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Gold complexes with mono- or di-chalcogenides of bis(diphenylphosphino)methanide ligands. X-ray crystal structure of $[Au(C_6F_5)_2\{(SPPh_2)_2C(AuAsPh_3)_2\}]ClO_4$

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Abstract—The reaction between the chalcogenide derivatives $[Au(C_6F_5)_3(PPh_2CH_2PPh_2E)]$ (E = S, O) and $[Au(acac)PPh_3]$ or $[Au(TfO)PPh_3]$ leads to the dinuclear compounds $[Au(C_6F_5)_3\{PPh_2CH(AuPPh_3)PPh_2E\}]$ (E = S, O) or $[Au(C_6F_5)_3\{PPh_2CH_2PPh_2(SAuPPh_3)\}]$, respectively. When the phosphine disulphide complex $[Au(C_6F_5)_3(SPPh_2CH_2PPh_2S)]$ is employed, the reaction with $[Au(acac)PPh_3]$ promotes the double substitution of the methylenic protons. The reaction of $[Au(acac)L]$ (L = PPh_3, $AsPh_3$) with the six-membered auracycle $[Au(C_6F_5)_2\{(SPPh_2)_2CH_2\}]ClO_4$ leads to the double substitution of both methylenic protons by $[AuL]^+$ fragments, keeping the auracycle intact. The crystal structure of one such product, $[Au(C_6F_5)_2\{(SPPh_2)_2C(AuAsPh_3)_2\}]ClO_4$ has been established by X-ray diffraction studies. Starting from the methanide derivative $[Au(C_6F_5)_2(SPPh_2CHPPh_2S)]$, the reaction with $[Au(acac)PPh_3]$ leads to the synthesis of the four-membered ring methanide $[Au(C_6F_5)_2\{SPPh_2C(AuPPh_3)PPh_2S\}]$ © 1998 Elsevier Science Ltd. All rights reserved

Keywords: gold; diphosphinedichalcogenide; diphosphinemonochalcogenide; methanide; crystal structure.

In the last few years there has been a renewed interest in the chemistry of diphosphine chalcogenide ligands and their methanide derivatives [1–5], which can be attributed to the tendency of the diphosphine chalcogenides to charge delocalization, thus enhancing the acidity of the methylenic protons as well as the lability of the chalcogen–metal bonds [6]. This lability can give rise to dynamic processes and thus renders these ligands appropiate for catalytic applications [7–10].

The introduction of oxygen or sulfur atoms at one or both phosphorus centres in bis(diphenylphosphino)methane after or prior to metal complexation can change the character of the donor atom or lead to metallacycle ring expansion, depending on the starting complex employed. This may have a significant influence on the coordination properties or on the reactivity of these products.

The present paper reports the synthesis of some gold(III) derivatives containing mono- or di-chalcogenides of bis(diphenylphosphino)methane and their reactivity towards reagents of the type [Au (acac)L] (acac = acetylacetonate) forming methanide complexes. We employed tris(pentafluorophenyl)gold(III) derivatives, which afford non-cyclic methanides in a different way from that recently described [11] or $[Au(C_6F_5)_2(SPPh_2CH_2PPh_2S)]ClO_4$ [12], from which we have synthesized methanediide species containing a six-membered metallacycle. These last products are not accessible through other

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classical methods, which lead instead to the formation of four-membered rings.

RESULTS AND DISCUSSION

The reaction of $[Au(C_6F_5)_3(PPh_2CH_2PPh_2)]$ and equimolecular amounts of sulfur leads to the sulfuration of the free phosphorus to give $[Au(C_6F_5)_3(PPh_2CH_2PPh_2S)]$ (**1**) (see Scheme 1).

Compound **1** is stable to air and moisture, soluble in most common organic solvents and insoluble in hexane. The IR spectrum of this compound shows the characteristic pattern of tris(pentafluorophenyl) gold(III) groups [13]. Besides, a weak band at 611 cm^{-1} corresponding to the ν(P—S) vibration appears [14]. The $^{31}P\{^1H\}$ and ^{19}F NMR spectra of this compound are also in accordance with the proposed structure (see Experimental section).

The presence of the chalcogenide atom near the phosphorus increases the acidity of the methylenic protons of the phosphine and this increase is greater for the sulfur than for the oxygen derivative. Thus, the resonance of the methylene group in complex **1** appears at $\delta = 3.66$ (t), shifted downfield compared to the starting material ($\delta = 3.2$) and making it appropriate for further deprotonations.

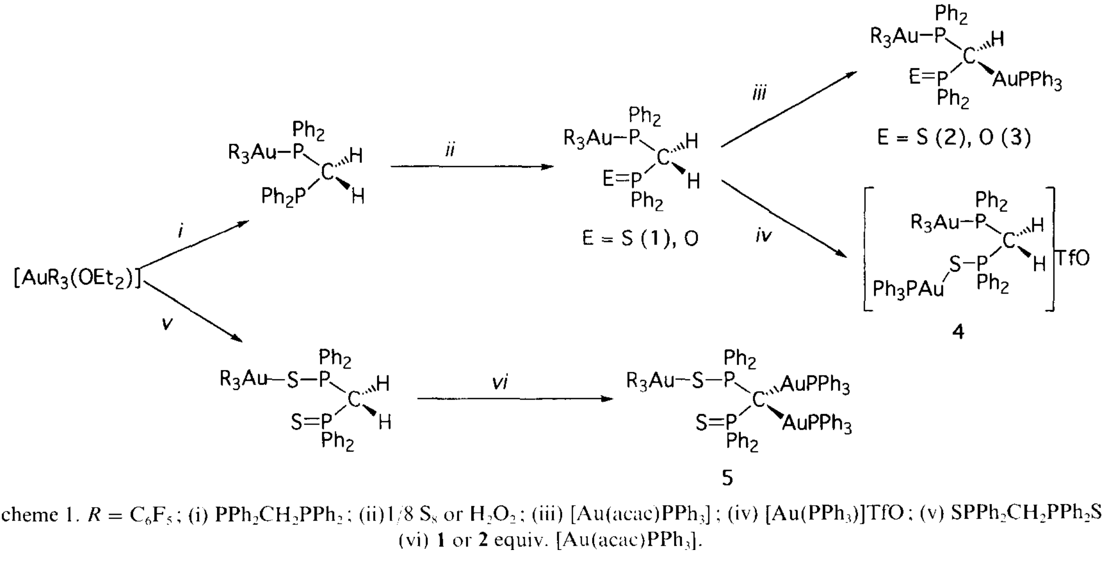
When complex **1** or the corresponding oxygen derivative $[Au(C_6F_5)_3(PPh_2CH_2PPh_2O)]$ [15] are treated with equimolecular amounts of $[Au(acac)PPh_3]$ in dichloromethane, a methylenic proton is substituted by an $[AuPPh_3]^+$ group, affording the dinuclear species $[Au(C_6F_5)_3\{PPh_2CH(AuPPh_3)PPh_2E\}]$ (E = S (**2**), O (**3**)) (Scheme 1). As we already observed in previous studies [16], the substitution of a methylenic proton by an $[AuL]^+$ fragment (L = tertiary phosphine) also increases the acidity of the second methylenic H atom. However, in this case an excess of $[Au(acac)PPh_3]$ does not produce the double substitution.

Complexes **2** and **3** are air and moisture-stable solids, soluble in chlorinated solvents, acetone and diethyl ether and insoluble in hexane. Their analytical and spectroscopic data are in accordance with the proposed formulation; e.g. they display three resonances with relative intensities 1 : 1 : 1 in their $^{31}P\{^1H\}$ spectra.

The reaction of complex **1** with the aurating agent $[Au(TfO)PPh_3]$ (TfO = trifluoromethanesulfonate), prepared *in situ* by reaction of $[AuClPPh_3]$ and AgTfO in dichloromethane, leads to the dinuclear complex $[Au(C_6F_5)_3\{PPh_2CH_2PPh_2(SAuPPh_3)\}]TfO$ (**4**), in which the coordination of the new $[AuPPh_3]^+$ fragment takes place at the sulfur atom.

When the phosphine disulphide derivative $[Au(C_6F_5)_3(SPPh_2CH_2PPh_2S)]$ [12] is employed instead of the monosulphide, its reaction with $[Au(acac)PPh_3]$ leads to the synthesis of the di-substituted product $[Au(C_6F_5)_3\{SPPh_2C(AuPPh_3)_2PPh_2S\}]$ (**5**), whatever the molar ratio of the gold(I) derivative and without formation of the monosubstituted species $[Au(C_6F_5)_3\{SPPh_2CH(AuPPh_3)PPh_2S\}]$ (Scheme 1). This result is probably attributable to two factors: (i) the increase of the acidity that the second sulfur atom produces in the methylenic protons and (ii) the increase of the length of the phosphine ligand, reducing the steric restrictions that prevented the synthesis of disubstituted non-cyclic methanides as reported in a previous paper [11].

Complex **5** is obtained as a pale yellow stable solid soluble in acetone, ether and chlorinated solvents and insoluble in hexane. Its $^{31}P\{^1H\}$ NMR spectrum dis-



Scheme 1. $R = C_6F_5$; (i) $PPh_2CH_2PPh_2$; (ii) 1/8 S_8 or H_2O_2; (iii) $[Au(acac)PPh_3]$; (iv) $[Au(PPh_3)]TfO$; (v) $SPPh_2CH_2PPh_2S$; (vi) **1** or **2** equiv. $[Au(acac)PPh_3]$.

plays two different resonances for the diphosphine phosphorus and a pseudo-triplet at $\delta = 35.2$ from both phosphorus atoms of the PPh_3 groups.

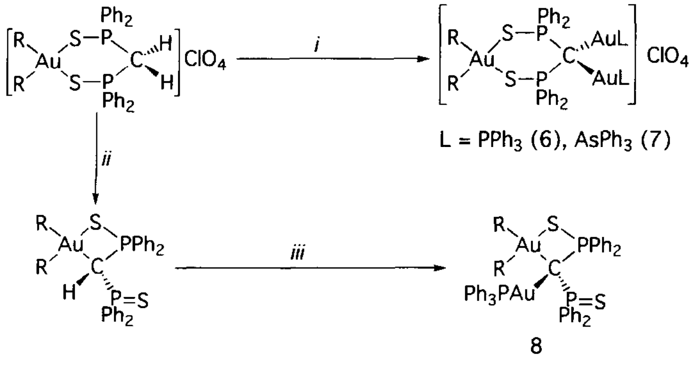
In the case of the diaryl complex $[Au(C_6F_5)_2(SPPh_2CH_2PPh_2S)]ClO_4$ [12], which contains the phosphine disulphide as a chelate, the increase of acidity produced by the sulfur centres is also demonstrated by its reaction with [Au(acac)L] (L = PPh_3, $AsPh_3$). Treatment of one equivalent of the starting complex with two equivalents of [Au(acac)L] results in the substitution of both methylenic protons by two $[AuL]^+$ groups with formation of $[Au(C_6F_5)_2\{(SPPh_2)_2C(AuL)_2\}]ClO_4$ (L = PPh_3 (**6**), $AsPh_3$ (**7**)) (Scheme 2). This is a surprising result in view of our previous studies with the same starting complex, because the employment of stronger deprotonating agents, such as NaH, led to the formation of four membered rings [12].

Complexes **6** and **7** are pale yellow solids, moisture and air stable. They are soluble in chlorinated solvents and acetone and they behave as 1 : 1 electrolytes in this solvent. Their analytical and spectroscopic data are in accordance with their formulation. The resonance from the phosphorus of the diphosphine sulphide appears as a triplet at $\delta = 43.9$ (**6**) or as a singlet at $\delta = 42.6$ (**7**) in their $^{31}P\{^1H\}$ NMR spectra. In the spectrum of the triphenylphosphine derivative **6** the signal corresponding to the PPh_3 groups is located at $\delta = 36.3$ and appears as a triplet because of the coupling with both phosphorus of the chelating ligand.

The crystal structure of complex **7** has been determined. The cation is shown in Fig. 1, with selected bond lengths and angles in Table 1. The complex crystallizes with two independent formula units; the overall distances and angles are very similar and consequently we will comment on only one of them. The precision is not very good for reasons discussed below. The coordination around the gold(III) center is slightly distorted from square planar, whereby the wide bite of the diphosphine disulphide ligand represents the major deviation from ideal geometry, S(2)—Au(1)—S(1) 102.0(2)°. This bite angle is unusually high for a chelating ligand in gold(III) complexes, compared with other examples such as $[Au(C_6F_5)_2(SPPh_2CHPPh_2)]$ (S—Au—P 89.6(1)°) [17] or $[Au(C_6F_5)_2\{(PPh_2)_2C(AuPPh_3)_2\}]ClO_4$ (P—Au—P 70.5(3)°) [16]. The gold(III) atom is coplanar with the C(11), C(21), S(1) and S(2) atoms. The Au—S distances, 2.390(7) and 2.357(8) Å, are longer than those found in $[Au(C_6F_5)_2(SPPh_2CHPPh_2)]$ (2.345(2) Å). The P—S bond lengths are 2.029(11) and 2.050(10) Å corresponding to a slightly shortened single bond. The gold(I) atoms exhibit essentially linear geometry and lie only 2.873(2) Å from each other. These short gold–gold contacts are very frequent in this type of polynuclear methanide complexes e.g., $[Au(C_6F_5)_2\{(PPh_2)_2C(AuPPh_3)_2\}]ClO_4$(Au···Au 2.826(2) Å) or $[Au_2\{(PPh_2)_2C(AuPPh_3)_2\}_2](ClO_4)_2$ [18] (Au···Au 2.920(2)–2.987(2) Å). The Au—As bond lengths 2.365(3) and 2.370(3) Å are similar to those in the complexes $[Au(CH_3)(AsPh_3)]$ (2.3800(11) Å) [19] or $[Au(CH_2CH_3\text{-}closo\text{-}C_2B_{10}H_{10})(AsPh_3)]$ [19] (2.3740(8) Å) which also have a carbon donor ligand *trans* to the Au—As bond.

Using the same starting complex we have synthesized another methanide featuring a four-membered ring instead a six-membered one. This is made possible by treating it first with NaH, which causes a change in the coordination of the chelating ligand: one sulfur atom is replaced by the new methanide carbon atom at the gold(III) centre. If this product is now treated with one equivalent of $[Au(acac)PPh_3]$, the second methylenic proton is then removed and the $[AuPPh_3]^+$ takes its place (see Scheme 2).

Complex **8** is a yellow solid stable to air and moisture. It is soluble in chlorinated solvents and insoluble in diethyl ether or hexane. The IR spectrum shows two bands at 575 (w) and 625 (m) cm^{-1} due to the ν(P—S) vibration, in accordance with the presence of a free and a coordinated sulfur atom [20]. In the $^{31}P\{^1H\}$ NMR spectrum the signals corresponding to the three non equivalent phosphorus appear at $\delta = 46.9$, 37.5 and 34.8 with 1 : 1 : 1 relative intensity and no coupling between the different phosphorus is observed.



Scheme 2. $R = C_6F_5$; (i) **2** [Au(acac)L]; (ii) NaH; (iii) $[Au(acac)PPh_3]$.

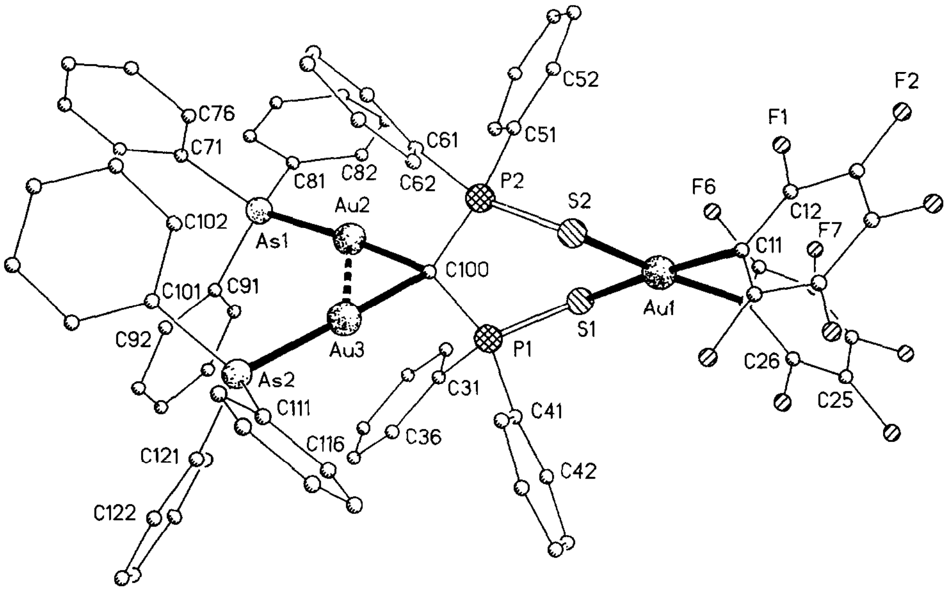


Fig. 1. The cation of complex **7** in the crystal with the atom labelling scheme. H atoms are omitted for clarity, radii are arbitrary.

EXPERIMENTAL

General

NMR spectra were recorded on a Bruker ARX 300 spectrometer in $CDCl_3$ solutions. Chemical shifts are quoted relative to $SiMe_4$ (^{1}H, external), $CFCl_3$ (^{19}F, external) and H_3PO_4 (85%) (^{31}P, external). All experiments were carried out at room temperature and under nitrogen except for **1**.

$[Au(C_6F_5)_3(PPh_2CH_2PPh_2S)]$ (**1**)

To a toluene solution of $(Au(C_6F_5)_3(PPh_2CH_2PPh_2)]$ [13] (0.27 g, 0.25 mmol) was added S (0.009 g, 0.3 mmol). The mixture was refluxed for 24 h and the solvent was evaporated to dryness. The dry solid was then treated with diethyl ether and insoluble material was filtered off over celite. The solution was concentrated to ca 5 cm^3 and hexane was added to give complex **1** as a white solid. Yield: 77%. m.p. 123°C. $C_{43}H_{22}AuF_{10}P_2S$ (1114.583). Calc: C, 46.3; H, 2.0; S, 2.9. Found: C, 46.9; H, 2.15; S, 2.4. $^{31}P\{^1H\}$ NMR: $\delta = 8.5$ (m, 1P, Au(III)-*P*Ph$_2$) and 33.2 (d, 1P, S*P*Ph$_2$, [^2J(P—P) = 17.2 Hz]); ^{1}H NMR: $\delta = 3.6$ ("t", 2H, C*H*$_2$, *N* = 11.3 Hz); ^{19}F NMR: $\delta = -118.9$ (m, 4F, *o*-F), −119 (m, 2F, *o*-F), −156.4 (t, 2F, *p*-F, [^3J(FF) = 20.1 Hz]), −157.2 (t, 1F, *p*-F, [^3J(FF) = 19.9 Hz]), −160.5 (m, 4F, *m*-F) and −160.6 (m, 2F, *m*-F).

$[Au(C_6F_5)_3\{PPh_2CH(AuPPh_3)PPh_2E\}]$ (E = S (**2**), O (**3**))

To a dichloromethane solution of $[Au(C_6F_5)_3(PPh_2CH_2PPh_2E]$ (0.278 g, 0.25 mmol, *E* = *S* (**1**)) or (0.274 g, 0.25 mmol, *E* = *O* [11]) was added $[Au(acac)PPh_3]$ (0.139 g, 0.25 mmol). After stirring for 2 h the mixture was filtered through a layer of celite and the solvent was evaporated to ca 5 cm^3. Addition of 20 ml of hexane led to the precipitation of **2** or **3** as a pale yellow solids. Yield: 60% **2,** 66% **3**. m.p. 113°C, **2,** 78°C, **3**. $C_{61}H_{36}Au_2F_{10}SP_3$ (1572.833) **2**. Calc: C, 46.6; H, 2.3; S, 2.03. Found: C, 46.8; H, 2.6; S, 2.15. $C_{61}H_{36}Au_2F_{10}OP_3$ (1556.768) **3**. Calc: C, 47.1; H, 2.3. Found: C, 47.2; H, 2.9. NMR **2**: $^{31}P\{^1H\}$: $\delta = 21.8$ (m, 1P, Au(III)-*P*Ph$_2$) 41.3 (dd, 1P, S*P*Ph$_2$, [^2J(P-P) = 37.8 Hz], [^3J(P-P) = 12.8 Hz]) and 38.6 ("t", 1P, *P*Ph$_3$, *N* = 11 Hz). ^{1}H: $\delta = 3.75$ ("c", 1H, C*H*, *N* = 7.33 Hz). ^{19}F: $\delta = -118.4$ (m, 4F, *o*-F), −121.2 (m, 2F, *o*-F), −157.8 (t, 1F, *p*-F, [^3J(FF) = 19.9 Hz]), −158.1 (t, 2F, *p*-F, [^3J(FF) = 19.9 Hz]), −160.9 (m, 4F, *m*-F) and −161 (m, 2F, *m*-F). NMR **3**: $^{31}P\{^1H\}$: $\delta = 21.6$ (m, 1P, Au(III)-*P*Ph$_2$), 29.4 (dd, 1P, S*P*Ph$_2$, [^2J(P−P) = 33.9 Hz], [^3J(P-P) = 11.3 Hz]) and 38.6 ("t", 1P, *P*Ph$_3$, *N* = 11.3 Hz). ^{1}H: $\delta = 3.79$ ("q", 1H, C*H*, [*N*(HP) = 8.57 Hz]). ^{19}F: $\delta = -119.4$ (m, 4F, *o*-F), −121.1 (m, 2F, *o*-F), −157.8 (t, 1F, *p*-F, [^3J(FF) = 20.1 Hz]), −158.1 (t, 2F, *p*-F, [^3J(FF) = 19.9 Hz]), −161.5 (m, 4F, *m*-F) and −161.6 (m, 2F, *m*-F).

$[Au(C_6F_5)_3\{PPh_2CH_2PPh_2(SAuPPh_3)\}]$ TfO (**4**)

To a freshly prepared dichloromethane solution of $[Au(TfO)PPh_3]$ (0.25 mmol) was added $[Au(C_6F_5)_3(PPh_2CH_2PPh_2S)]$ (0.278 g, 0.25 mmol) and the mixture was stirred for 2 h. Evaporation of the solvent to

Table 1. Selected bond lengths (Å) and angles (°) for complex **7**

Au(1)—C(11)	2.02(3)	Au(1)—C(21)	2.08(4)
Au(1)—S(2)	2.357(8)	Au(1)—S(1)	2.390(7)
Au(2)—C(100)	2.10(3)	Au(2)—As(1)	2.370(3)
Au(2)—Au(3)	2.873(2)	Au(3)—C(100)	2.04(3)
Au(3)—As(2)	2.365(3)	As(1)—C(81)	1.91(2)
P(1)—S(1)	2.029(11)	P(2)—S(2)	2.050(10)
Au(4)—C(141)	2.02(2)	Au(4)—C(131)	2.05(3)
Au(4)—S(3)	2.375(7)	Au(4)—S(4)	2.385(7)
Au(5)—C(200)	2.13(3)	Au(5)—As(3)	2.371(3)
Au(5)—Au(6)	2.840(2)	Au(6)—C(200)	2.07(3)
Au(6)—As(4)	2.368(3)	P(3)—S(3)	2.007(10)
P(4)—S(4)	2.047(11)		

C(11)—Au(1)—C(21)	84.9(10)	C(11)—Au(1)—S(2)	84.8(7)
C(21)—Au(1)—S(2)	169.6(8)	C(11)—Au(1)—S(1)	173.2(7)
C(21)—Au(1)—S(1)	88.3(8)	S(2)—Au(1)—S(1)	102.0(2)
C(100)—Au(2)—As(1)	175.3(7)	C(100)—Au(2)—Au(3)	45.2(7)
As(1)—Au(2)—Au(3)	130.31(9)	C(100)—Au(3)—As(2)	177.6(7)
C(100)—Au(3)—Au(2)	47.0(7)	As(2)—Au(3)—Au(2)	130.63(9)
C(81)—As(1)—Au(2)	113.4(7)	C(71)—As(1)—Au(2)	114.8(6)
C(91)—As(1)—Au(2)	113.0(7)	C(121)—As(2)—Au(3)	112.4(6)
C(101)—As(2)—Au(3)	113.2(6)	C(111)—As(2)—Au(3)	112.5(7)
C(100)—P(1)—S(1)	115.8(10)	C(31)—P(1)—S(1)	105.3(8)
C(41)—P(1)—S(1)	107.6(8)	C(100)—P(2)—S(2)	113.9(10)
C(61)—P(2)—S(2)	105.9(8)	C(51)—P(2)—S(2)	107.1(8)
P(1)—S(1)—Au(1)	102.9(4)	P(2)—S(2)—Au(1)	104.8(4)
P(2)—C(100)—P(1)	112.4(14)	P(2)—C(100)—Au(3)	116(2)
P(1)—C(100)—Au(3)	111.9(14)	P(2)—C(100)—Au(2)	115.1(14)
P(1)—C(100)—Au(2)	111.0(14)	Au(3)—C(100)—Au(2)	87.8(10)
C(141)—Au(4)—C(131)	89.4(8)	C(141)—Au(4)—S(3)	172.2(6)
C(131)—Au(4)—S(3)	82.8(6)	C(141)—Au(4)—S(4)	86.1(6)
C(131)—Au(4)—S(4)	175.0(6)	S(3)—Au(4)—S(4)	101.7(2)
C(200)—Au(5)—As(3)	174.2(7)	C(200)—Au(5)—Au(6)	46.7(7)
As(3)—Au(5)—Au(6)	128.02(9)	C(200)—Au(6)—As(4)	173.8(7)
C(200)—Au(6)—Au(5)	48.4(7)	As(4)—Au(6)—Au(5)	125.66(9)
C(191)—As(3)—Au(5)	110.2(8)	C(201)—As(3)—Au(5)	113.0(7)
C(211)—As(3)—Au(5)	118.2(7)	C(241)—As(4)—Au(6)	115.6(8)
C(231)—As(4)—Au(6)	115.3(7)	C(221)—As(4)—Au(6)	108.0(6)
C(200)—P(3)—S(3)	112.0(10)	C(151)—P(3)—S(3)	105.4(7)
C(161)—P(3)—S(3)	107.9(8)	C(200)—P(4)—S(4)	114.7(10)
C(181)—P(4)—S(4)	107.6(8)	C(171)—P(4)—S(4)	106.3(8)
P(3)—S(3)—Au(4)	102.0(4)	P(4)—S(4)—Au(4)	102.8(4)
P(4)—C(200)—P(3)	112.6(14)	P(4)—C(200)—Au(6)	112.8(14)
P(3)—C(200)—Au(6)	116.9(14)	P(4)—C(200)—Au(5)	115.4(14)
P(3)—C(200)—Au(5)	111.5(14)	Au(6)—C(200)—Au(5)	85.0(10)

ca 5 cm^3 and addition of 20 cm^3 of hexane led to the precipitation of **4** as a microcrystalline white solid. Yield: 55%. m.p. 114°C. $C_{62}H_{37}Au_2F_{13}O_3P_3S_2$ (1722.909). Calc: C, 43.2; H, 2.15; S, 3.7. Found: C, 43.6; H, 2.2; S, 3.6. Λ_m $(5\times10^{-4}$ M$)$ = 133 $(ohm^{-1}\cdot cm^2\cdot mol^{-1})$. $^{31}P\{^1H\}$ NMR: $\delta = 5.1$ (m, 1P, Au(III)-*P*Ph$_2$), 36.4 (m, 1P, S*P*Ph$_2$) and 43.6 (m, 1P, *P*Ph$_3$). ^1H NMR: $\delta = 4.55$ ("t", 2H, CH_2, $N = 10.4$ Hz). ^{19}F NMR: $\delta = -117.6$ (m, 4F, *o*-F), -120.5 (m, 2F, *o*-F), -155.5 (t, 2F, *p*-F, [^3J(FF) = 19.9 Hz]), -156.5 (t, 1F, *p*-F, [^3J(FF) = 19.9 Hz]), -160.0 (m, 4F, *m*-F), -161.0 (m, 2F, *m*-F) and -120.4 (CF_3SO_3).

$[Au(C_6F_5)_3\{SPPh_2C(AuPPh_3)_2PPh_2S\}]$ (**5**)

To a dichloromethane solution of $[Au(C_6F_5)_3(SPPh_2CH_2PPh_2S)]$ (0.286 g, 0.25 mmol) was added $[Au(acac)PPh_3]$ (0.279 g, 0.50 mmol). After stirring for 1 h the mixture was filtered through a layer of celite and the solvent was evaporated to ca 5 cm^3.

Addition of 20 cm^3 of hexane led to the precipitation of **5** as a pale yellow solid. Yield: 71%. m.p. 110°C. $C_{79}H_{50}Au_3F_{10}S_2P_4$ (2063.147). Calc: C, 46.0; H, 2.4; S, 3.1. Found: C, 46.4; H, 2.1; S, 2.9. $^{31}P\{^1H\}$ NMR: $\delta = 47.0$ (m, 1P, Au(III)-*P*Ph$_2$), 50.6 (m, 1P, S*P*Ph$_2$) and 35.2 ("t", 1P, *P*Ph$_3$, $N = 7.3$ Hz). ^{19}F NMR: $\delta = -121.2$ (m, 4F, *o*-F), -122.2 (m, 2F, *o*-F), -158.6 (t, 1F, *p*-F, [^3J(FF) = 19.9 Hz]), -158.8 (t, 2F, *p*-F, [^3J(FF) = 19.9 Hz]), -162 (m, 4F, *m*-F) and -163.4 (m, 2F, *m*-F).

$[Au(C_6F_5)_2\{(SPPh_2)_2C(AuL)_2\}]\ ClO_4$ (L = PPh$_3$ (**6**), AsPh$_3$ (**7**))

A solution of $[Au(C_6F_5)_2(SPPh_2CH_2PPh_2S)]ClO_4$ (0.27 g, 0.25 mmol) in 25 cm^3 of dichloromethane was treated with [Au(acac)PPh$_3$] (0.279 g, 0.50 mmol (**6**)) or [Au(acac)AsPh$_3$] (0.30 g, 0.50 mmol (**7**)). After stirring for 2 h the mixture was filtered through a layer of celite and the solvent was evaporated to ca 5 cm^3. Addition of 20 cm^3 of diethyl ether led to the precipitation of **6** or **7** as a pale yellow solids. Yield: 80% **6,** 74% **7**. $C_{73}H_{50}Au_3ClF_{10}O_4P_4S_2$ (1995.56) **6**. Calc: C, 43.95; H, 2.5. Found: C, 43.65; H, 2.35. $C_{73}H_{50}Au_3As_2ClF_{10}O_4P_2S_2$ (2083.457) **7**. Calc. C, 42.1; H, 2.4; S, 3.1. Found: C, 42.5; H, 2.1; S, 3.4. Λ_m ($5 \cdot 10^{-4}$ M): 143 (**6**), 140 (**7**) (ohm$^{-1}\cdot$cm$^2\cdot$mol^{-1}). NMR **6**: $^{31}P\{^1H\}$: $\delta = 43.9$ (t, 2P, Au(III)-S*P*Ph$_2$, [^{3}J(P-P) = 5.6 Hz]) and 36.3 (t, 2P, *P*Ph$_3$, [^3J(P-P) = 5.6 Hz]). NMR **7**: $^{31}P\{^1H\}$: $\delta = 42.6$ (s, 2P, Au(III)-*P*Ph$_2$); ^{19}F: $\delta = -121.8$ (m, 4F, *o*-F), -155.7 (t, 2F, *p*-F, [^3J(FF) = 19.9 Hz]) and -160.5 (m, 4F, *m*-F).

$[Au(C_6F_5)_2\{SPPh_2C(AuPPh_3)PPh_2S\}]$ (**8**)

To a dichloromethane solution of $[Au(C_6F_5)_2(SPPh_2CHPPh_2S)]$ (0.195 g, 0.20 mmol) was added [Au(acac)PPh$_3$] (0.112 g, 0.20 mmol). After stirring for 1 h the mixture was filtered through a layer of celite and the solvent was evaporated to ca 5 cm^3. Addition of 20 cm^3 of hexane led to the precipitation of **8** as a yellow solid. Yield: 53%. $C_{55}H_{35}Au_2F_{10}P_3S_2$ (1436.85). Calc: C, 45.95; H, 2.45. Found: C, 45.65; H, 2.8. $^{31}P\{^1H\}$ NMR: $\delta = 46.9$ (m, 1P, Au(III)-*P*Ph$_2$), 34.8 (m, 1P, S*P*Ph$_2$) and 37.5 (s, 1P, *P*Ph$_3$).

Crystal structure determination of $7 \cdot 2CH_2Cl_2$

Crystal data. $C_{74}H_{52}As_2Au_3Cl_3F_{10}O_4P_2S_2$, $M_r = 2168.31$, monoclinic, space group $P2_1/n$, $a = 18.134(4)$, $b = 15.805(3)$, $c = 51.489(9)$ Å, $\beta = 95.52(2)°$, $V = 14689(9)$ Å^3, $Z = 8$, $D_c = 1.961$ Mg m^{-3}, $\mu = 7.156$ mm^{-1}, $F(000) = 8272$, $T = -100$°C. Colourless prism $0.40 \times 0.30 \times 0.20$ mm.

Data collection and reduction. The crystal was mounted in inert oil on a glass fibre. Data were collected using monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å) on a Siemens P4 diffractometer with an LT-2 low temperature attachment to $2\theta_{max} = 45°$. 19,516 intensities were collected of which 18,818 ($R_{int} = 0.070$) were independent. An absorption correction based on Ψ-scans gave transmissions factors 0.693–0.904. Cell constants were refined from setting angles of 55 reflection in the 2θ range 6–23°.

The structure was solved by direct methods and subjected to full-matrix least-squares refinement on F^2 (program SHELXL-93) [21]. Au, P, As, S and F atoms were refined anisotropically, others isotropically. Hydrogen atoms were included using a riding model. The final $\omega R(F^2)$ was 0.211 for 18,789 reflections, 751 parameters and 358 restraints, conventional $R(F)$ 0.0812. $S = 1.028$, maximum $\Delta\rho$ 1.94 e Å^{-3}. The poor R value is caused by two factors: (i) the disorder of an perchlorate with very badly defined O atoms (the dichloromethane molecules also display high U values) and, more seriously, (ii) the reflection overlap caused by the long axis (despite narrow reflections and the use of ω scans). A systems of restraints to P, S and F atom displacement-factor components and local ring symmetry was used. CCDC reference number 100612.

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