Mono- and Bi-nuclear Four-membered Methanide Auracycles; Synthesis and Reactivity. *X*-Ray Structure of *cis*-$[Au(C_6F_5)_2(SPPh_2O)(CH_2PPh_2Me)]$*

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The complexes $[Au(C_6F_5)_2Cl(SPh_2PCH_2PPh_2CH_2R)]ClO_4$ (R = H or Ph) react with Na_2CO_3 or NaH to give four-membered methanide auracycles $[Au(C_6F_5)_2(SPh_2PCHPPh_2CH_2R)]ClO_4$ or $[Au(C_6F_5)_2(SPh_2PCPPh_2CH_2R)]$, respectively; these complexes can be interconverted by reaction with with NaH or $HClO_4$. The neutral derivatives can be used to form homobinuclear complexes $[Au(C_6F_5)_2\{SPh_2PC(AuX)PPh_2Me\}]$ (X = C_6F_5 or Cl) and $[Au(C_6F_5)_2\{SPh_2PC(AuPPh_3)PPh_2Me\}]BF_4$ and react with water to give $[Au(C_6F_5)_2(SPPh_2O)(CH_2PPh_2CH_2R)]$. The structure of $[Au(C_6F_5)_2(SPPh_2O)(CH_2PPh_2Me)]$ has been solved by *X*-ray crystallography.

Sodium hydride deprotonates the following gold(I) or gold(III) complexes containing bis(diphenylphosphino)methane (dppm) or its derivatives: $[Au(C_6F_5)_2(Ph_2PCH_2PPh_2)]ClO_4$,[1] $[Au(C_6F_5)_2(SPh_2PCH_2PPh_2S)]ClO_4$,[2] $[Au(C_6F_5)(Ph_2PCH_2PPh_2CH_2R)]ClO_4$ (R = H,[3] Ph,[4] or C_6F_5[4]), $[Au(C_6F_5)_3(Ph_2PCH_2PPh_2CH_2R)]ClO_4$ (R = H),[3] $[Au(C_6F_5)_2Cl(Ph_2PCH_2PPh_2CH_2R)]ClO_4$ (R = H,[3] Ph, C_6F_5,[4] or CO_2Me[5]) to give neutral methanide complexes. In these cases, only single deprotonation is achieved (from the CH_2 group between the two P atoms). The precursor $[Au(C_6F_5)_2Cl(Ph_2PCH_2PPh_2CH_2CO_2Me)]ClO_4$ can be doubly deprotonated,[5] the additional proton coming from the other CH_2 group, α to the CO_2Me substituent.

In the present paper we report the deprotonation (single or double) of $[Au(C_6F_5)_2Cl(SPh_2PCH_2PPh_2CH_2R)]ClO_4$ (R = H or Ph) with Na_2CO_3 or NaH, which leads to the formation of four-membered methanide auracycles. These can be used as C-donor ligands to afford homobinuclear gold complexes; they also react with water to form ylide complexes by ring opening. The structure of the ylide $[Au(C_6F_5)_2(SPh_2O)(CH_2PPh_2Me)]$ has been established by *X*-ray diffraction.

Results and Discussion

The phosphonium phosphine sulphide perchlorates were prepared from the salts $[Ph_2PCH_2PPh_2CH_2R]X$ (R = H, X = I;[6] R = Ph, X = Br[7]) according to equation (1). By treating the salt (**1**) or (**2**) with the dimer $[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]$ (2:1 ratio), the monomeric cationic gold(III) complexes (**3**) and (**4**) can be obtained [Scheme, (*i*)].

$$[Ph_2PCH_2PPh_2CH_2R]X + AgClO_4 \longrightarrow AgX + [Ph_2PCH_2PPh_2CH_2R]ClO_4 \xrightarrow{1/8S_8} [SPh_2PCH_2PPh_2CH_2R]ClO_4 \quad (1)$$

(**1**) R = H

(**2**) R = Ph

Complexes (**3**) and (**4**) react at room temperature with the mild deprotonating agent Na_2CO_3 to give auracycles (**5**) and (**6**), as a result of deprotonation of the methylene group between the P atoms and simultaneous elimination of the chloride ligand, thereby vacating a co-ordination site which is occupied by the methanide C atom to form a four-membered auracycle [Scheme (*ii*)]. If the stronger deprotonating agent NaH is used, the same methylene group is doubly deprotonated, both the chloride ligand and the perchlorate anion are eliminated as the sodium salts, and the neutral complexes (**7**) and (**8**) are formed [Scheme, (*iii*)].

Addition of $HClO_4$ to the methanide complex (**7**) or (**8**) (1:1 ratio) gives the cationic (**5**) or (**6**) [Scheme, (*iv*)] which regenerate the neutral (**7**) or (**8**) on reaction with NaH [(*v*)].

The white compounds (**1**)—(**6**) are air- and moisture-stable in the solid state or in solution. The yellow (**7**) and (**8**) are stable in the solid state but their solutions are very sensitive to moisture. In the presence of a trace of water the solutions become pale; H_2O adds to the C–PPh_2 bond, leading to ring opening and formation of the monothiophosphinate(ylide) derivative (**9**) or (**10**).

The structure of (**9**) has been solved by *X*-ray diffraction. Single crystals were obtained by slow diffusion of n-hexane into a diethyl ether solution of the complex. However, they were of moderate quality and the precision attained is correspondingly low.

The gold atom shows the expected square-planar geometry (Figure). The Au–C bond lengths are equal to within *ca.* 1 estimated standard deviation. The Au–S bond length [2.363(7) Å] is the first reported for an Au^{III}–S–P group; it is very similar to the 2.367(3), 2.377(3) Å in an Au^{II}–S–P system.[8] In gold(III) dithiolate complexes the usual values are *ca.* 2.29—2.32 Å.[9] However, a detailed comparison is not possible because of the different groups *trans* to the S atoms. The P–O and P–S bonds may be regarded as double and single respectively[10] [1.467(18) and 2.026(12) Å].

The excess of electron density on the methanide C atom in complexes (**7**) and (**8**) leads to reaction with gold(I) complexes $[Au(C_6F_5)(tht)]$, $[AuCl(tht)]$ (tht = tetrahydrothiophene), or $[\{Au(PPh_3)\}_3O]BF_4$, to give binuclear complexes (**11**)—(**13**) [Scheme (*vii*), (*viii*)] which were isolated as white stable solids.

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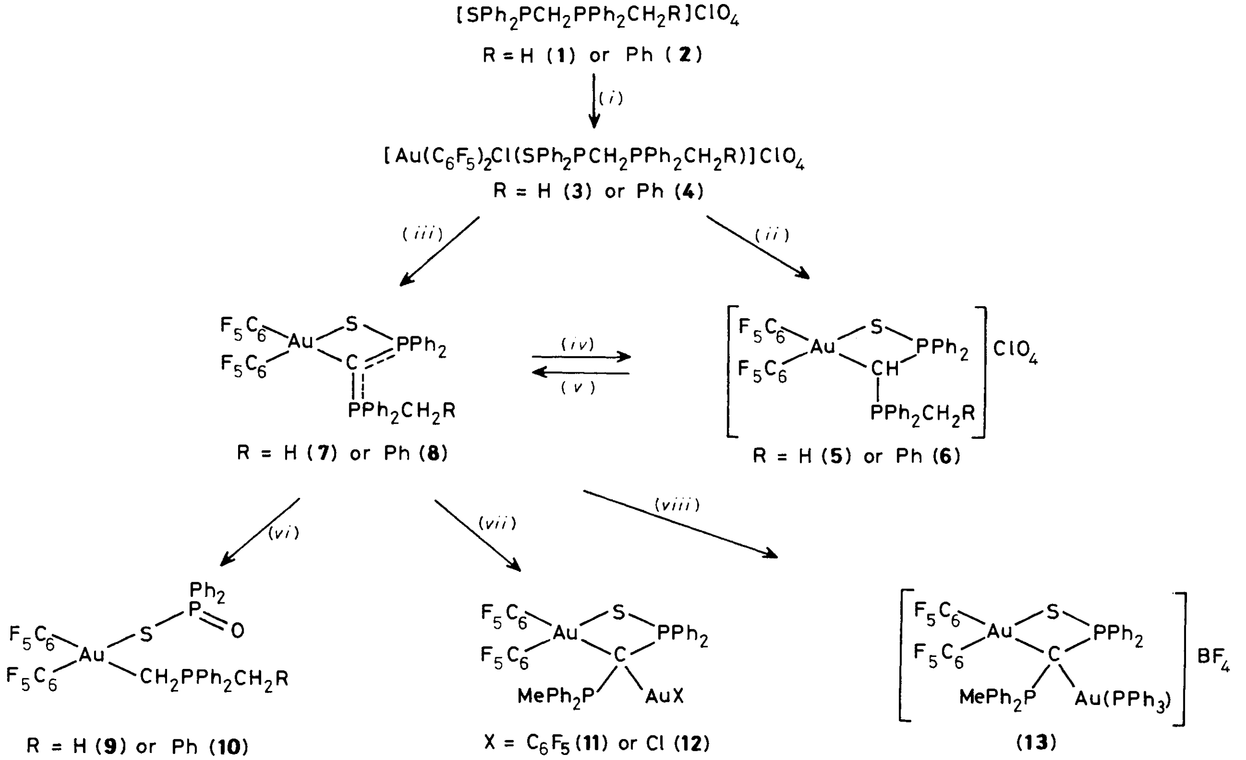
* *cis*-Diphenylthiophosphinato[(methyldiphenylphosphonio)-methanide]bis(pentafluorophenyl)gold(III).

Supplementary data available from Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, West Germany, by quoting a full literature citation and the reference number CSD 52905.



Scheme. (*i*) $[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]$; (*ii*) Na_2CO_3; (*iii*). (*iv*) $HClO_4$; (*v*) NaH; (*vi*) water; (*vii*) [AuX(tht)]; (*viii*) $[\{Au(PPh_3)\}_3O]BF_4$

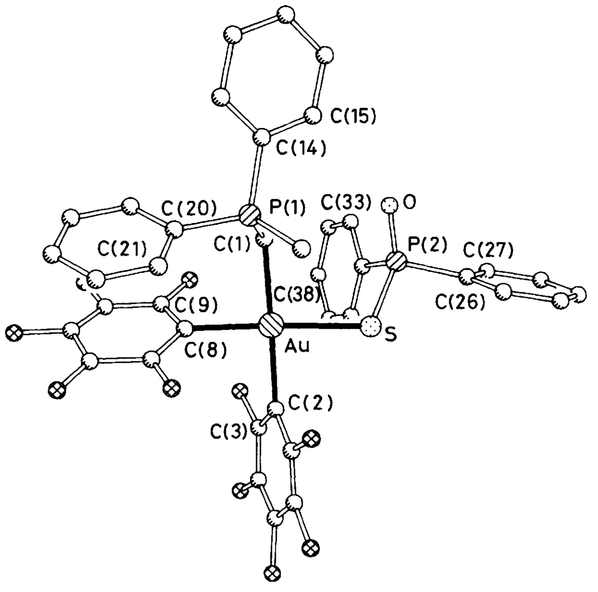


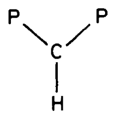
Figure. The molecule of complex (**9**) in the crystal. Radii arbitrary, H atoms omitted for clarity

Acetone solutions of compounds (**1**)—(**6**) and (**13**) behave as 1:1 electrolytes,[11] whilst solutions of (**7**)—(**12**) are non-conducting. In chloroform solution (**7**)—(**12**) are monomeric (Table 1) in agreement with the proposed formula.

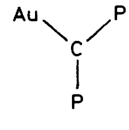
Additional information comes from the i.r. spectra. The ν(Au–Cl) vibrations appear at higher energy for complexes (**3**) and (**4**) (320 and 315 cm^{-1}) than in the spectrum of the chloride-bridged dimer $[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]$[12] (290 cm^{-1}). This vibration is not present in the spectra of complexes (**5**) and (**6**), showing that the anion eliminated simultaneously with the first deprotonation is the co-ordinated chloride and not the perchlorate; moreover the absorptions due[13] to the ClO_4^- anion appear at 1 100vs, br and 620m cm^{-1}. They are also present in the spectra of complexes (**1**)—(**4**), but not in those of (**7**) and (**8**), the double deprotonation of the methylene group [Scheme (*iii*) or (*v*)] requiring the elimination of two anionic groups (chloride and perchlorate).

The i.r. spectrum of complex (**13**) shows absorptions at 1 100 and 1 060 cm^{-1} due[14] to BF_4^-.

The ν(P–S) vibrations[2,15,16] of complexes (**3**) and (**4**) containing the unidentate ligands are shifted towards lower energies (Δν *ca.* 35 cm^{-1}) with respect to the free ligands (**1**) and (**2**), but in the auracycles (**5**)—(**8**) and (**11**)—(**13**) the shift is less marked (Δν *ca.* 15—25 cm^{-1}). One absorption between 600 and 520 cm^{-1} due to ν(Au–C) is expected[1-5] for complexes (**5**)—(**12**), but only (**5**) (550), (**6**) (545), and (**11**) (565 cm^{-1}) show bands which can be assigned to this vibration. For the other complexes, this vibration would be masked by the stronger ν(P–S).



(I)



(II)

We have often observed[4,5] that complexes containing the moieties (I) and (II), *i.e.* a three-co-ordinated methanide carbon atom, display a strong absorption between 1 100—1 200 cm^{-1}, which disappears upon protonation or co-ordination of the C atom to another metal centre. Thus, complexes (**7**) and (**8**) display a strong absorption at 1 150 and 1 135 cm^{-1} respectively, which is not present in the spectra of complexes (**5**), (**6**), and (**9**)—(**13**).

Table 1. Analytical data for the new compounds ($X = C_6F_5$)

Compound	Yield (%)	Analysis (%)[a] C	H	Au	Λ_M[b]/Ω^{-1} cm^2 mol^{-1}	M.p. (°C)	M[a]
(**1**) $[SPh_2PCH_2PPh_2Me]ClO_4$	80	58.4 (58.8)	4.65 (4.75)		119	114	
(**2**) $[SPh_2PCH_2PPh_2CH_2Ph]ClO_4$	75	63.0 (63.3)	4.9 (4.8)		126	242	
(**3**) $[AuX_2Cl(SPh_2PCH_2PPh_2Me)]ClO_4$	88	41.1 (41.6)	2.25 (2.3)	17.6 (17.95)	130	180 (decomp.)	
(**4**) $[AuX_2Cl(SPh_2PCH_2PPh_2CH_2Ph)]ClO_4$	70	45.4 (45.05)	2.6 (2.5)	16.35 (16.8)	134	175 (decomp.)	
(**5**) $[AuX_2(SPh_2PCHPPh_2Me)]ClO_4$	79[c] 86[c]	43.0 (43.0)	2.3 (2.3)	18.7 (18.55)	118	218 (decomp.)	
(**6**) $[AuX_2(SPh_2PCHPPh_2CH_2Ph)]ClO_4$	65[c] 84[c]	46.9 (46.5)	2.65 (2.5)	16.9 (17.3)	111	197 (decomp.)	
(**7**) $[AuX_2(SPh_2PCPPh_2Me)]$	87	47.85 (47.5)	2.65 (2.4)	20.6 (20.5)	12	217	924 (960.5)
(**8**) $[AuX_2(SPh_2PCPPh_2CH_2Ph)]$	70	51.05 (51.0)	3.2 (2.65)	18.45 (19.0)	17	192	1 011 (1 036.5)
(**9**) $[AuX_2(SPPh_2O)(CH_2PPh_2Me)]$	65	47.45 (46.65)	2.9 (2.65)	20.85 (20.15)	0.5	198	952 (979)
(**10**) $[AuX_2(SPPh_2O)(CH_2PPh_2CH_2Ph)]$	62	50.55 (50.1)	2.30 (2.75)	19.2 (18.7)	0.2	231	996 (1055)
(**11**) $[AuX_2\{SPh_2PC(AuX)PPh_2Me\}]$	91	39.9 (39.95)	1.9 (1.75)	29.95 (29.75)	1	196 (decomp.)	1 274 (1 325)
(**12**) $[AuX_2\{SPh_2PC(AuCl)PPh_2Me\}]$	81	38.25 (38.25)	2.15 (1.95)	32.25 (33.0)	1	191 (decomp.)	1 145 (1 193)
(**13**) $[AuX_2\{SPh_2PC(AuPPh_3)PPh_2Me\}]BF_4$	55	44.45 (44.65)	2.55 (2.55)	26.6 (26.15)	100	129	

[a] Calculated values are given in parentheses. [b] In acetone solutions. [c] See text.

Table 2. N.m.r. data[a] and ν(P–S) vibrations

Compound	^{1}H P–CH$_2$–P or P–CH–P	^2J(P–H)	P–CH$_2$–Ph or P–Me	J(P–H)	^{31}P-{^{1}H} S–P	C–P–C	^2J(P–P)	$\tilde{\nu}$(P–S)/cm^{-1}
(**1**)	4.41 (dd)	12.6, 15.4	2.70 (d)	13.7	33.68 (d)	21.50 (d)	9.1	605
(**2**)	4.29 (dd)	10.5, 14.5	4.62 (d)	14.4	33.53 (d)	23.44 (d)	7.8	610
(**3**)	5.53 (t)	15.5	2.54 (d)	13.7	39.43 (d)	20.80 (d)	14.2	570
(**4**)	5.50 (t)	15.0	4.53 (d)	14.1	40.13 (d)	24.11 (d)	17.1	575
(**5**)	3.95 (dd)	3.9, 11.9	2.18 (d)	12.8	60.61 (d)	25.13 (d)	11.6	585
(**6**)	3.86 (dd)	12.5, 15.6	4.55 (dd)	6.9, 10.9	57.72 (d)	28.80 (d)	12.1	590
(**7**)			1.70 (d)	12.4	61.34 (d)	7.75 (d)	29.0	582
(**8**)			3.19 (d)	14.0	60.80 (d)	12.62 (d)	24.1	588
(**9**)	2.77 (d)[b]	14.6	2.64 (d)	13.9	45.93 (s)	28.51 (s)		575
(**10**)	2.78 (d)[b]	14.9	4.53 (d)	13.9	46.11 (s)	32.70 (s)		580
(**11**)			1.97 (d)	12.1	66.35 (s)	15.62 (s, br)		590
(**12**)			2.04 (d)	12.1	69.70 (s)	16.14 (s, br)		582
(**13**)			2.33 (d)	11.6	72.47 (d)	38.12 (m)[c]	12.0	592

[a] In $CDCl_3$, resonances in p.p.m. and J in Hz. [b] Assignable to Au–CH$_2$–P protons. [c] Au–PPh$_3$ appears at 21.18 (s) p.p.m.

Complexes (**9**) and (**10**) show absorptions at 1 165 and 1 170 cm^{-1} respectively, assignable to ν(P=O).[16]

Complexes (**3**)—(**13**) show absorptions at 1 150, 970, and two more (or one broad band at 800 cm^{-1}), which are characteristic of *cis*-bis(pentafluorophenyl) derivatives.[12] Complex (**11**) also shows absorptions at 975 and 765 cm^{-1} from the additional Au–C_6F_5 group.

Table 2 presents ^{1}H and ^{31}P-{^{1}H} n.m.r. data for the complexes. Signals from the phenylic protons (which appear as multiplets between 7 and 8 p.p.m.) have been omitted. The ^{1}H n.m.r. signals of the P–CH$_3$ or P–CH$_2$Ph groups appear at similar δ values for all complexes except the doubly deprotonated (**7**) and (**8**), where they are shifted to higher field.

The behaviour of the signals from the groups P–CH$_2$–P and P–CH–P is consistent (Table 2, column 1) with the proposed formula.

The ^{31}P-{^{1}H} n.m.r. spectra show, except for complexes (**9**) and (**10**), two doublets corresponding to two mutually coupled P nuclei. The S*P* resonances change upon co-ordination of the free ligands, and especially so when the P atom is part of a four-membered auracycle.[2,17] The coupling constants ^2J(P–P) show markedly higher values for the doubly deprotonated complexes (**7**) and (**8**).

Finally, complexes (**9**) and (**10**) show singlets for each P atom; the binuclear derivatives (**11**) and (**12**) [^2J(P–P) *ca.* 0] show a broadening of the signal from the quaternary P atom, possibly due to some coupling with ^{19}F of the C_6F_5 group *trans* to the methanide C atom. Complex (**13**) has ^2J(P–P) 12.0, a

Table 3. Atomic co-ordinates (× 10^4) for complex (**9**)

Atom	*x*	*y*	*z*
Au	3 555(1)	1 084.0(5)	1 934.1(6)
S	2 899(8)	1 110(4)	3 063(4)
P(1)	672(8)	1 818(4)	1 144(4)
P(2)	3 418(9)	1 889(4)	3 443(4)
C(1)	2 586(22)	1 857(11)	1 625(13)
C(2)	4 657(21)	333(12)	2 233(13)
C(3)	6 132(39)	261(15)	2 263(16)
C(4)	6 892(41)	−229(15)	2 426(16)
C(5)	6 070(46)	−673(18)	2 541(19)
C(6)	4 628(42)	−605(17)	2 536(18)
C(7)	3 897(38)	−146(14)	2 342(15)
C(8)	4 094(28)	1 010(13)	950(13)
C(9)	5 108(33)	1 359(13)	762(16)
C(10)	5 552(33)	1 316(12)	107(17)
C(11)	4 853(36)	946(15)	−358(19)
C(12)	3 851(40)	548(17)	−203(21)
C(13)	3 410(37)	588(15)	489(18)
C(15)	58(20)	2 822(9)	1 717(8)
C(16)	−594	3 351	1 707
C(17)	−1 434	3 563	1 078
C(18)	−1 621	3 247	459
C(19)	−970	2 719	469
C(14)	−130	2 506	1 097
C(21)	−256(18)	1 089(8)	19(10)
C(22)	−270	898	−666
C(23)	520	1 187	−1 106
C(24)	1 324	1 667	−861
C(25)	1 339	1 859	−176
C(20)	549	1 570	264
C(27)	4 611(18)	2 055(8)	4 870(11)
C(28)	4 560	2 023	5 588
C(29)	3 360	1 754	5 805
C(30)	2 211	1 518	5 304
C(31)	2 262	1 549	4 586
C(26)	3 462	1 818	4 369
C(33)	5 767(24)	2 590(8)	3 245(10)
C(34)	7 260	2 703	3 208
C(35)	8 312	2 271	3 281
C(36)	7 871	1 726	3 391
C(37)	6 378	1 612	3 429
C(32)	5 326	2 044	3 356
F(3)	6 958(17)	711(8)	2 113(9)
F(4)	8 442(24)	−243(9)	2 433(11)
F(5)	6 849(29)	−1 191(9)	2 678(11)
F(6)	3 913(26)	−1 089(9)	2 654(10)
F(7)	2 434(22)	−133(7)	2 335(9)
F(9)	5 833(15)	1 742(7)	1 191(9)
F(10)	6 534(19)	1 667(9)	−82(9)
F(11)	5 192(24)	893(11)	−1 022(10)
F(12)	3 164(22)	157(8)	−624(10)
F(13)	2 455(20)	226(7)	637(9)
C(38)	−416(30)	1 399(11)	1 608(15)
O	2 421(21)	2 345(8)	3 134(10)

Table 4. Selected bond lengths (Å) and angles (°) for complex (**9**)

Au–S	2.363(7)	Au–C(1)	2.086(23)
Au–C(2)	2.084(27)	Au–C(8)	2.056(26)
S–P(2)	2.026(12)	P(1)–C(1)	1.802(21)
P(1)–C(14)	1.796(22)	P(1)–C(20)	1.779(21)
P(1)–C(38)	1.768(25)	P(2)–C(26)	1.785(22)
P(2)–C(32)	1.806(24)	P(2)–O	1.467(18)
C(1)–Au–S	94.2(7)	C(2)–Au–S	87.8(8)
C(2)–Au–C(1)	176.2(10)	C(8)–Au–S	176.5(9)
C(8)–Au–C(1)	88.6(10)	C(8)–Au–C(2)	89.6(10)
P(2)–S–Au	105.9(4)	C(14)–P(1)–C(1)	108.5(11)
C(20)–P(1)–C(1)	112.5(10)	C(20)–P(1)–C(14)	108.0(9)
C(38)–P(1)–C(1)	110.1(12)	C(38)–P(1)–C(14)	106.7(12)
C(38)–P(1)–C(20)	110.7(12)	C(26)–P(2)–S	103.4(7)
C(32)–P(2)–S	108.3(7)	C(32)–P(2)–C(26)	106.1(9)
O–P(2)–S	117.3(9)	O–P(2)–C(26)	111.6(11)
O–P(2)–C(32)	109.5(11)	P(1)–C(1)–Au	114.2(13)

quaternary P signal similar to that of (**11**) and (**12**), and an additional singlet from the P atom of the Au–PPh_3 group.

Experimental

Instrumentation and general experimental techniques were as described earlier.[4] The yields, melting points, C, H, and Au analyses, conductivities, and molecular weights of the complexes are listed in Table 1. Proton and $^{31}P-\{^1H\}$ n.m.r. and ν(P–S) data are listed in Table 2. All the reactions were run at room temperature. The salts $[Ph_2PCH_2PPh_2Me]I$,[6] $[Ph_2PCH_2PPh_2CH_2Ph]Br$,[7] and $[Ph_2PCH_2PPh_2Me]ClO_4$[3] were prepared as described earlier; $[Ph_2PCH_2PPh_2CH_2Ph]ClO_4$ was prepared similarly.

$[SPh_2PCH_2PPh_2CH_2R]ClO_4$ [R = H (**1**) *or* Ph (**2**)].—To a suspension of $[Ph_2PCH_2PPh_2Me]ClO_4$ (0.499 g, 1 mmol) or $[Ph_2PCH_2PPh_2CH_2Ph]ClO_4$ (0.576 g, 1 mmol) in toluene (30 cm^3) was added S_8 (0.08 g, 0.313 mmol), and the mixture was stirred for 6 h at reflux temperature. The resulting white solid was filtered off, washed with CS_2 (3 × 3 cm^3), and recrystallized from dichloromethane–diethyl ether.

$[Au(C_6F_5)_2Cl(SPh_2PCH_2PPh_2CH_2R)]ClO_4$ [R = H (**3**) *or* Ph (**4**)].—To a suspension of $[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]$[12] (0.227 g, 0.2 mmol) in CH_2Cl_2 (20 cm^3) was added salt (**1**) (0.213 g, 0.4 mmol) or (**2**) (0.243 g, 0.4 mmol). After stirring for 3 h, a slight turbidity was removed by filtration through a layer of Kieselguhr (1 cm). Concentration to *ca.* 5 cm^3 and addition of Et_2O led to the precipitation of complexes (**3**) and (**4**), as white solids.

$[Au(C_6F_5)_2(SPh_2PCHPPh_2CH_2R)]ClO_4$ [R = H (**5**) *or* Ph (**6**)].—These complexes can be obtained in two different ways.

(*a*) To a solution of complex (**3**) (0.219 g, 0.2 mmol) or (**4**) (0.235 g, 0.2 mmol) in dichloromethane (20 cm^3) was added Na_2CO_3 (0.3 g, 2.8 mmol), and the mixture was stirred for 3 h. The excess of Na_2CO_3 and the precipitated NaCl were filtered off and the solution was evaporated to 2 cm^3; addition of Et_2O gave (**5**) or (**6**).

(*b*) To a yellow solution of complex (**7**) (see below) (0.096 g, 0.1 mmol) or (**8**) (see below) (0.104 g, 0.1 mmol) was added $HClO_4$ (0.011 cm^3 of a 9 mol dm^{-3} solution, 0.1 mmol). The solution immediately turned white, and the white solid (**5**) or (**6**) was filtered off.

$[Au(C_6F_5)_2(SPh_2PCPPh_2CH_2R)]$ [R = H (**7**) *or* Ph (**8**)].—These complexes can be obtained in two different ways.

(*a*) To a diethyl ether (20 cm^3) suspension of NaH (0.3 g, 12.5 mmol) was added 0.2 mmol of complex (**3**) (0.219 g) or (**4**) (0.235 g), and the mixture was stirred for 2 h. The excess of NaH and the precipitated $NaClO_4$ and NaCl were filtered off under N_2 and the solution was evaporated to *ca.* 2 cm^3; addition of n-hexane (10 cm^3) gave (**7**) or (**8**) as yellow solids.

(*b*) Starting from complex (**5**) (0.106 g, 0.1 mmol) or (**6**) (0.114 g, 0.1 mmol) and working as described above with NaH (0.3 g, 12.5 mmol), complex (**7**) or (**8**) was obtained.

$[Au(C_6F_5)_2(SPPh_2O)(CH_2PPh_2CH_2R)]$ [R = H (**9**) *or* Ph (**10**)].—To a yellow solution of complex (**7**) (0.096 g, 0.1 mmol) or (**8**) (0.104 g, 0.1 mmol) in Et_2O (15 cm^3) was added one drop of water. The solution turned white in 1 h. Evaporation to *ca.* 5 cm^3 and addition of hexane (20 cm^3) led to complex (**9**) or (**10**) as white solids.

$[\overline{Au(C_6F_5)_2\{SPh_2PC}(AuX)PPh_2Me\}]$ [X = C_6F_5 (**11**) *or* Cl (**12**)].—To a solution of complex (**7**) (0.096 g, 0.1 mmol) in diethyl ether (20 cm^3) was added $[Au(C_6F_5)(tht)]$[18] (0.045 g, 0.1 mmol) or $[AuCl(tht)]$[15] (0.032 g, 0.1 mmol). After stirring for 2 h, the solution was evaporated to *ca.* 5 cm^3 and addition of hexane (20 cm^3) gave (**11**) or (**12**) as white solids.

$[\overline{Au(C_6F_5)_2\{SPh_2PC}(AuPPh_3)PPh_2Me\}]BF_4$ (**13**).—To a solution of complex (**7**) (0.096 g, 0.1 mmol) in dichloromethane (20 cm^3) was added $[\{Au(PPh_3)\}_3O]BF_4$[19] (0.148 g, 0.1 mmol). After stirring for 3 h the solution was evaporated to *ca.* 5 cm^3; addition of Et_2O (20 cm^3) gave a brown solid that was filtered off. Concentration to *ca.* 3 cm^3 and addition of hexane (15 cm^3) gave (**13**) as a white solid.

X-*Ray Structure Determination of Complex* (**9**).—*Crystal data.* $C_{38}H_{25}AuF_{10}OP_2S$, $M = 978.55$, monoclinic, $a = 9.055(4)$, $b = 23.956(7)$, $c = 19.264(7)$ Å, $\beta = 101.22(4)°$, $U = 4\,099$ Å^3 (by refinement of 2θ values of 38 reflections in the range 19—23°), space group $P2_1/c$, $Z = 4$, $D_c = 1.59$ g cm^{-3}, $F(000) = 1\,904$, colourless prism 0.3 × 0.1 × 0.1 mm, $\mu(Mo\text{-}K_\alpha) = 3.7$ mm^{-1}.

Data collection and processing. Stoe-Siemens four-circle diffractometer, monochromated Mo-K_α radiation ($\lambda = 0.710\,69$ Å). 6 442 Profile-fitted intensities[20] to $2\theta_{max.}$ 45°, 5 339 unique (R_{int} 0.044), 2 389 with $F > 4\sigma(F)$ used for all calculations (modified SHELX system). Absorption correction based on ψ scans (transmissions 0.58—0.64). Three check reflections, *ca.* 4% decay, appropriate scaling.

Structure analysis and refinement. Heavy-atom method. Refinement on *F* to *R* 0.089, *R′* 0.072 with Au, S, P, O, and F anisotropic, C and H isotropic. Phenyl (but not C_6F_5) groups idealized to C–C 1.395, C–O 0.96 Å. Other H included using a riding model. 250 Parameters, weighting scheme $w^{-1} = \sigma^2(F) + 0.0006\ F^2$, maximum shift/e.s.d. 0.08, maximum residual electron density 1 e Å^{-3}.

Final atomic parameters are given in Table 3, selected bond lengths and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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