inorg. Chem*., 1984, **3,** 51.
4. Chaudret, B., Delavaux, B. and Poilblanc, R., *Coord. Chem. Rev*., 1988, **86,** 191.
5. Anderson, G.K., *Adv. Organomet. Chem*., 1993, **35,** 1.
6. Davila, R. M., Elduque, A., Grant, T., Staples, R. J., Fackler, J. P. Jr., *Inorg. Chem*., 1993, **32,** 1749.
7. Nakamoto, M., Schier, A. and Schmidbaur, H., *J. Chem. Soc. Dalton Trans*., 1993, 1347.
8. Gimeno, M. C., Jones, P. G., Laguna, A., Laguna, M. and Terroba, R., *Inorg. Chem*., 1994, **33,** 3932.
9. Yip, H. K., Schier, A., Riede, J. and Schmidbaur, H., *J. Chem. Soc. Dalton Trans*., 1994, 2333.
10. Blake, A. J., Greig, J. A., Holder, A. L., Hyde, T. I., Taylor, A. and Schröder, M., *Angew. Chem. Int. Ed. Engl*., 1990, **29,** 197.
11. Heinrich, D. H., Fackler, J. P. Jr., *Inorg. Chem*., 1990, **29,** 4402.
12. Cerrada, E., Fernández, E. J., Jones, P. G., Laguna, A., Laguna, M. and Terroba, R., *Organometallics*, 1995, **14,** 5537.
13. Shaw, C. F. III., Isab, A. A., Hoeschele, J. D., Starich, M., Jocke, J., Schulteis, P. and Xiao, J., *J. Am. Chem. Soc*., 1994, **116,** 2254.
14. Graham, G. C., Champion, G. D. and Ziegher, J. B., *Inflammopharmacology*, 1991, **1,** 99.
15. Sadler, P. J. in, *Metal complexes in Cancer Chemotherapy*, ed. K. B. Keppler. VCH, Weinheim, 1993.
16. Okada, T., Patterdon, B. K., Ye, O. S. and Gurney, M. E., *Virology*, 1993, **192,** 631.
17. Blough, H. A., Richetti, M. and Montagnier, B. H., *Chem. Abstr*., 1991, **115,** 174630.
18. Cerrada, E., Fernández, E. J., Gimeno, M. C., Laguna, A., Laguna, M., Terroba, R. and Villacampa, M. D., *J. Organomet. Chem*., 1995, **492,** 105.
19. Allen, E. A. and Wilkinson, W., *Spectrochim. Acta*, 1972, **28A,** 2257.
20. Usón, R., Laguna, A. and Vicente, J., *J. Chem. Soc. Chem. Commun*., 1976, 353.
21. Danopoulos, A. A., Wilkinson, G., Hussain-Bate, M. B. and Hursthouse, M. B., *J. Chem. Soc. Dalton Trans*., 1991, 1855.
22. Sheldrick, G. M., *Acta Crystallogr. A*, 1990, **46,** 467.
23. Sheldrick, G. M., *Program for Crystal Structure Refinement*. University of Götingen, 1993.
24. Walker, N. P. C., Stuart, D., *Acta Crystallogr. A*, 1983, **39**, 158 (adapted for FAST geometry by Karaulov, A., University of Wales, Cardiff, 1991).
25. Cerrada, E., Laguna, A., Laguna, M. and Jones, P. G., *J. Chem. Soc. Dalton Trans*., 1994, 1325.
26. Narayanaswamy, R., Young, M. A., Parkhurst, E., Oullette, M., Kerr, M. E., Ho, D. M., Elder, R. C., Bruce, A. E. and Bruce, M. R. M., *Inorg. Chem*., 1993, **32,** 2506.
27. Noordik, J. H. and Beurskens, P. T., *J. Cryst. Mol. Struct*., 1971, **1,** 339.
28. Nakamoto, M., Koijman, H., Paul, M., Hiller, W. and Schmidbaur, H., *Z. Anorg. Allg. Chem*., 1993, **619,** 1341.
29. Usón, R., Laguna, A., Laguna, M., Lázaro, I., Morata, A., Jones, P. G. and Sheldrick, G. M., *J. Chem. Soc. Dalton Trans*., 1986, 669.