

1,1'-Bis(diphenylthiophosphoryl)ferrocene complexes of gold(I) and gold(III)

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Received 18 June 1999

Abstract

Linear and three-coordinate gold(I) complexes with the ferrocenyl derivative 1,1'-bis(diphenylthiophosphoryl)ferrocene (dtpf) of the type $[(\mu\text{-dtpf})(\text{AuX})_2]$ ($\text{X} = \text{Cl}$, **1**; C_6F_5 , **2**), $[(\mu\text{-dtpf})(\text{AuPPh}_3)_2](\text{ClO}_4)_2$ or $[\text{Au}(\text{dtpf})(\text{PPh}_3)]\text{ClO}_4$ have been obtained. Oxidation of **1** with chlorine gave the mixed gold(I)–gold(III) compound $[\text{Au}(\text{dtpf})][\text{AuCl}_4]$. The dinuclear gold(III) complexes $[(\mu\text{-dtpf})\{\text{Au}(\text{C}_6\text{F}_5)_3\}_2]$ or $[(\mu\text{-dtpf})\{\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}\}_2]$ were obtained from the corresponding gold precursors and dtpf. The crystal structures of $[\text{Au}(\text{dtpf})][\text{AuCl}_4]$ and $[(\mu\text{-dtpf})\{\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}\}_2]$ have been determined by X-ray diffraction studies. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Gold; Ferrocene; Bis(diphenylthiophosphoryl)ferrocene

1. Introduction

Recently, the chemistry of ferrocene-containing complexes has received much attention associated with their increasing applications in organic synthesis, production of fine chemicals, homogeneous catalysis, and materials science [1–4]. Ferrocene has become a versatile building block for the synthesis of compounds with tailor-made properties, and numerous derivatives have been reported in which the cyclopentadienyl rings are bound to organic groups containing one or more donor atoms [1]. A good example is the diphosphine 1,1'-bis(diphenylphosphine)ferrocene (dppf); it is a very flexible ligand that can modify its steric bite in order to adapt to different geometric requirements of the metal centres. This has facilitated the synthesis of a great number of mononuclear (with trigonal planar or tetrahedral geometry) or polynuclear gold or silver derivatives [5–10].

The sulfuration product of the diphosphine, bis(diphenylthiophosphoryl)ferrocene (dtpf), is a ligand with a longer and more flexible backbone that permits

the formation of the species $[\text{M}(\text{dtpf})]^+$ ($\text{M} = \text{Cu}$, Ag , Au) with dtpf acting as a *trans*-chelating ligand [11,12]. Here we report on the coordination chemistry of dtpf with gold(I) and -(III) centres. Mono- and di-nuclear derivatives are reported in which the S-donor ligand acts as bridging or chelating ligand.

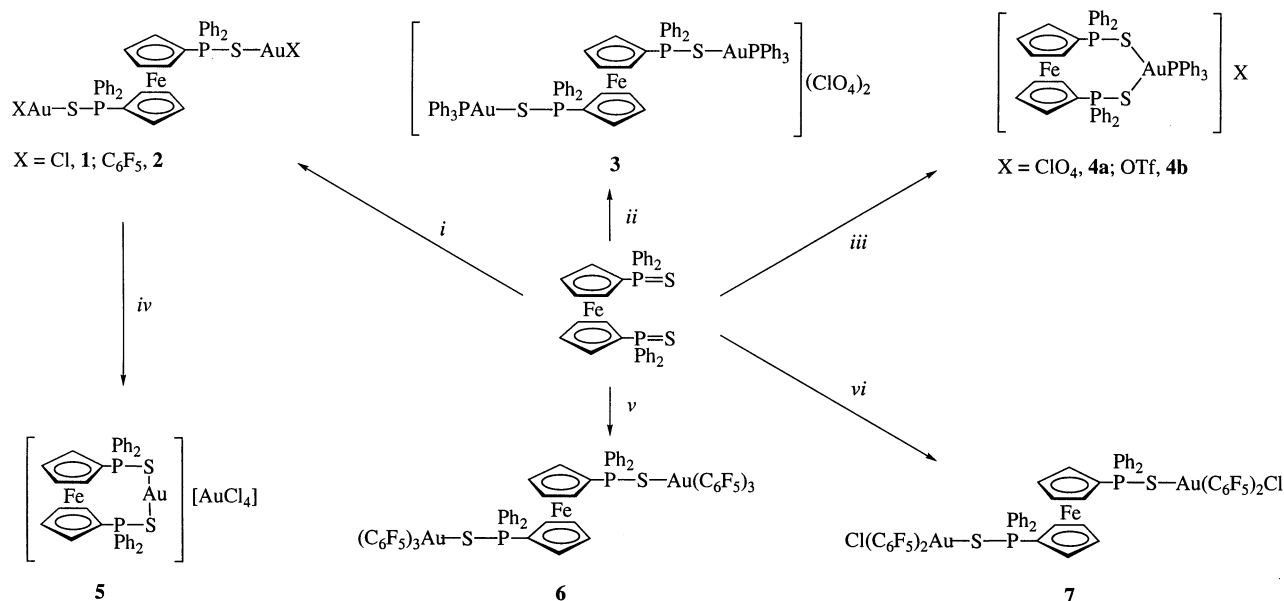
2. Results and discussion

The reaction of dtpf with the gold complexes $[\text{AuX}(\text{tht})]$ (tht = tetrahydrothiophene; molar ratio 1:2) gives the dinuclear complexes $[(\mu\text{-dtpf})(\text{AuX})_2]$ ($\text{X} = \text{Cl}$, **1**; C_6F_5 , **2**) (see Scheme 1). They are yellow air- and moisture-stable solids and are non-conducting in acetone solutions. Their IR spectra show the vibration $\nu(\text{Au}-\text{Cl})$ at $341(\text{m})\text{ cm}^{-1}$ (**1**) and the bands arising from the pentafluorophenyl group at $1502(\text{vs})$, $959(\text{vs})$ and $796(\text{m})\text{ cm}^{-1}$ (**2**). The positive liquid secondary ion mass spectra (LSIMS) do not show the cation molecular peak; however, the cation $[\text{Au}(\text{dtpf})]^+$ appears at $m/z = 815$ (**1**, 100; **2**, 13%).

The ^1H -NMR spectra show two multiplets for the α and β protons of the substituted cyclopentadienyl groups. The ^{19}F -NMR spectrum of **2** presents three resonances for the *ortho*-, *meta*- and *para*-fluorines of

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Scheme 1. (i) $2[\text{AuX}(\text{tht})]$; (ii) $2[\text{Au}(\text{OClO}_3)(\text{PPh}_3)]$; (iii) $[\text{Au}(\text{OClO}_3)(\text{PPh}_3)]$; (iv) Cl_2 ; (v) $2[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)]$; (vi) $[\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}]_2$.

the C_6F_5 group. The $^{31}\text{P}\{-^1\text{H}\}$ -NMR spectra at room temperature show a singlet for **1** and a multiplet for **2**, due to the coupling with the fluorine atoms.

The treatment of dptpf with $[\text{Au}(\text{OClO}_3)(\text{PPh}_3)]$ in the molar ratio 1:2 or 1:1 gives the dinuclear $[(\mu\text{-dptpf})(\text{AuPPh}_3)_2](\text{ClO}_4)_2$ (**3**) or the mononuclear $[\text{Au}(\text{dptpf})(\text{PPh}_3)]\text{ClO}_4$ (**4a**), respectively. The complex $[\text{Au}(\text{dptpf})(\text{PPh}_3)]\text{OTf}$ (**4b**) ($\text{OTf} = \text{CF}_3\text{SO}_3$) can be obtained by reaction of $[\text{Au}(\text{dptpf})]\text{OTf}$ with PPh_3 . These are yellow–brown air- and moisture-stable solids and behave as 1:2 (**3**) or 1:1 (**4a**, **4b**) electrolytes in acetone solution. Their IR spectrum shows, apart from the bands arising from the dptpf and phosphine ligands, those of the perchlorate at 1096(vs, br) and 623(m) cm^{-1} or triflate at 1265(vs, br), 1225(s) and 1155(s) cm^{-1} . The positive-ion LSIMS exhibit a peak corresponding to the cation $[\text{Au}_2(\text{dptpf})(\text{PPh}_3)]^+$ [$m/z = 1273$ (19%)] for complex **3** and the cation molecular peak $[\text{Au}(\text{dptpf})(\text{PPh}_3)]^+$ [$m/z = 1077$, 20%] for complexes **4a** and **4b**. The most intense peak in these spectra is the fragment $[\text{Au}(\text{dptpf})]^+$, which appears at $m/z = 815$.

The ^1H -NMR spectra show, apart from the multiplet from the phenyl protons, two multiplets of the cyclopentadienyl ring. The $^{31}\text{P}\{-^1\text{H}\}$ -NMR spectra present two singlets at 41.7 and 37.4 ppm (**3**) or 45.1 and 37.6 ppm (**4**), for the two different phosphorus environments.

The oxidative addition of chlorine to dinuclear gold(I) derivatives is a standard synthesis of dinuclear gold(II) complexes with gold–gold bonds. We therefore studied the reaction of complex **1** with an equimolar amount of chlorine. The yellow solution of **1** in dichloromethane turns orange–red on addition of the halogen, but the solution slowly fades to yellow and the

ionic complex $[\text{Au}(\text{dptpf})][\text{AuCl}_4]$ (**5**) is isolated. We believe that the intermediate orange–red product should be the dinuclear gold(II) derivative, $[(\mu\text{-dptpf})(\text{AuCl}_2)_2]$, but that it isomerises to the mixed gold(I)–gold(III) derivative. Complex **5** behaves as a 1:1 electrolyte in acetone solution. In the IR spectrum the $\nu(\text{Au}–\text{Cl})$ vibration appears at 359(m) cm^{-1} . The $^{31}\text{P}\{-^1\text{H}\}$ -NMR spectrum presents a singlet at 45.7 ppm.

The structure of complex **5** has been confirmed by an X-ray crystal diffraction study (Fig. 1, Table 1). The asymmetric unit consists of one cation on a general position and two half anions, in each of which the gold and two chlorine atoms lie on a two-fold axis. In the cation the gold atom is linearly coordinated with an angle $\text{S}–\text{Au}–\text{S}$ of $174.5(2)^\circ$, which is marginally more bent than in the complex $[\text{Au}(\text{dptpf})]\text{OTf}$ ($176.43(12)^\circ$).

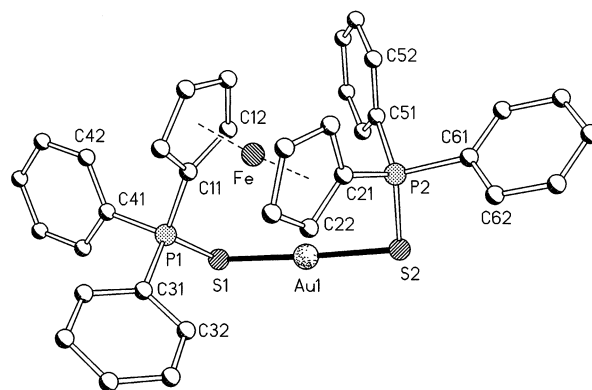


Fig. 1. Molecular structure of the cation of complex **5** in the crystal showing the atom numbering scheme. Hydrogen atoms are omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complex **5**^a

Bond lengths			
Au(1)–S(1)	2.281(5)	Au(1)–S(2)	2.299(5)
Fe–C(15)	2.014(12)	Fe–C(25)	2.022(12)
Fe–C(11)	2.025(12)	Fe–C(14)	2.031(12)
Fe–C(21)	2.031(12)	Fe–C(24)	2.035(12)
Fe–C(12)	2.049(12)	Fe–C(22)	2.049(13)
Fe–C(23)	2.052(13)	Fe–C(13)	2.052(13)
P(1)–C(11)	1.780(10)	P(1)–C(41)	1.804(10)
P(1)–C(31)	1.804(10)	P(1)–S(1)	2.023(7)
P(2)–C(61)	1.800(9)	P(2)–C(21)	1.813(10)
P(2)–C(51)	1.826(10)	P(2)–S(2)	1.986(7)
Au(2)–Cl(3)	2.271(9)	Au(2)–Cl(1)	2.280(6)
Au(2)–Cl(2)	2.280(8)	Au(3)–Cl(5)	2.272(11)
Au(3)–Cl(4)	2.278(6)	Au(3)–Cl(6)	2.287(9)
Bond angles			
S(1)–Au(1)–S(2)	174.5(2)	P(1)–S(1)–Au(1)	103.6(3)
C(61)–P(2)–C(51)	107.0(6)	C(61)–P(2)–C(51)	106.6(6)
C(21)–P(2)–C(51)	111.4(6)	C(61)–P(2)–S(2)	107.8(5)
C(21)–P(2)–S(2)	110.2(5)	C(51)–P(2)–S(2)	113.4(5)
P(2)–S(2)–Au(1)	97.5(2)	C(15)–C(11)–P(1)	125.3(8)
C(12)–C(11)–P(1)	125.4(8)	C(25)–C(21)–P(2)	125.5(8)
C(22)–C(21)–P(2)	126.4(8)	C(32)–C(31)–P(1)	118.7(8)
C(36)–C(31)–P(1)	121.1(8)	C(42)–C(41)–P(1)	120.3(8)
C(46)–C(41)–P(1)	119.6(8)	C(52)–C(51)–P(2)	120.3(7)
C(56)–C(51)–P(2)	119.5(7)	C(62)–C(61)–P(2)	116.8(7)
C(66)–C(61)–P(2)	123.2(7)	Cl(3)–Au(2)–Cl(1)	90.3(2)
Cl(1) # 1–Au(2)–Cl(1)	179.5(3)	Cl(3)–Au(2)–Cl(2)	180.0
Cl(1)–Au(2)–Cl(2)	89.7(2)	Cl(5)–Au(3)–Cl(4)	89.9(2)
Cl(4)–Au(3)–Cl(4) # 2	179.7(4)	Cl(5)–Au(3)–Cl(6)	180.0
Cl(4)–Au(3)–Cl(6)	90.1(2)		

^a Symmetry transformations used to generate equivalent atoms: (# 1) $-x, -x+y, -z-1/3$; (# 2) $y, x, -z$.

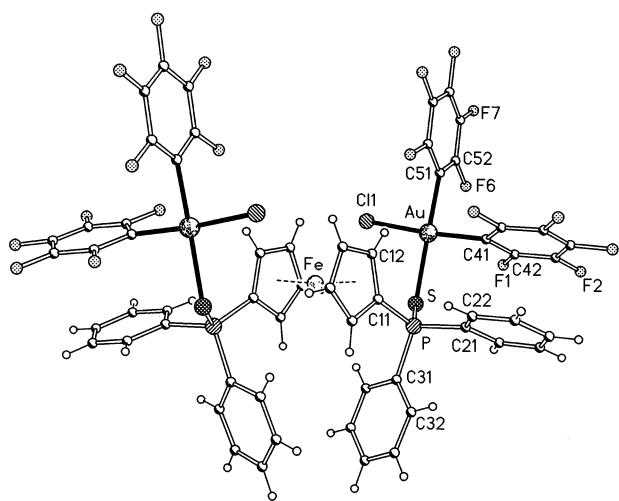


Fig. 2. The structure of complex **7** in the crystal with the atom labelling scheme.

and 178.26(11), two independent molecules) [6]. The Au–S bond distances are 2.281(5) and 2.299(5) Å, which are also in the same range as those in [Au(dtpf)]OTf (2.280(3)–2.302(3) Å). The coordination of the gold(III) atoms is square-planar as expected. The

two P=S bonds are *gauche* to each other, with the torsion angle P1–S1···S2–P2 = 41.9(4)°. Noteworthy features of the crystal packing are several interactions of the form C–H···Cl with H···Cl between 2.64 and 3.05 Å; the shortest is H62···Cl6 ($x, -1+y, z$), with a C–H···Cl angle of 165°. These contacts can reasonably be assigned as hydrogen bonds [13,14].

The cyclopentadienyl rings adopt an almost eclipsed orientation with a torsion angle C(12)–centre–centre–C(21) of 10.1°. The intramolecular gold–iron contact is 3.869 Å, but there are no short gold–gold interactions, the shortest Au···Au distance being 4.75 Å.

The gold(III) complexes [(μ-dtpf){Au(C₆F₅)₃}₂] (**6**) or [(μ-dtpf){Au(C₆F₅)₂Cl}]₂ (**7**) have been obtained by reaction of dtpf with [Au(C₆F₅)₂Cl]₂ or [Au(C₆F₅)₃-(OEt₂)], respectively, in a 1:2 molar ratio. They are orange (**6**) or yellow (**7**) air- and moisture-stable solids and are non-conducting in acetone solutions. In the IR spectrum of **6** the ν(Au–Cl) vibration appears at 349(m) cm^{−1}. The positive-ion LSIMS do not show the cation molecular peak; however the fragments [Au(C₆F₅)₃-(dtpf)]⁺ [m/z = 1316, 3%] or [Au(C₆F₅)₂ClH(dtpf)]⁺ [m/z = 1185, 1%] and [Au(C₆F₅)₂(dtpf)]⁺ [m/z = 1149, 40%] are present for complexes **6** or **7**, respectively.

The ¹H-NMR spectra show two multiplets for the α and β protons of the cyclopentadienyl ring, and the ³¹P-{¹H}-NMR spectra present only a singlet. The ¹⁹F-NMR spectra show six resonances corresponding to two types of pentafluorophenyl groups, in a ratio 1:1 (**7**, indicating a *cis* position for the two C₆F₅ groups) or 2:1 (**6**), due to the *ortho*, *meta* or *para* fluorine atoms.

The crystal structure of complex **7** has been established by an X-ray diffraction study (Fig. 2). A selection of bond lengths and angles are presented in Table 2. The iron atom lies on a two-fold axis and thus only half of the molecule corresponds to the asymmetric unit. The geometry of the gold atoms is square-planar with the two pentafluorophenyl groups occupying *cis* positions; the gold atom lies 0.021 Å out of the plane of

Table 2
Selected bond lengths (Å) and angles (°) for complex **7**

Bond lengths			
Au–C(41)	2.008(8)	S–P	2.020(3)
Au–C(51)	2.040(8)	P–C(11)	1.775(8)
Au–Cl(1)	2.316(2)	P–C(31)	1.805(9)
Au–S	2.386(2)	P–C(21)	1.816(8)
Bond angles			
C(41)–Au–C(51)	87.9(3)	C(11)–P–C(31)	106.2(4)
C(41)–Au–Cl(1)	174.6(2)	C(11)–P–C(21)	107.9(3)
C(51)–Au–Cl(1)	87.4(2)	C(31)–P–C(21)	106.9(3)
C(41)–Au–S	93.9(2)	C(11)–P–S	115.7(3)
C(51)–Au–S	174.4(2)	C(31)–P–S	106.8(3)
Cl(1)–Au–S	90.53(7)	C(21)–P–S	112.7(3)
P–S–Au	108.08(10)		

the four donor atoms. The Au–S distance is 2.386(2) Å and is of the same order as those in similar complexes such as $[\text{Au}(\text{C}_6\text{F}_5)_2\{(\text{SPPPh}_2)_2\text{CCH}_2\text{Cp}\}]$ (2.3552(9) and 2.3626(9) Å) [15]. The Au–Cl distance is 2.316(2) Å, similar to those in complexes such as $[\text{AuCl}_2(\eta^2\text{-S}_2\text{CCl})]$ [16], but longer than those in $[\text{AuCl}_4]^-$ salts (e.g. 2.281(3)–2.287(2) Å) [17], presumably because of the higher *trans* influence of the pentafluorophenyl group.

The gold–iron distance is 4.821 Å, longer than in complex **5**. The shortest Cl⋯H and F⋯H contacts are C36–H36⋯Cl1 (1–*x*, 1–*y*, 1–*z*; H⋯Cl 2.65 Å, angle 149°) and C23–H23⋯F2 (*x*, 1–*y*, 0.5+*z*; H⋯F 2.55 Å, angle 168°).

3. Experimental

IR spectra were recorded on a Perkin–Elmer 883 spectrophotometer, over the range 4000–200 cm^{-1} , using Nujol mulls between polyethylene sheets. Conductivities were measured in ca. 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. C, H, and S analyses were carried out with a Perkin–Elmer 2400 microanalyser. Mass spectra were recorded on a VG Autospec, with the LSIMS technique, using nitrobenzyl alcohol as matrix. ^1H -, ^{19}F - and ^{31}P - $\{^1\text{H}\}$ -NMR spectra were recorded on a Varian Unity 300, Bruker ARX 300 or Gemini 2000 apparatus in CDCl_3 solutions (kept with Na_2CO_3), if no other solvent is stated; chemical shifts are quoted relative to SiMe_4 (external, ^1H), CFCl_3 (external, ^{19}F) and 85% H_3PO_4 (external, ^{31}P).

The starting materials $[\text{AuCl}(\text{tht})]$ [18], $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ [18], $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)]$ [18], $[\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}]_2$ [19], and dptpf [20] were prepared by published procedures. $[\text{Au}(\text{OCIO}_3)(\text{PPh}_3)]$ was prepared from $[\text{AuCl}(\text{PPh}_3)]$ [18] by reaction with AgClO_4 in dichloromethane. All other chemicals used were commercially available and used without further purification. **Caution:** perchlorate salts with organic cations may be explosive.

3.1. Syntheses

3.1.1. $[(\mu\text{-dptpf})(\text{AuX})_2]$ (*X* = Cl, **1**; C_6F_5 , **2**)

To a solution of dptpf (0.062 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[\text{AuCl}(\text{tht})]$ (0.064 g, 0.2 mmol) or $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{tht})]$ (0.090 g, 0.2 mmol) and the mixture was stirred for 90 min. Concentration of the solution to ca. 5 cm^3 and addition of diethyl ether (10 cm^3) gave complexes **1** or **2** as yellow solids. Complex **1**: yield 82%. M_M 13 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Elemental analysis (%), Found: C, 38.05; H, 2.6; S, 5.5. Calc. for $\text{C}_{34}\text{H}_{28}\text{Au}_2\text{Cl}_2\text{FeP}_2\text{S}_2$: C, 37.65; H, 2.6; S, 5.9%. ^1H -NMR, δ : 4.65 (m, 4H), 4.70 (m, 4H), 7.4–7.7 (m, 20H, Ph). ^{31}P - $\{^1\text{H}\}$ -NMR, δ : 44.1 (s). Complex **2**: yield 60%. M_M 14 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Elemental analysis (%), Found: C, 40.95; H, 2.1; S, 4.75. Calc. for

$\text{C}_{46}\text{H}_{28}\text{Au}_2\text{F}_{10}\text{FeP}_2\text{S}_2$: C, 41.05; H, 2.1; S, 4.75%. ^1H -NMR, δ : 4.65 (m, 4H), 4.70 (m, 4H), 7.4–7.7 (m, 20H, Ph). ^{31}P - $\{^1\text{H}\}$ -NMR, δ : 46.7 (m). ^{19}F -NMR, δ : –116.7 (m, 2F, *o*-F), –160.3 (t, 1F, *p*-F, *J*(FF) 19.3 Hz), –163.3 (m, 2F, *m*-F).

3.1.2. $[(\mu\text{-dptpf})(\text{AuPPh}_3)_2](\text{ClO}_4)_2$ (**3**) or $[\text{Au}(\text{dptpf})(\text{PPh}_3)]\text{ClO}_4$ (**4a**)

To a solution of $[\text{Au}(\text{OCIO}_3)(\text{PPh}_3)]$ (0.2 or 0.1 mmol, respectively) in dichloromethane (20 cm^3) was added dptpf (0.062 g, 0.1 mmol) and the mixture was stirred for 90 min. Concentration of the solution to ca. 5 cm^3 and addition of diethyl ether (10 cm^3) gave complexes **3** and **4a** as yellow–brown solids. Complex **3**: yield 88%. M_M 200 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Elemental analysis (%), Found: C, 48.1; H, 3.3; S, 4.15. Calc. for $\text{C}_{70}\text{H}_{58}\text{Au}_2\text{Cl}_2\text{FeO}_8\text{P}_4\text{S}_2$: C, 48.45; H, 3.35; S, 3.7%. ^1H -NMR, δ : 4.59 (m, 4H), 4.71 (m, 4H), 7.3–7.78 (m, 50H, Ph). ^{31}P - $\{^1\text{H}\}$ -NMR, δ : 37.4 (s, PPh_3), 47.1 (s, dptpf). Complex **4a**: yield 62%. M_M 135 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Elemental analysis (%), Found: C, 52.8; H, 2.35; S, 5.19. Calc. for $\text{C}_{52}\text{H}_{43}\text{AuClFeO}_4\text{P}_3\text{S}_2$: C, 53.0; H, 2.4; S, 5.45%. ^1H -NMR, δ : 4.49 (m, 4H), 4.58 (m, 4H), 7.3–7.78 (m, 35H, Ph). ^{31}P - $\{^1\text{H}\}$ -NMR, δ : 37.6 (s, PPh_3), 45.1 (s, dptpf).

3.1.3. $[\text{Au}(\text{dptpf})(\text{PPh}_3)]\text{OTf}$ (**4b**)

To a solution of $[\text{Au}(\text{dptpf})]\text{OTf}$ (0.092 g, 0.1 mmol) in 20 cm^3 of dichloromethane was added PPh_3 (0.026 g, 0.1 mmol) and the mixture was stirred for 10 min. Concentration of the solution to ca. 5 cm^3 and addition of diethyl ether (10 cm^3) gave complex **4b** as a yellow–brown solid. Yield 77%. M_M 149 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Elemental analysis (%), Found: C, 50.95; H, 3.85; S, 4.85. Calc. for $\text{C}_{53}\text{H}_{43}\text{AuF}_3\text{FeO}_3\text{P}_3\text{S}_3$: C, 50.45; H, 3.6; S, 5.05%.

3.1.4. $[\text{Au}(\text{dptpf})][\text{AuCl}_4]$ (**5**)

To a solution of complex **1** (0.108 g, 0.1 mmol) in 30 cm^3 of dichloromethane was added a CCl_4 solution of chlorine (0.25 cm^3 , 0.4 N, 0.1 mmol) and the mixture was stirred for 10 min. Concentration of the solution to ca. 5 cm^3 and addition of diethyl ether (10 cm^3) gave complex **5** as a yellow solid. Yield 87%. M_M 139 $\text{ohm}^{-1} \text{cm}^2 \text{mol}^{-1}$. Elemental analysis (%), Found: C, 35.8; H, 2.55; S, 4.85. Calc. for $\text{C}_{34}\text{H}_{28}\text{Au}_2\text{Cl}_4\text{FeP}_2\text{S}_2$: C, 35.3; H, 2.45; S, 5.5%. ^1H -NMR, δ : 4.6 (m, 8H), 7.3–7.7 (m, 20H, Ph). ^{31}P - $\{^1\text{H}\}$ -NMR, δ : 45.7 (s).

3.1.5. $[(\mu\text{-dptpf})\{\text{Au}(\text{C}_6\text{F}_5)_3\}_2]$ (**6**) or $[(\mu\text{-dptpf})\{\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}\}_2]$ (**7**)

To a solution of $[\text{Au}(\text{C}_6\text{F}_5)_3(\text{OEt}_2)]$ (0.154 g, 0.2 mmol) or $[\text{Au}(\text{C}_6\text{F}_5)_2\text{Cl}]_2$ (0.113 g, 0.1 mmol) in dichloromethane (20 cm^3) was added dptpf (0.062 g, 0.1 mmol) and the mixture was stirred for 1 h. Concentra-

Table 3

Details of data collection and structure refinement for complexes **5** and **7**

Compound	5	7 .3CH ₂ Cl ₂
Chemical formula	C ₃₄ H ₂₆ Au ₂ Cl ₄ FeP ₂ S ₂	C ₆₁ H ₃₄ Au ₂ Cl ₈ F ₂₀ FeP ₂ S ₂
Crystal habit	Orange prism	Yellow prism
Crystal size (mm)	0.4 × 0.3 × 0.2	0.4 × 0.4 × 0.3
Crystal system	Trigonal	Monoclinic
Space group	<i>P</i> 3 ₂ 21	<i>C</i> 2/ <i>c</i>
<i>a</i> (Å)	12.715(2)	29.705(3)
<i>b</i> (Å)	12.715(2)	14.955(2)
<i>c</i> (Å)	38.197(6)	17.658(2)
<i>a</i> (°)	90	90
<i>β</i> (°)	90	115.113(12)
<i>γ</i> (°)	120	90
<i>U</i> (Å ³)	5348(2)	7103.1(14)
<i>Z</i>	6	4
<i>D</i> _{calc.} (Mg m ^{−3})	2.147	1.903
<i>M</i>	1152.19	2034.65
<i>F</i> (000)	3264	3904
<i>T</i> (°C)	−100	−100
2 θ _{max} (°)	50	50
μ (Mo–K α) (mm ^{−1})	2.147	4.843
Transmission	0.843–0.972	0.815–0.971
No. of reflections measured	6120	6499
No. of unique reflections	5614	6202
<i>R</i> _{int}	0.058	0.037
<i>R</i> ^a (<i>F</i> , <i>F</i> > 4 σ (<i>F</i>))	0.058	0.044
<i>wR</i> ^b (<i>F</i> ² , all reflections)	0.112	0.105
No. of parameters	173	447
No. of restraints	34	367
<i>S</i> ^c	0.842	0.908
Max. $\Delta\rho$ (e Å ^{−3})	1.424	1.97

$$^a R(F) = \frac{\sum \|F_o\| - |\sum F_c|}{\sum \|F_o\|}$$

^b $wR(F^2) = [\sum \{w(F_o^2 - F_c^2)^2\} / \sum \{w(F_o^2)^2\}]^{0.5}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, where $P = [F_o^2 + 2F_c^2]/3$ and *a* and *b* are constants adjusted by the program.

^c $S = [\sum \{w(F_o^2 - F_c^2)^2\} / (n - p)]^{0.5}$, where *n* is the number of data and *p* the number of parameters.

tion of the solution to ca. 5 cm³ and addition of diethyl ether (10 cm³) gave complexes **6** and **7** as orange or yellow solids, respectively. Complex **6**: yield 86%. *A*_M 14 ohm^{−1} cm² mol^{−1}. Elemental analysis (%), Found: C, 41.25; H, 0.95; S, 2.95. Calc. for C₇₀H₂₈Au₂F₃₀FeP₂S₂: C, 41.75; H, 1.4; S, 3.15%. ¹H-NMR, δ : 4.36 (m, 4H), 4.57 (m, 4H), 7.4–7.7 (m, 20H, Ph). ³¹P-{¹H}-NMR, δ : 40.4 (s). ¹⁹F-NMR, δ : −120.4 (m, 4F, *o*-F), −157.5 (t, 2F, *p*-F, *J*(FF) 20.6 Hz), −161.5 (m, 4F, *m*-F); −122.3 (m, 2F, *o*-F), −157.3 (t, 1F, *p*-F, *J*(FF) 20.6 Hz), −161.7 (m, 2F, *m*-F). Complex **7**: yield 78%. *A*_M 71 ohm^{−1} cm² mol^{−1}. Elemental analysis (%), Found: C, 40.05; H, 1.65; S, 3.55. Calc. for C₅₈H₂₈Au₂Cl₂F₂₀FeP₂S₂: C, 49.8; H, 1.6; S, 3.65%. ¹H-NMR, δ : 4.63 (m, 4H), 4.89 (m, 4H), 7.4–7.7 (m, 20H, Ph). ³¹P-{¹H}-NMR, δ : 45.7 (s). ¹⁹F-NMR, δ : −121.7 (m, 2F, *o*-F), −156.5 (t, 1F,

p-F, *J*(FF) 20 Hz), −161.0 (m, 2F, *m*-F); −122.9 (m, 2F, *o*-F), −157.2 (t, 1F, *p*-F, *J*(FF) 20.1 Hz), −161.6 (m, 2F, *m*-F).

3.2. Crystallography

The crystals were mounted in inert oil on a glass fibre and transferred to the cold gas stream of a Siemens P4 diffractometer equipped with an LT-2 low-temperature attachment. Data were collected using monochromated Mo–K α radiation ($\lambda = 0.71073$ Å). Scan type ω . Cell constants were refined from setting angles of ca. 60 reflections in the range 2 θ 10–25°. Psi-scans were applied for both complexes. The structures were solved by the heavy-atom method and refined on *F*² using the programs SHELXL-93 (**5**) or -97 (**7**) [21]. For **7**, all non-hydrogen atoms were refined anisotropically; for **5**, idealised isotropic rings were employed. Hydrogen atoms were included using a riding model.

3.2.1. Special refinement details

For **5**, the absolute structure (and thus the sense of the three-fold screw axis) was determined by an *x* refinement; *x* = 0.00(2). For both structures, a system of restraints to light-atom displacement-factor components and (for **7** additionally) to local ring symmetry was used. The solvent areas were ill defined; one molecule is disordered over an inversion centre. Further details of the data collection are given in Table 3.

4. Supplementary material

Complete crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre under the numbers CCDC 125989 (**5**) and CCDC 125988 (**7**). Copies can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

We thank the Dirección General de Enseñanza Superior (No. PB97-1010-C02-01) and the Fonds der Chemischen Industrie for financial support.

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