(Diphenylphosphinomethyl)diphenylphosphine Sulphide ($Ph_2PCH_2PPh_2S$) and its Methanide Anion $Ph_2PCHPPh_2S^-$ as Ligands in Organogold Chemistry. *X*-Ray Crystal Structure of *cis*-$[\overline{\text{Au}(C_6F_5)_2(PPh_2CHPPh_2\text{S}})]$†

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Stable gold complexes containing uni- or bi-dentate $Ph_2PCH_2PPh_2S$ are described. Deprotonation of the ligand yields complexes containing the anionic ligand $Ph_2PCHPPh_2S^-$, which acts either as a P,S-chelating ligand or as a P, C, S-bridging six-electron ligand. The molecular structure of $[Au(C_6F_5)_2(Ph_2PCHPPh_2S)]$ has been established by *X*-ray crystallography. The P–C bond lengths are appreciably shorter than in complexes containing chelating $Ph_2PCH_2PPh_2$.

The co-ordination chemistry of the ligand $Ph_2P(S)CH_2(S)PPh_2$ (dppmds) has been the subject of recent attention and one paper dealing with gold compounds has been published.[1] Related gold monosulphide derivatives have only been prepared with the ligand $SPPh_2CH_2PPh_2Me^+$ where the second P atom had been blocked by incorporating it into a phosphonium group.[2] The monosulphide $PPh_2CH_2PPh_2S$ [(diphenylphosphinomethyl)diphenylphosphine sulphide, dppms] has been scarcely used in organotransition metal chemistry: only one paper, reporting the preparation of $[M(CO)_4(dppms)]$ (M = Cr, Mo, or W) has appeared.[3] The synthesis of the ligand was originally patented by Seyferth[4] and has since been modified.[5] It involves a multi-step procedure and the overall yield is low (*ca.* 30%), which has possibly hindered the study of the co-ordination chemistry of this ligand.

If the ligand $Ph_2PCH_2PPh_2$ (dppm) is acting as a unidentate ligand, *i.e.* with one of the phosphorus atoms firmly attached to a metal centre, it may be possible to add a sulphur atom to the unco-ordinated P atom, thereby creating the P-co-ordinated monosulphide. In fact, the reaction of *cis*-$[Au(C_6F_5)_2Cl(dppm)]$ with elemental sulphur leads to *cis*-$[Au(C_6F_5)_2Cl(dppms)]$ (**1**), and starting from (**1**) complexes with P,S-chelating dppms or with the anionic ligand $Ph_2PCHPPh_2S^-$ can be prepared. Moreover, the anionic ligand can also act as a P,C,S-bridging six-electron ligand.

The structure of $[Au(C_6F_5)_2(PPh_2CHPPh_2S)]$ has been established by *X*-ray diffractometry. This is the only fully characterized gold(III) methanide.

Results and Discussion

The reaction of *cis*-$[Au(C_6F_5)_2Cl(dppm)]$ with elemental S (1:1.05 molar ratio) in refluxing toluene gives *cis*-$[Au(C_6F_5)_2Cl(dppms)]$ (**1**) in good yield (86%), equation (1). Using

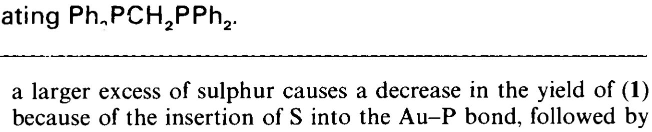
$$[Au(C_6F_5)_2Cl(dppm)] + \tfrac{1}{8}S_8 \longrightarrow \underset{(\mathbf{1})}{[Au(C_6F_5)_2Cl(dppms)]} \quad (1)$$

a larger excess of sulphur causes a decrease in the yield of (**1**) because of the insertion of S into the Au–P bond, followed by rearrangement, equation (2). For instance, a 1:1.8 ratio leads to

$$2[Au(C_6F_5)_2Cl(dppm)] + \tfrac{1}{4}S_8 \longrightarrow \underset{(\mathbf{2})}{cis,cis\text{-}[Au(C_6F_5)_2(dppmds)][Au(C_6F_5)_2Cl_2]} + \text{dppmds} \quad (2)$$

a mixture of (**1**) (60%) and (**2**) (25%) (see below).

Complexes (**1**) and (**2**) are air- and moisture-stable white solids. Complex (**1**) is monomeric in chloroform solution (isopiestic method) and its ^{31}P n.m.r. spectrum (room temperature) shows two broad signals centred at 43.0 and 23.8 p.p.m. At −40 °C, the ^{31}P n.m.r. spectrum shows a doublet at 60.25 p.p.m. [J(P–P) = 34.2 Hz] assignable to P–S and a broad unresolved multiplet at 38.18 p.p.m. due to the coupling of P–Au with ^{19}F nuclei of the *trans* C_6F_5 group. Since these values are very similar to those observed for $[Au(C_6F_5)_2(dppms)]ClO_4$ (**3**), we ascribe this to the equilibrium (3) (R = C_6F_5) which is apparently displaced to the right at lower temperatures to give either a five-co-ordinated gold complex or a four-co-ordinated cationic complex with the chloride displaced from the co-ordination sphere. The i.r. spectrum of solid (**1**) (Nujol mull) shows ν(Au–Cl) at 320 cm^{-1}, and its acetone solutions are non-conducting, in contrast to complex (**3**) (see below).



(3)

Addition of $AgClO_4$ to dichloromethane solutions of (**1**) gives the cation (**3**), equation (4). Complex (**3**) is an air- and moisture-stable white solid; its acetone solutions are conducting (1:1 electrolyte)[6] and its i.r. spectrum shows bands at 1 100s,br and 620m cm^{-1} from ionic ClO_4^- (T_d).[7]

$$[Au(C_6F_5)_2Cl(dppms)] + AgClO_4 \longrightarrow AgCl + \underset{(\mathbf{3})}{[Au(C_6F_5)_2(dppms)]ClO_4} \quad (4)$$

By stirring a diethyl ether suspension of complex (**3**) and NaH, the methanide (**4**) can be obtained, equation (5). Complex

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† [(Diphenylphosphino)(diphenylthiophosphinoyl)methanido-*P,S*]-bis(pentafluorophenyl)gold(III).

Supplementary data available: complete bond lengths and angles, H-atom co-ordinates, thermal parameters, structure factors have been deposited with the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany. Any request for this material should quote the reference number CSD 53168 and a full literature citation.

Table 1. Analytical data and properties of the complexes (**1**)—(**12**)

	Complex[a]	Yield (%)	Analysis[b] (%) C	H	Au	Λ_M[c]	M.p. (°C)	M[b,d]
(**1**)	$[AuR_2Cl(dppms)]$	86	45.2	2.5	19.95	10	120	1 032
			(45.25)	(2.25)	(20.05)			(982)
(**2**)	$[AuR_2(dppmds)][AuR_2Cl_2]$	*e*	37.35	1.65	24.6	104	165	
			(37.2)	(1.4)	(24.9)			
(**3**)	$[AuR_2(dppms)]ClO_4$	75	42.7	2.2	18.3	127	192[f]	
			(42.5)	(2.1)	(18.85)			
(**4**)	$[AuR_2(PPh_2CHPPh_2S)]$	60	47.1	2.35	21.15	5	175	977
			(46.95)	(2.25)	(20.8)			(946)
(**5**)	$[AuR_2\{PPh_2CH(AuR)PPh_2S\}]$	80	39.6	1.65	30.45	10	155[f]	1 267
			(39.4)	(1.6)	(30.05)			(1 310)
(**6**)	$[AuR_2\{PPh_2CH(AuCl)PPh_2S\}]$	80	37.25	2.05	33.2	10	160[f]	1 200
			(37.7)	(1.8)	(33.4)			(1 179)
(**7**)	$[AuR_2\{PPh_2CH(AuR_3)PPh_2S\}]$	70	40.35	1.4	23.75	15	120	1 700
			(40.15)	(1.3)	(23.95)			(1 645)
(**8**)	$[AuR_2\{PPh_2CH(AuR_2Cl)PPh_2S\}]$	65	39.05	1.5	25.95	15	82	1 450
			(38.9)	(1.4)	(26.05)			(1 513)
(**9**)	$[AuR_2\{PPh_2CH(AgPPh_3)PPh_2S\}]ClO_4$	90	46.75	2.75	21.7	130	136	
			(46.65)	(2.55)	(21.5)			
(**10**)	$[\{AuR_2(PPh_2CHPPh_2S)\}_2Au]ClO_4$	60	40.4	2.1	27.3	94	235[f]	
			(40.6)	(1.95)	(27.0)			
(**11**)	$[\{AuR_2(PPh_2CHPPh_2S)\}_2Ag]ClO_4$	60	41.95	2.26	23.4	135	170[f]	
			(42.3)	(2.0)	(23.9)			
(**12**)	$[\{AuR_2(PPh_2CHPPh_2S)\}_2AuR_2]ClO_4$	80	41.05	2.0	23.6	130	180[f]	
			(40.95)	(1.7)	(23.4)			

[a] $R = C_6F_5$. [b] Calculated values are given in parentheses. [c] In acetone, values in Ω^{-1} cm^2 mol^{-1}. [d] In choroform. [e] See text. [f] With decomposition.

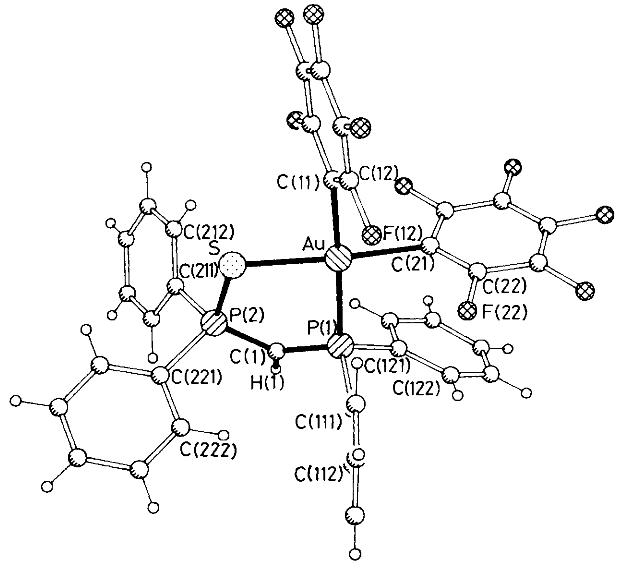


Figure. The molecule of complex (**4**) in the crystal, showing the atom numbering scheme; radii are arbitrary

$$\underset{(3)}{[Au(C_6F_5)_2(PPh_2CH_2PPh_2S)]ClO_4} + NaH \longrightarrow H_2 + NaClO_4 + \underset{(4)}{[Au(C_6F_5)_2(PPh_2CHPPh_2S)]} \quad (5)$$

(**4**) is an air- and moisture-stable white solid. Under an N_2 atmosphere it is also stable in solution, but a white turbidity slowly develops if the solution is exposed to moist air.

No bands assignable to perchlorate are present in the i.r. spectrum of (**4**); instead, a strong absorption appears at 1 173 cm^{-1} which, according to previous observations[8,9] can be assigned to the P–CH–P system. The ^1H n.m.r. spectrum shows (Table 2) a signal at 2.26 p.p.m. [1 H, dd, J(P–H) = 3.8 and 15 Hz] corresponding to the proton of that system, confirming that the methylene group in the starting complex (**3**) undergoes deprotonation in the reaction with NaH, equation (5).

Only three gold methanide complexes, $[CH(Ph_2PAuPPh_2)_2CH]$,[10] $[Au(C_6F_5)(PPh_2CHPPh_2Me)]$,[9] and $[HC(Ph_2PAuCH_2)_2PBu^t_2]$,[11] have been structurally characterized, so far. Crystals of (**4**) suitable for *X*-ray studies were grown by slow diffusion of n-hexane into a saturated diethyl ether solution of the complex. The structure is represented in the Figure and shows the square-planar environment of the gold(III) centre (mean deviation 0.07 Å). The P–C(1) distances [1.715(6) and 1.699(6) Å] are shorter than in complexes containing chelating dppm, *e.g.* 1.845(9) Å in $[Au(C_6F_5)_2(dppm\text{-}PP')]ClO_4$,[12] as a consequence of the delocalized electron density in the P–C–P system. The P–S bond length of 2.055(2) Å corresponds to a slightly shortened single bond. The chelate ring is however far from planar, with torsion angles about Au–P(1) 28, P(1)–C(1) −30, C(1)–P(2) 15, P(2)–S 8, S–Au −19°. The atoms C(1) and P(2) lie 0·7 Å out of the ligand plane on opposite sides. The C_6F_5 rings show the narrowing of the *ipso* C–C–C angle typical of such complexes[13] (114.8, 116.7°).

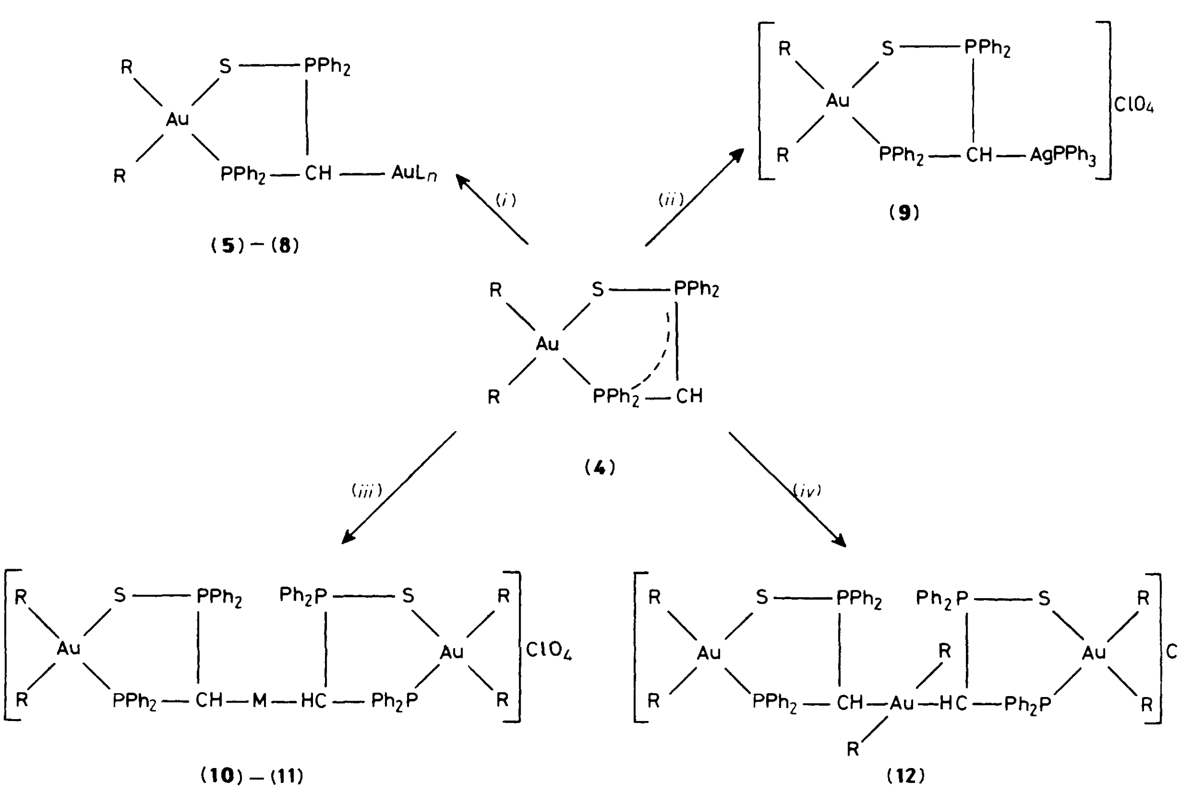
The methanide carbon atom in (**4**) has an excess of electron density, which can be donated to other metal centres, *e.g.* in reactions with gold or silver complexes containing readily displaceable ligands: [AuCl(tht)] (tht = tetrahydrothiophene), $[Au(C_6F_5)(tht)]$, $[Au(C_6F_5)_3(OEt_2)]$, $[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]$, or $[Ag(OClO_3)(PPh_3)]$ (see Scheme).

Complexes (**5**)—(**9**) are air- and moisture-stable solids. They are white [(**5**), (**6**), (**9**)] or pale yellow [(**7**), (**8**)]. Complexes (**5**)—

Table 2. N.m.r. data and some i.r. absorptions

Complex	$^1H^a$ (CH_2 or CH)	$^{31}P-\{^1H\}^b$ Au–P	P–S	ν(P–S)[c]	ν(C–Au)[c]
(1)	4.85 (at, 12.8)	32.18 (m)	60.25 (d, 34.2)	602m	
(2)	5.47 (at, 12.8)		38.27 (s)	565s	
(3)	5.22 (at, 11.7)	31.14 (dm)	59.78 (d, 35.6)	562s	
(4)	2.26 (dd, 15.0, 3.8)	38.62 (dm)	55.34 (d, 84.9)	555s	
(5)	3.6 (dd, 14.1, 21.7)	45.49 (dm)	69.66 (d, 39.6)	560s	550 (sh)
(6)	3.9 (dd, 13.6, 21.5)	42.68 (dm)	64.65 (d, 43.1)	572m	555m
(7)	4.7 (at, 11.9)	28.88 (dm)	59.59 (d, 35.0)	560m	525w
(8)	5.1 (at, 16.0)	29.96 (dm)	59.81 (d, 35.8)	555m	520w
(9)[d,e]	5.89 (at,br, 12.6)	42.14 (m)	62.22 (m)	560m	535w
(10)[d,f]	5.07 (at, 2.7)	45.79 (dm)	70.02 (d, 37.7)	575m	550m
(11)	5.94 (at,br, 12.0)	32.8 (m)	60.5 (d, 34.7)	560m	535w
(12)	5.23 (at, 12.1)	30.98 (m)	59.77 (d, 34.7)	560m	525w

[a] In p.p.m., recorded in $CDCl_3$ at 200 MHz with reference to internal $SiMe_4$, unless otherwise specified; s = singlet, d = doublet, at = apparent triplet, m = multiplet, dm = doublet of multiplets, br = broad. All complexes show a multiplet in the region 7—8 p.p.m. corresponding to Ph groups. Coupling constants (Hz) are given in parentheses. [b] Referred to external H_3PO_4. [c] For i.r. data: s = strong, m = medium, w = weak. [d] Recorded in $(CD_3)_2CO$. [e] Ag–*P*Ph_3 at 16.44 p.p.m. (dm, *J* 343 Hz). [f] See text.



Scheme. R = C_6F_5. (*i*) [AuR(tht)] gives **(5)**, [AuCl(tht)] gives **(6)**, [$AuR_3(OEt_2)$] gives **(7)**, $\frac{1}{2}$[{Au(μ-Cl)R_2}$_2$] gives **(8)**; (*ii*) [Ag($OClO_3$)(PPh_3)]; (*iii*) [$Au(tht)_2$]ClO_4 gives **(10)**, $\frac{1}{2}$ $AgClO_4$ gives **(11)**; (*iv*) $\frac{1}{2}$[$AuR_2(OEt_2)_2$]ClO_4

(8) are non-conducting in acetone solution and monomeric in chloroform solutions. Acetone solutions of **(9)** are conducting (1 : 1 electrolyte).[6]

The (2:1) reactions of complex **(4)** with ligand-free metal centres ($AgClO_4$) or complexes containing two readily displaceable ligands {[$Au(tht)_2$]ClO_4 or *cis*-[$AuR_2(OEt_2)_2$]-ClO_4} lead to the cationic trinuclear derivatives **(10)**—**(12)**, which are air- and moisture-stable white [**(10)**, **(11)**] or yellow [**(12)**] solids.

In the i.r. spectra of the polynuclear complexes **(5)**—**(12)** the absorption at 1 173 cm^{-1} characteristic of the methanide **(4)** is lacking and a new absorption appears at 550 cm^{-1}, due to ν(M–C) (M = Au or Ag) (Table 2). The ν(P–S) absorption at 560 cm^{-1} is not significantly modified after co-ordination of the methanide C atom to a metal centre.

Table 2 presents ^1H and $^{31}P-\{^1H\}$ n.m.r. data for the reported complexes. The resonances due to the proton of the methanide group appear at higher fields than that of both the CH_2 group in complex **(3)** and in the polynuclear derivatives **(5)**—**(12)**. In all cases, the pattern is either a doublet of doublets or an apparent triplet. In the $^{31}P-\{^1H\}$ spectra, the P atom bonded to the S resonates (as a doublet) at lower field than the P–Au, which

Table 3. Atomic co-ordinates (× 10^4) for complex (**4**)

Atom	*x*	*y*	*z*
Au	2 069.9(2)	856.5(1)	2 535.8(1)
P(1)	899(1)	1 655.2(6)	1 807(1)
P(2)	−686(1)	1 083.6(7)	2 993(1)
S	498(1)	375.4(6)	3 072(1)
C(1)	−232(5)	1 733(2)	2 439(4)
C(111)	464(5)	1 445(2)	531(4)
C(112)	−292(6)	1 831(3)	−47(5)
C(113)	−782(7)	1 646(3)	−959(5)
C(114)	−515(7)	1 075(3)	−1 339(5)
C(115)	249(7)	690(3)	−784(5)
C(116)	739(6)	880(3)	149(5)
C(121)	1 586(5)	2 414(3)	1 777(4)
C(122)	2 053(6)	2 623(3)	979(5)
C(123)	2 601(8)	3 184(4)	997(7)
C(124)	2 702(8)	3 542(4)	1 798(9)
C(125)	2 280(8)	3 353(4)	2 639(7)
C(126)	1 688(6)	2 787(3)	2 624(5)
C(211)	−1 003(5)	1 280(2)	4 204(4)
C(212)	−304(6)	1 104(3)	5 042(4)
C(213)	−559(7)	1 303(3)	5 957(4)
C(214)	−1 476(7)	1 666(3)	6 016(5)
C(215)	−2 184(6)	1 844(3)	5 185(5)
C(216)	−1 943(5)	1 647(3)	4 276(4)
C(221)	−1 974(5)	726(3)	2 375(4)
C(222)	−2 204(6)	760(3)	1 368(5)
C(223)	−3 157(7)	464(4)	870(6)
C(224)	−3 877(7)	152(4)	1 397(7)
C(225)	−3 679(6)	132(3)	2 368(7)
C(226)	−2 714(6)	410(3)	2 880(5)
C(11)	3 023(5)	94(3)	3 110(4)
C(12)	3 334(5)	−368(3)	2 487(4)
C(13)	3 917(6)	−912(3)	2 821(5)
C(14)	4 222(6)	−1 000(3)	3 803(6)
C(15)	3 941(5)	−552(3)	4 439(5)
C(16)	3 353(5)	−22(3)	4 107(4)
F(12)	3 055(4)	−300(2)	1 517(3)
F(13)	4 193(4)	−1 343(2)	2 189(3)
F(14)	4 782(4)	−1 520(2)	4 139(3)
F(15)	4 246(3)	−643(2)	5 416(3)
F(16)	3 095(4)	394(2)	4 772(2)
C(21)	3 500(5)	1 305(3)	2 206(5)
C(22)	3 894(6)	1 297(3)	1 326(5)
C(23)	4 852(7)	1 643(4)	1 154(7)
C(24)	5 410(7)	1 981(4)	1 908(8)
C(25)	5 039(6)	2 007(3)	2 797(7)
C(26)	4 089(5)	1 669(3)	2 933(5)
F(22)	3 357(4)	961(2)	570(3)
F(23)	5 182(5)	1 617(3)	265(4)
F(24)	6 367(4)	2 291(2)	1 757(5)
F(25)	5 602(4)	2 342(2)	3 520(4)
F(26)	3 753(3)	1 709(2)	3 808(3)

shows a doublet of multiplets. This is not well resolved in complexes (**1**), (**9**), (**11**), and (**12**), because of the coupling with the other P atom and with the ^{19}F nuclei of the *trans* C_6F_5 group, thus confirming the *cis* structure of all these complexes. The *J*(P–P) values are *ca.* 35 Hz with the exception of the methanide (84.9 Hz), in agreement with previous observations in other methanide complexes.[8,9]

When co-ordinated to gold or silver [complexes (**5**)—(**9**)] the methanide C atoms are chiral centres, but the n.m.r. spectra cannot distinguish between *R*- and *S*-enantiomers. Moreover, because of the two chiral centres in complexes (**10**)—(**12**), three isomers are possible in each case.[14] The simple ^{31}P spectra rule out the presence of diastereoisomers in our samples, which consist of either one isomer or an enantiomeric mixture. Only in the case of complex (**10**) does a further doublet (not included in Table 2) at 69.02 p.p.m. [*J*(P–P) = 38.0 Hz], with 12% of the intensity of the other doublet, indicate the presence of another diastereoisomer.

Experimental

Instrumentation and general experimental techniques were as described earlier.[9,15] The yields, melting points, C, H, and Au analyses, conductivities, and molecular weights are listed in Table 1. Proton and ^{31}P-{^{1}H} n.m.r. data, ν(P–S) and ν(Au–C) are listed on Table 2. All the reactions were run at room temperature unless otherwise stated.

Preparation of the Complexes.—[AuR_2Cl(dppms)] (**1**) *and* [AuR_2(dppmds)][AuR_2Cl_2] (**2**) (R = C_6F_5). To a toluene solution (20 cm^3) of [$Au(C_6F_5)_2Cl$(dppm)][12] (0.475 g, 0.5 mmol) was added S_8 (0.017 g, 0.525 mmol S) (1:1.05 molar ratio) and the mixture was refluxed for 4 h. The resulting mixture was evaporated to dryness and the white residue was extracted (3 × 3 cm^3) with CS_2. Extraction with diethyl ether (2 × 10 cm^3) gave a cloudy solution which was filtered and concentrated to 5 cm^3. Addition of n-hexane gave (**1**) (0.4223 g, 86% yield).

Table 4. Selected bond lengths (Å) and angles (°) for complex (**4**)

Au–P(1)	2.331(1)	Au–S	2.345(2)
Au–C(11)	2.069(5)	Au–C(21)	2.061(6)
P(1)–C(1)	1.715(6)	P(1)–C(111)	1.816(5)
P(1)–C(121)	1.809(6)	P(2)–S	2.055(2)
P(2)–C(1)	1.699(6)	P(2)–C(211)	1.810(6)
P(2)–C(221)	1.816(6)		
P(1)–Au–S	89.6(1)	P(1)–Au–C(11)	175.2(1)
S–Au–C(11)	87.8(2)	P(1)–Au–C(21)	92.0(2)
S–Au–C(21)	174.4(2)	C(11)–Au–C(21)	90.9(2)
Au–P(1)–C(1)	108.6(2)	Au–P(1)–C(111)	108.1(2)
C(1)–P(1)–C(111)	112.1(3)	Au–P(1)–C(121)	114.2(2)
C(1)–P(1)–C(121)	108.5(3)	C(111)–P(1)–C(121)	105.4(3)
S–P(2)–C(1)	110.8(2)	S–P(2)–C(211)	110.5(2)
C(1)–P(2)–C(211)	110.4(3)	S–P(2)–C(221)	104.5(2)
C(1)–P(2)–C(221)	115.6(3)	C(211)–P(2)–C(221)	104.7(3)
Au–S–P(2)	103.9(1)	P(1)–C(1)–P(2)	118.3(3)
C(12)–C(11)–C(16)	114.8(5)	C(22)–C(21)–C(26)	116.7(6)

If a larger amount of sulphur is used, a more substantial amount of a white material remains undissolved [complex (**2**)]. For instance, using a 1:1.8 molar ratio of the reactants, complexes (**1**) (60%) and (**2**) (25%) can be isolated.

[$Au(C_6F_5)_2$(dppms)]ClO_4 (**3**). To a dichloromethane solution (20 cm^3) of (**1**) (0.098 g, 0.1 mmol) was added $AgClO_4$ (0.021 g, 0.1 mmol) and the mixture stirred for 1 h after addition of diethyl ether (5 cm^3). The precipitated AgCl was filtered off and the solution was evaporated to *ca.* 5 cm^3; addition of n-hexane (10 cm^3) gave (**3**) as a white solid.

[$Au(C_6F_5)_2$(dppms)] (**4**). A diethyl ether (20 cm^3) suspension of NaH (0.1 g, 4.20 cm^3) and complex (**3**) (0.105 g, 0.1 mmol) was stirred for 1 h. The excess NaH and the precipitated $NaClO_4$ and NaCl were filtered off under N_2, and the solution was evaporated to *ca.* 5 cm^3; addition of n-hexane (10 cm^3) gave (**4**) as a yellow solid.

[$Au(C_6F_5)_2${$PPh_2CH(AuL_n)PPh_2S$}] [L_n = C_6F_5 (**5**), Cl (**6**), $(C_6F_5)_3$ (**7**), *or* $(C_6F_5)_2Cl$ (**8**)]. To a dichloromethane solution (20 cm^3) of (**4**) (0.095 g, 0.1 mmol) was added $[Au(C_6F_5)(tht)]$[16] (0.045 g, 0.1 mmol), $[AuCl(tht)]$[17] (0.030 g, 0.1 mmol), $[Au(C_6F_5)_3(OEt_2)]$[1] (0.077 g, 0.1 mmol) or $[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]$[18] (0.057 g, 0.05 mmol). After stirring for 30 min, the solution was evaporated to *ca.* 5 cm^3 and addition of hexane (10 cm^3) gave white solids (**5**) or (**6**), or yellow solids (**7**) or (**8**).

$[Au(C_6F_5)_2\{PPh_2CH(AgPPh_3)PPh_2S\}]ClO_4$ (**9**). Using the method described for complexes (**5**)—(**8**), but starting from $[Ag(OClO_3)(PPh_3)]$[19] (0.047 g, 0.1 mmol) gave (**9**) as a white solid.

$[\{Au(C_6F_5)_2(PPh_2CHPPh_2S)\}_2M]ClO_4$ [M = Au (**10**) *or* Ag (**11**)]. To a dichloromethane solution (15 cm^3) of (**4**) (0.189 g, 0.2 mmol) was added $[Au(tht)_2]ClO_4$[20] (0.047 g, 0.1 mmol) or $AgClO_4$ (0.021 g, 0.1 mmol) and the mixture stirred for 1 h. The solution was evaporated to *ca.* 5 cm^3 and addition of diethyl ether (10 cm^3) gave (**10**) or (**11**) as white solids.

$[\{Au(C_6F_5)_2(PPh_2CHPPh_2S)\}_2Au(C_6F_5)_2]ClO_4$ (**12**). To a diethyl ether suspension (20 cm^3) of *trans*-$[NBu_4][Au(C_6F_5)_2Cl_2]$[21] (0.084 g, 0.1 mmol) was added $AgClO_4$ (0.041 g, 0.2 mmol) and the mixture stirred for 1 h. The precipitated AgCl and $[NBu_4]ClO_4$ were filtered off. To the diethyl ether solution was added (**4**) (0.189 g, 0.2 mmol) and the mixture stirred for 1 h. Partial evaporation to *ca.* 5 cm^3 gave (**12**) as a yellow solid.

X-Ray Structure Determination of Complex (**4**).—*Crystal data.* $C_{37}H_{21}AuF_{10}P_2S$, $M = 946.5$, monoclinic, space group $P2_1/c$, $a = 11.942(2)$, $b = 21.203(5)$, $c = 13.767(3)$ Å, $\beta = 98.11(2)°$, $U = 3\,451$ Å^3, $Z = 4$, $D_c = 1.82$ g cm^{-3}, $F(000) = 1\,832$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu = 4.5$ mm^{-1}. Orange prism, 0.8 × 0.5 × 0.4 mm.

Data collection and reduction. Stoe-Siemens four-circle diffractometer with monochromated Mo-K_α radiation. 9 163 Profile-fitted intensities[22] to $2\theta_{max.}$ 55°, 7 906 unique ($R_{int.}$ 0.023), 6 007 with $F > 4\sigma(F)$ used for all calculations (program system SHELX 76,[23] locally modified by Professor G. M. Sheldrick). Absorption correction based on ψ-scans; transmission factors 0.79—0.96. Cell constants refined from 2θ values of 46 reflections in the range 20—23°.

Structure solution and refinement. Heavy-atom method, followed by full-matrix refinement on F to R 0.044, R' 0.040. All non-H atoms anisotropic; H atoms included using a riding model. Weighting scheme $w^{-1} = \sigma^2(F) + 0.0003F^2$. 460 Parameters; max. Δ/σ 0.007; max. $\Delta\rho$ 1 e Å^{-3} near Au; S 1.43.

Final atomic co-ordinates are presented in Table 3, with selected bond lengths and angles in Table 4. Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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