Synthesis of (Diphenylphosphinothioyl)methyldiphenylphosphoniomethanide Complexes of Gold and Silver. *X*-Ray Structure of $[Au(C_6F_5)\{SPh_2PCH[Au(C_6F_5)]PPh_2Me\}]$‡

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Both $[Au(C_6F_5)_3(SPh_2PCHPPh_2Me)]$ {obtained from $[Au(C_6F_5)_3(OEt_2)]$ and $[SPh_2PCH_2PPh_2Me]ClO_4$, followed by deprotonation with NaH} and the free methanide $SPPh_2CHPPh_2Me$ react with gold(I) or silver(I) complexes $[Au(C_6F_5)(tht)]$ (tht = tetrahydrothiophene), $[Au(tht)_2]ClO_4$, and $[Ag(OClO_3)(PPh_3)]$ to afford binuclear complexes of the types $[Au(C_6F_5)\{SPh_2PCH[Au(C_6F_5)]PPh_2Me\}]$ or $[\{M(SPh_2PCHPPh_2Me)\}_2][ClO_4]_2$ (M = Au or Ag). The silver complex can also be obtained by deprotonation of $[\{Ag(SPh_2PCH_2PPh_2Me)\}_2][ClO_4]_2$ with Na_2CO_3. Oxidative addition of chlorine to the gold derivative gives the binuclear gold(II) complex $[\{AuCl(SPh_2PCHPPh_2Me)\}_2]$. The structure of $[Au(C_6F_5)\{SPh_2PCH[Au(C_6F_5)]PPh_2Me\}]$ has been established by *X*-ray crystallography [space group $P2_1/c$, with a = 15.392(4), b = 12.643(5), c = 21.965(7) Å, β = 107.95(2)°, and R' = 0.072 for 3 166 unique observed reflections]. The molecule adopts a folded conformation with parallel, eclipsed C_6F_5 rings and a corresponding short Au ··· Au contact of 3.224 Å.

We have recently reported the preparation of methanide complexes of gold and their use in synthesizing homo- and heteropolynuclear complexes.[1] In this paper we describe the preparation of $[Au(C_6F_5)_3(SPh_2PCHPPh_2Me)]$ and the free methanide $SPh_2PCHPPh_2Me$, and their reactions with several gold(I) and silver(I) complexes. The structure of the binuclear complex $[Au(C_6F_5)\{SPPh_2CH[Au(C_6F_5)]PPh_2Me\}]$ has been established by single-crystal *X*-ray analysis.

Results and Discussion

Although the sulphur donor tetrahydrothiophene (tht) is readily displaced from complexes such as $[Au(C_6F_5)_3(tht)]$ and $[Au(C_6F_5)(tht)]$ by a variety of other neutral ligands, no reaction was observed with $[SPh_2PCH_2PPh_2Me]ClO_4$. However, if $[Au(C_6F_5)_3(OEt_2)]$ is used instead of the tht complex, the more weakly co-ordinating OEt_2 is readily displaced and the complex $[Au(C_6F_5)_3(SPh_2PCH_2PPh_2Me)]ClO_4$ (**1**) can be obtained (see Scheme 1). At room temperature complex (**1**) is an air- and moisture-stable solid; it is soluble in acetone (1:1 electrolyte, see Table 1) and dichloromethane, and insoluble in diethyl ether and n-hexane. Its i.r. spectrum (Nujol mull) shows two bands at 1 100s, br and 620m cm^{-1} from the ClO_4^- anion,[2] and two other bands (810s and 790s cm^{-1}) that are characteristic for tris(pentafluorophenyl)gold(III) complexes.[3] The ν(P–S) band is shifted to lower frequencies than for the free ligand (605 cm^{-1}).

Complex (**1**) reacts with NaH to give the neutral methanide complex (**2**), which can be isolated as an air- and moisture-stable pale yellow solid. Its molecular weight (1 146 in chloroform, calc. 1 128) is in agreement with the proposed stoicheiometry. Its i.r. spectrum does not exhibit the bands at 1 100 and 620 cm^{-1} observed for the precursor; instead, a new band at 1 185s cm^{-1} confirms the formation of the methanide moiety P–CH–P, a behaviour already observed as in other methanide systems.[1,4]

The reaction of complex (**2**) with $[Au(C_6F_5)(tht)]$ (1:2) leads to a mixture of $[Au(C_6F_5)\{SPh_2PCH[Au(C_6F_5)]PPh_2Me\}]$ (**3**) and $[Au(C_6F_5)_3(tht)]$, which can be separated because of the lower solubility of complex (**3**). This shows that the gold(III) atom in the $Au(C_6F_5)_3$ fragment bonds more strongly to the S atom of tht than to the same atom in the starting methanide (**2**) (Scheme 2); indeed, the same mixture is also obtained using a 1:1 molar ratio, albeit with lower yield (30%, *cf.* 65% with molar ratio 1:2).

The binuclear complex (**3**) can also be obtained by another method, *viz.* the (2:1) reaction of $[Au(C_6F_5)(tht)]$ with a diethyl ether solution of the free ligand $SPh_2PCHPPh_2Me$, prepared[1] by addition of LiBu^n to a diethyl ether suspension of $[SPh_2PCH_2PPh_2Me]ClO_4$ (Scheme 1).

At room temperature, complex (**3**) is a stable white solid; it is soluble in acetone (non-conducting), slightly soluble in dichloromethane, and insoluble in diethyl ether and n-hexane. As is usual for Au–C(methanide) complexes, the absorption at 1 185 cm^{-1} is not present in the i.r. spectrum of (**3**), and a new band appears at 550m cm^{-1}, assignable to ν(Au–C) by analogy with observations for other methanide[1,4] or ylide[5–7] complexes of gold.

The structure of complex (**3**) was determined by *X*-ray diffraction methods. Single crystals were grown by slow diffusion of n-hexane into a dichloromethane solution of (**3**). However, the weakly diffracting nature of the crystals limited

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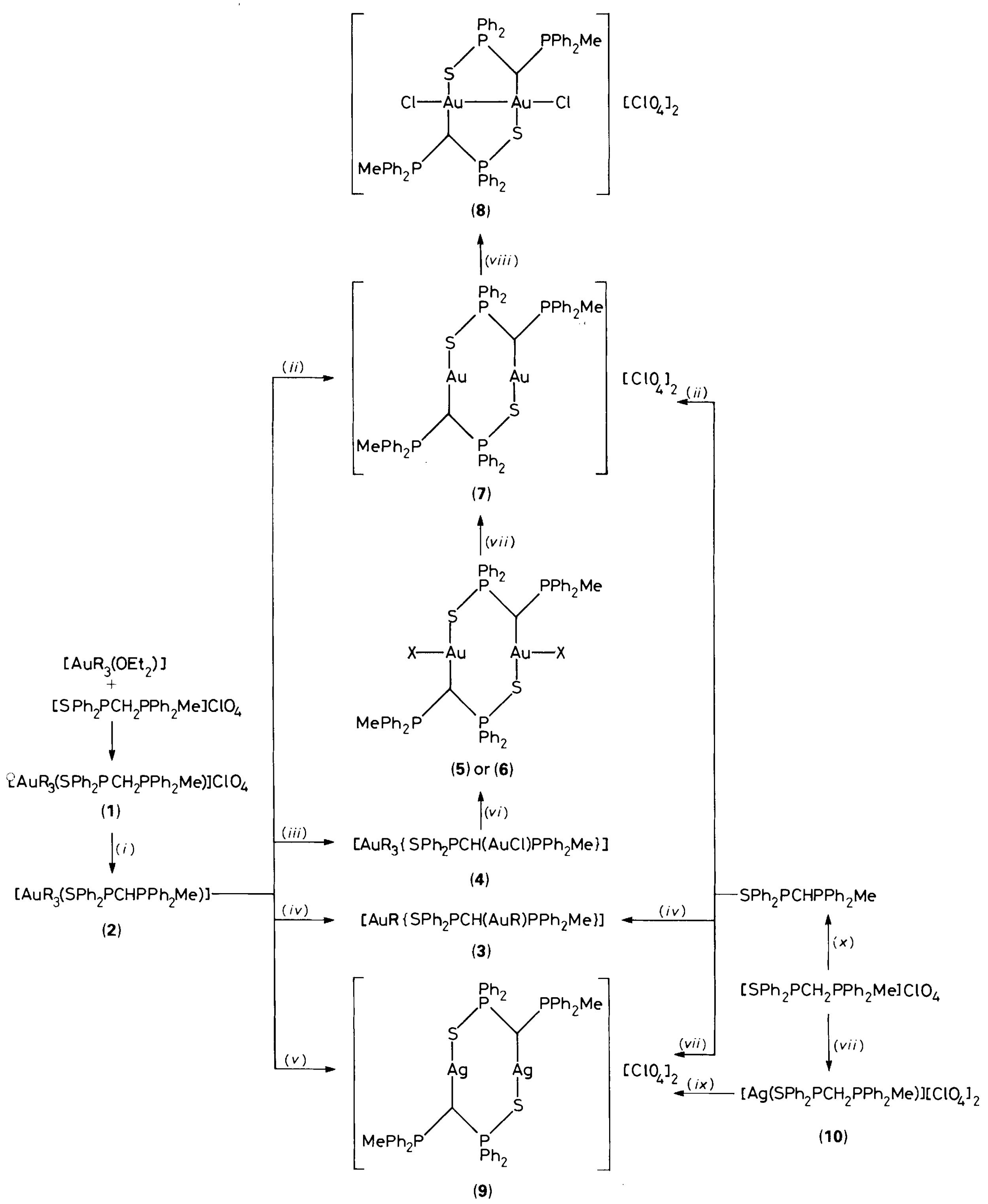
‡ μ-[Diphenylphosphinothioyl(methyldiphenylphosphonio)methanide-*CS*]-bis[(pentafluorophenyl)gold(I)].

Supplementary data available: complete bond lengths and angles, thermal parameters, structure factors, and H-atom co-ordinates can be obtained from the Fachinformationszentrum Energie Physik Mathematik, 7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany by quoting a full literature citation and the reference number CSD 53908.



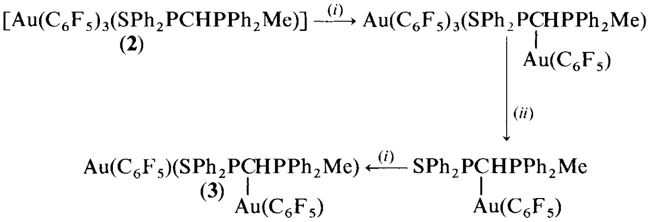
Scheme 1. R = C_6F_5. (*i*) NaH; (*ii*) $[Au(tht)_2]ClO_4$; (*iii*) [AuCl(tht)]; (*iv*) [AuR(tht)]; (*v*) $[Ag(OClO_3)(PPh_3)]$; (*vi*) $[N(PPh_3)_2]Cl$ gives (**5**), $[NBu_4]Br$ gives (**6**); (*vii*) $AgClO_4$; (*viii*) Cl_2; (*ix*) Na_2CO_3; (*x*) LiBu

the precision of the structure. The observed structure (Figure) is very different from that found[4] for the analogous $[Au(C_6F_5)\{Ph_2PCH[Au(C_6F_5)]PPh_2Me\}]$, because the two C_6F_5 rings of (**3**) adopt a parallel, eclipsed conformation with a corresponding short Au···Au separation of 3.224(2) Å (dihedral angle between rings 8°). The co-ordination geometry at gold is linear, as expected: C(37)–Au(1)–C(1) 175(1), C(31)–Au(2)–S 175(1)°. The bond lengths Au–C_6F_5 2.04(3) and 1.98(3), and Au(1)–C(1) 2.076(25) Å are in the expected range,[8] although the poor precision precludes detailed comparisons. The Au(2)–S bond, *trans* to a carbon ligand, is rather long[8] at 2.312(8) Å [*cf.* 2.323(3) Å in another C–Au–S system[9]]. The dimensions associated with the methanide function [P(1)–C(1) 1.82(3), P(2)–C(1) 1.79(2) Å, and P–C–P 117.7(14)°] are comparable to the corresponding values in the above-mentioned analogue:[4] 1.804(11), 1.790(10) Å, and 114.9(6)°. The P–S bond

Table 1. Analytical data for complexes (**1**)—(**10**)

Complex[a]	Yield (%)	Analysis[b] (%) C	H	Au	Λ[c]	M.p. (°C)
(**1**) $[AuR_3(SPh_2PCH_2PPh_2Me)]ClO_4$	91	43.6 (43.0)	2.4 (2.05)	15.95 (16.05)	141	138
(**2**) $[AuR_3(SPh_2PCHPPh_2Me)]$	85	46.4 (46.85)	2.4 (2.15)	16.95 (17.45)	20	100
(**3**) $[AuR\{SPh_2PCH(AuR)PPh_2Me\}]$	65	39.1 (39.4)	2.15 (2.1)	34.55 (34.0)	2	170[e]
(**4**) $[AuR_3\{SPh_2PCH(AuCl)PPh_2Me\}]$	65	38.45 (38.85)	1.75 (1.8)	28.6 (28.95)	8	210[e]
(**5**) $[\{AuCl(SPh_2PCHPPh_2Me)\}_2]$	45	46.7 (47.1)	3.7 (3.65)	30.3 (29.65)	40	150[e]
(**6**) $[\{AuBr(SPh_2PCHPPh_2Me)\}_2]$	40	43.8 (44.2)	3.3 (3.4)	27.4 (27.8)	25	190[e]
(**7**) $[\{Au(SPh_2PCHPPh_2Me)\}_2][ClO_4]_2$	90	42.4 (42.9)	3.20 (3.3)	27.95 (27.05)	240	150[e]
(**8**) $[\{AuCl(SPh_2PCHPPh_2Me)\}_2][ClO_4]_2$	65	40.3 (40.9)	3.15 (3.15)	25.0 (25.8)	*d*	155[e]
(**9**) $[\{Ag(SPh_2PCHPPh_2Me)\}_2][ClO_4]_2$	60	48.6 (48.9)	3.6 (3.8)		*d*	120[e]
(**10**) $[Ag(SPh_2PCH_2PPh_2Me)][ClO_4]_2$	91	42.5 (42.3)	3.9 (3.4)		253	208[e]

[a] R = C_6F_5. [b] Calculated values are given in parentheses. [c] In acetone, values in $ohm^{-1}\ cm^2\ mol^{-1}$. [d] Not soluble enough. [e] With decomposition.



Scheme 2. (*i*) $+[Au(C_6F_5)(tht)]$, −tht; (*ii*) +tht, $-[Au(C_6F_5)_3(tht)]$

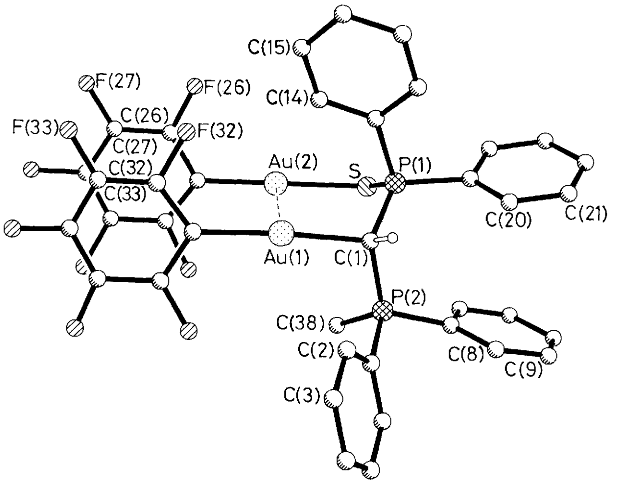


Figure. The molecule of complex (**3**) in the crystal, showing the atom numbering scheme; radii are arbitrary, phenyl H atoms omitted for clarity

length of 2.022(11) Å corresponds to a somewhat shortened single bond. The C_6F_5 rings display narrow angles at the *ipso* carbons.[10]

Complex (**2**) reacts with [AuCl(tht)] to give the mixed-valence binuclear complex $[Au(C_6F_5)_3\{SPh_2PCH(AuCl)PPh_2Me\}]$ (**4**), together with $[Au(C_6F_5)_3(tht)]$ (*ca.* 20%). Complex (**4**) is soluble in dichloromethane, acetone (non-conducting), and chloroform (*M* 1 320, calc. 1 361). Its i.r. spectrum shows ν(Au–Cl) at 320m cm^{-1}.

Complex (**4**) reacts with salts of bulky cations, $[N(PPh_3)_2]Cl$ and $[NBu_4]Br$, with cleavage of the Au^{III}–S bond to give a mixture of $[\{AuX(SPh_2PCHPPh_2Me)\}_2]$ [X = Cl (**5**) or Br (**6**)] (Scheme 1) and $[N(PPh_3)_2][Au(C_6F_5)_3Cl]$ or $[NBu_4][Au(C_6F_5)_3Br]$. The halide complexes (**5**) and (**6**) are white solids, which decompose slowly at room temperature but are stable at 0 °C. They are slightly soluble in dichloromethane, chloroform, and acetone and insoluble in diethyl ether and n-hexane. In acetone solution, the ligands X dissociate to some extent, as has previously been found for other three-co-ordinate gold(I) complexes.[11,12] No ν(Au–X) absorptions were found in the i.r. spectra; they probably lie below the limit of our apparatus (200 cm^{-1}).[11–13]

The chloro complex (**5**) reacts with $AgClO_4$ to give the cationic complex $[\{Au(SPh_2PCHPPh_2Me)\}_2][ClO_4]_2$ (**7**) in 90% yield. The same compound can also be obtained in 80% yield by the reaction between free $SPh_2PCHPPh_2Me$ and $[Au(tht)_2]ClO_4$, and in 61% yield by the reaction of complex (**2**) with $[Au(tht)_2]ClO_4$. At room temperature the white solid (**7**) decomposes slowly. It is slightly soluble in acetone, dichloromethane, and chloroform but insoluble in diethyl ether and n-hexane. The presence of ionic ClO_4^- in (**7**) is demonstrated by two i.r. bands at 1 100s, br and 620m cm^{-1}.

Complex (**7**) reacts with chlorine (1:1) to afford the gold(II) complex (**8**), an air- and moisture-stable yellow solid, which is slightly soluble in acetone, dichloromethane, and chloroform and insoluble in diethyl ether and n-hexane. Its i.r. spectrum shows a band at 260m cm^{-1}; values below 300 cm^{-1} are characteristic for ν(Au–Cl) in gold(II) complexes.[13–16]

Complex (**2**) reacts with $[Ag(OClO_3)(PPh_3)]$ (1:1) to afford a mixture of $[\{Ag(SPh_2PCHPPh_2Me)\}_2][ClO_4]_2$ (**9**) and $[Au(C_6F_5)_3(PPh_3)]$, because of ligand rearrangement. The lower solubility of complex (**9**) in acetone allows its isolation in 60% yield. Complex (**9**) can also be obtained in 80% yield by treating $AgClO_4$ with the free methanide $SPh_2PCHPPh_2Me$, and in 78% yield by the deprotonation with Na_2CO_3 of $[Ag(SPh_2PCH_2PPh_2Me)][ClO_4]_2$ (**10**) {prepared by the

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

	^{1}H N.m.r. (δ)[a,b]		^{31}P-{^{1}H} N.m.r. (δ)[b,c]		I.r. (cm^{-1})	
Complex	CH_2 or CH	Me	P–S	P–Me	ν(P–S)	ν(Au–C)
(**1**)	4.5 (t, 5.2)	2.39 (d, 13.6)	38.89(d)	20.24 (d, 15.7)	570	
(**2**)	3.17 (t, 8.3)	1.93 (d, 13.0)	38.47(d)	15.30 (d, 19.0)	560	
(**3**)	4.18 (dd, 11.5, 15.5)	3.29 (d, 13.7)	43.87(d)	22.56 (d, 6.9)	585	550
(**4**)	4.78 (dd, 10.8, 16.7)	2.27 (d, 13.4)	44.30(d)	22.90 (d, 6.3)	605	550
(**5**)	5.31 (dd, 13.4, 15.1)	2.84 (d, 13.7)	42.85(d)	21.11 (d, 4.9)	600	545
(**7**)	4.48 (dd, 12.6, 14.8)	2.72 (d, 13.8)	44.33(d)	23.22 (d, 7.2)	600	545
(**8**)			44.37(d)	22.87 (d, 5.7)	600	550
(**9**)	4.51 (dd, 11.0, 15.5)	3.08 (d, 14.5)	42.29(d)	21.99 (d, 6.5)	590	
(**10**)	5.18 (dd, 13.7, 16.1)	3.04 (d, 14.2)	38.83(d)	22.90 (d, 10.9)	587	

[a] Recorded in $CDCl_3$ at 200 MHz with reference to internal $SiMe_4$. [b] All complexes show a multiplet in the region δ 7.8 corresponding to Ph groups. Coupling constants in Hz are shown in parentheses. d = Doublet, t = triplet, and dd = doublet of doublets. [c] Referred to external H_3PO_4.

reaction (1:1) between $AgClO_4$ and $[SPh_2PCH_2PPh_2Me]ClO_4$ (Scheme 1)}.

Complex (**9**) is an air- and moisture-stable but light-sensitive white solid. It is slightly soluble in acetone, dichloromethane, and chloroform, and insoluble in diethyl ether and n-hexane. Its i.r. spectrum shows bands[2] corresponding to unco-ordinated ClO_4^- (1 100s, br and 620m cm^{-1}). In the spectrum of complex (**10**) these bands are broadened and show a shoulder at 1 145 cm^{-1}, indicating co-ordination of at least one perchlorato group to the silver atom.

Complexes (**3**) and (**4**) possess one chiral centre, but in the absence of other chiral species the n.m.r. spectra cannot distinguish *R* and *S* enantiomers. Complexes (**5**)—(**9**) have two chiral centres, and the four possible isomers should give rise to two sets of signals (each 50%) if there is no preferred configuration. Proton and ^{31}P-{^{1}H} n.m.r. spectra show, however, a major set of signals corresponding to only one isomer or enantiomeric mixture. For complexes (**5**), (**6**), (**8**), and (**9**), another set of signals (*ca.* 5—7% of the intensity of the major set) is observed in the ^{31}P-{^{1}H} spectra or in the ^{1}H spectra from the methyl group (P–Me). Table 2 collates the ^{1}H and ^{31}P-{^{1}H} n.m.r. data for the complexes (or for the more abundant isomer). The signals from the P atoms are often doublets, corresponding to two inequivalent and mutually coupled P atoms. Since the coupling constants are low (*ca.* zero in some cases) the signals are sometimes broad singlets. For complex (**2**) the coupling constant is higher (19 Hz) than for the complexes containing the C(methanide) centre co-ordinated to a metal atom. In all cases, the CH_2 and CH groups resonate as doublets of doublets or apparent triplets, and the CH_3 groups appear as doublets.

The minor sets of n.m.r. signals (not included in Table 2) are as follows: complex (**6**), ^{31}P-{^{1}H}, δ 41.55 (s, br) and 22.23 p.p.m. (s, br) and ^{1}H, P–Me at δ 2.75 [d, *J*(P–H) 12.5 Hz]; complex (**7**), ^{31}P-{^{1}H}, δ 41.59(d) and 22.66 p.p.m. [d, *J*(P–P) 12.4 Hz]; complex (**9**), ^{31}P-{^{1}H}, δ 43.80 (s, br) and 23.25 p.p.m. (s, br); complex (**10**), ^{1}H, P–Me at δ 3.05 [d, *J*(P–H) 15.4 Hz].

Experimental

Instrumentation and general experimental techniques were as described earlier.[6] The yields, melting points, C, H, and Au analyses, and conductivities of the new complexes are listed in Table 1. Proton and ^{31}P-{^{1}H} n.m.r. data are listed in Table 2. All the reactions were performed at room temperature unless otherwise stated.

Preparations.—$[SPh_2PCH_2PPh_2Me]ClO_4$. To a suspension of $[Ph_2PCH_2PPh_2Me]ClO_4$[4] (0.050 g, 0.1 mmol) in toluene (25 cm^3) was added S_8 (0.08 g, 0.3 mmol) and the mixture was stirred at reflux temperature for 6 h. The yellow solid that formed was filtered off and washed with 3 × 5 cm^3 of toluene, carbon disulphide, and hexane. Recrystallization from dichloromethane–diethyl ether gave white crystals (80% yield), m.p. 114 °C (Found: C, 58.4; H, 4.65. $C_{26}H_{25}ClO_4P_2S$ requires C, 58.8; H, 4.75%). Λ_M = 119 ohm^{-1} cm^2 mol^{-1} (*ca.* 5 × 10^{-4} mol dm^{-3} in acetone). N.m.r.: ^{1}H, δ 7.5 (m, 20 H, Ph), 4.41 [dd, 2 H, CH_2, *J*(HP) 12.6 and 15.1], and 2.70 [d, 3 H, CH_3, *J*(HP) 13.7 Hz]; ^{31}P-{^{1}H}, δ 33.68 (d, P–S) and 21.50 p.p.m. [d, P–Me, *J*(PP) 9.1 Hz].

Ether solutions of $SPh_2PCHPPh_2Me$. To a suspension of $[SPh_2PCH_2PPh_2Me]ClO_4$ (0.106 g, 0.2 mmol) in diethyl ether (20 cm^3) was added a solution of $LiBu^n$[17] in diethyl ether (0.2 cm^3, 1 mol dm^{-3}); a yellow solution immediately appeared.

$[Au(C_6F_5)_3(SPh_2PCH_2PPh_2Me)]ClO_4$ (**1**). A mixture of $[Au(C_6F_5)_3(OEt_2)]$[18] (0.077 g, 0.1 mmol) and $[SPh_2PCH_2PPh_2Me]ClO_4$ (0.053 g, 0.1 mmol) in dichloromethane (20 cm^3) was stirred for 1 h. Concentration to 2 cm^3 and addition of hexane (15 cm^3) gave complex (**1**).

$[Au(C_6F_5)_3(SPh_2PCHPPh_2Me)]$ (**2**). A diethyl ether (20 cm^3) suspension of NaH (0.08 g, 3 mmol) and complex (**1**) (0.123 g, 0.1 mmol) was stirred for 1 h under a nitrogen atmosphere. The excess of NaH and the precipitated $NaClO_4$ were filtered off and the solution was evaporated to *ca.* 2 cm^3; addition of hexane (10 cm^3) gave complex (**2**).

$[Au(C_6F_5)\{SPh_2PCH[Au(C_6F_5)]PPh_2Me\}]$ (**3**). The following procedures were used.

(*a*) To a solution of complex (**2**) (0.113 g, 0.1 mmol) in dichloromethane (10 cm^3) was added $[Au(C_6F_5)(tht)]$[19] (0.090 g, 0.2 mmol) and the mixture was stirred for 1 h. Partial concentration to *ca.* 5 cm^3 and addition of hexane (15 cm^3) led to precipitation of the white complex (**3**) (65% yield), which was filtered off. Evaporation of the ether–hexane solution to *ca.* 5 cm^3 gave $[Au(C_6F_5)_3(tht)]$ (70% yield).

(*b*) To a freshly prepared diethyl ether solution (20 cm^3) of $SPh_2PCHPPh_2Me$ (0.2 mmol) was added $[Au(C_6F_5)(tht)]$[19] (0.180 g, 0.4 mmol) and the mixture was stirred for 1 h. A white precipitate [complex (**3**)] was formed and filtered off, then recrystallized from dichloromethane–diethyl ether (65% yield).

$[Au(C_6F_5)_3\{SPh_2PCH(AuCl)PPh_2Me\}]$ (**4**). A mixture of complex (**2**) (0.118 g, 0.1 mmol) and $[AuCl(tht)]$[19] (0.032 g, 0.1 mmol) in dichloromethane (5 cm^3) was stirred for 15 min. On addition of hexane (5 cm^3) the white solid (**4**) precipitated and was filtered off (65% yield). Evaporation of the dichloromethane–hexane solution to dryness gave $[Au(C_6F_5)_3(tht)]$, which was recrystallized from ether–hexane (20% yield).

$[\{AuX(SPh_2PCHPPh_2Me)\}_2]$ [X = Cl (**5**) *or* Br (**6**)]. To a solution of complex (**4**) (0.272 g, 0.2 mmol) in acetone (7 cm^3)

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

Atom	*x*	*y*	*z*
Au(1)	4 286.3(7)	6 666(1)	3 120.2(6)
Au(2)	3 915.9(8)	4 213(1)	2 723.3(6)
S	5 380(5)	4 118(6)	2 648(4)
P(1)	5 680(5)	5 629(6)	2 488(4)
P(2)	6 300(5)	6 249(6)	3 914(4)
C(1)	5 627(15)	6 545(21)	3 111(12)
C(2)	5 838(11)	8 331(16)	4 137(7)
C(3)	5 872	9 192	4 540
C(4)	6 419	9 150	5 177
C(5)	6 932	8 245	5 412
C(6)	6 898	7 383	5 009
C(7)	6 351	7 426	4 371
C(8)	8 172(16)	6 564(13)	4 176(10)
C(9)	9 056	6 233	4 225
C(10)	9 228	5 170	4 137
C(11)	8 516	4 437	4 001
C(12)	7 632	4 767	3 952
C(13)	7 460	5 831	4 040
C(14)	3 983(12)	6 108(13)	1 617(8)
C(15)	3 407	6 587	1 068
C(16)	3 776	7 162	665
C(17)	4 720	7 258	810
C(18)	5 297	6 780	1 359
C(19)	4928	6 205	1 762
C(20)	7 395(11)	6 420(11)	2 517(7)
C(21)	8 202	6 386	2 355
C(22)	8 386	5 518	2 022
C(23)	7 764	4 686	1 851
C(24)	6 957	4 720	2 014
C(25)	6 772	5 588	2 347
C(26)	1 907(18)	4 068(23)	2 255(14)
C(27)	1 009(23)	4 121(26)	2 278(19)
C(28)	846(26)	4 121(30)	2 843(19)
C(29)	1 561(22)	4 163(28)	3 369(18)
C(30)	2 442(19)	4 187(24)	3 329(15)
C(31)	2 664(20)	4 150(26)	2 794(16)
C(32)	2 193(18)	6 908(22)	2 692(15)
C(33)	1 333(18)	6 895(21)	2 726(14)
C(34)	1 218(21)	6 809(26)	3 302(17)
C(35)	1 923(21)	6 754(25)	3 836(16)
C(36)	2 849(17)	6 712(23)	3 791(13)
C(37)	3 006(21)	6 871(24)	3 191(16)
C(38)	5 807(18)	5 169(21)	4 265(13)
F(26)	1 978(12)	4 113(17)	1 665(9)
F(27)	265(14)	4 112(18)	1 765(11)
F(28)	−37(13)	4 117(20)	2 877(13)
F(29)	1 456(13)	4 231(18)	3 987(10)
F(30)	3 144(12)	4 217(16)	3 887(9)
F(32)	2 300(10)	6 942(15)	2 100(8)
F(33)	609(11)	6 884(17)	2 217(10)
F(34)	399(11)	6 806(18)	3 374(11)
F(35)	1 898(14)	6 667(22)	4 433(10)
F(36)	3 576(10)	6 682(18)	4 328(8)

Table 4. Selected bond lengths (Å) and angles (°) for complex (**3**)

Au(1) • • • Au(2)	3.224(2)	Au(1)–C(1)	2.076(25)
Au(1)–C(37)	2.04(3)	Au(2)–S	2.312(8)
Au(2)–C(31)	1.98(3)	S–P(1)	2.022(11)
P(1)–C(1)	1.82(3)	P(1)–C(19)	1.809(17)
P(1)–C(25)	1.801(20)	P(2)–C(1)	1.788(23)
P(2)–C(7)	1.782(20)	P(2)–C(13)	1.801(25)
P(2)–C(38)	1.84(3)		
C(1)–Au(1)–C(37)	175.2(10)	S–Au(2)–C(31)	174.7(10)
Au(2)–S–P(1)	104.1(4)	S–P(1)–C(1)	113.9(10)
S–P(1)–C(19)	114.5(7)	C(1)–P(1)–C(19)	104.0(10)
S–P(1)–C(25)	106.2(6)	C(1)–P(1)–C(25)	114.2(9)
C(1)–P(2)–C(7)	107.0(10)	C(1)–P(2)–C(13)	117.3(12)
C(1)–P(2)–C(38)	112.3(12)	C(7)–P(2)–C(38)	109.6(12)
C(13)–P(2)–C(38)	103.6(11)	Au(1)–C(1)–P(1)	109.3(11)
Au(1)–C(1)–P(2)	106.3(14)	P(1)–C(1)–P(2)	117.7(14)
C(26)–C(31)–C(30)	112(3)	C(32)–C(37)–C(36)	112(3)

was added $[N(PPh_3)_2]Cl$[20] (0.115 g, 0.2 mmol) or $[NBu_4]Br$ (0.065 g, 0.2 mmol) and the mixture was stirred for 2 h. Complex (**5**) or (**6**) precipitated as a white solid. A second crop was obtained on addition of hexane (10 cm^3).

$[\{Au(SPh_2PCHPPh_2Me)\}_2][ClO_4]_2$ (**7**). The following procedures were used.

(*a*) To a dichloromethane solution (30 cm^3) of complex (**5**) (0.133 g, 0.1 mmol) was added $AgClO_4$ (0.041 g, 0.2 mmol). After stirring for 1 h AgCl was filtered off and the filtrate concentrated to *ca.* 5 cm^3. Addition of hexane (10 cm^3) led to the precipitation of complex (**7**) (90% yield).

(*b*) A mixture of complex (**2**) (0.226 g, 0.2 mmol) and $[Au(tht)_2]ClO_4$[21] (0.095 g, 0.2 mmol) in acetone (7 cm^3) was stirred for 1 h. A white precipitate of (**7**) was formed and on addition of hexane (5 cm^3) a second crop was obtained (61% yield). Evaporation of the acetone–hexane solution to dryness gave $[Au(C_6F_5)_3(tht)]$ which was recrystallized from ether–hexane (80% yield).

(*c*) To a freshly prepared diethyl ether solution (20 cm^3) of $SPh_2PCHPPh_2Me$ (0.2 mmol) was added $[Au(tht)_2]ClO_4$[21] (0.095 g, 0.2 mmol) and the mixture stirred for 1 h. A white precipitate of (**7**) was formed (80% yield).

$[\{AuCl(SPh_2PCHPPh_2Me)\}_2][ClO_4]_2$ (**8**). To a suspension of complex (**7**) (0.145 g, 0.1 mmol) in dichloromethane (15 cm^3) was added 1 cm^3 of a solution of Cl_2 (0.1 mmol) in chloroform. An orange colour immediately appeared and the mixture was stirred for 30 min. Concentration to *ca.* 5 cm^3 and addition of hexane (10 cm^3) led to the precipitation of yellow crystals of complex (**8**).

$[\{Ag(SPh_2PCHPPh_2Me)\}_2][ClO_4]_2$ (**9**). The following procedures were used.

(*a*) To a solution of complex (**2**) (0.226 g, 0.2 mmol) in acetone (1 cm^3) was added $[Ag(OClO_3)(PPh_3)]$[22] (0.094 g, 0.2 mmol). A white precipitate of (**9**) immediately appeared and the mixture was stirred for 1 h. Addition of hexane (5 cm^3) gave a second crop (60% yield). Evaporation of the acetone–hexane solution to dryness gave $[Au(C_6F_5)_3(PPh_3)]$, which was recrystallized from diethyl ether–hexane (80% yield).

(*b*) To a freshly prepared diethyl ether solution (20 cm^3) of $SPh_2PCHPPh_2Me$ (0.2 mmol) was added $AgClO_4$ (0.041 g, 0.2 mmol) and the mixture stirred for 1 h. Complex (**9**) precipitated as a white solid (80% yield).

(*c*) A mixture of complex (**10**) (0.184 g, 0.25 mmol) and Na_2CO_3 (0.106 g, 1 mmol) in dichloromethane (30 cm^3) was stirred for 4 h. The excess of Na_2CO_3 and the precipitated $NaClO_4$ were filtered off and the solution was evaporated to *ca.* 5 cm^3. Addition of hexane (15 cm^3) gave complex (**9**) (78% yield).

$[Ag(SPh_2PCH_2PPh_2Me)][ClO_4]_2$ (**10**). To a solution of $AgClO_4$ (0.104 g, 0.5 mmol) in acetone (25 cm^3) was added $[SPh_2PCH_2PPh_2Me]ClO_4$ (0.265 g, 0.5 mmol) and the mixture stirred for 3 h. Concentration to *ca.* 10 cm^3 and addition of diethyl ether (15 cm^3) gave the white complex (**10**).

X-Ray Structure Determination of Complex (**3**).—*Crystal data.* $C_{38}H_{24}Au_2F_{10}P_2S$, $M = 1\,158.5$, monoclinic, space group $P2_1/c$, $a = 15.392(4)$, $b = 12.643(5)$, $c = 21.965(7)$ Å, $\beta = 107.95(2)°$, $U = 4\,066$ Å^3 (refined from 2θ values of 44 reflections in the range 20—23°), $Z = 4$, $D_c = 1.89$ g cm^{-3}, $F(000) = 2\,184$, $\lambda(\text{Mo-}K_\alpha) = 0.710\,69$ Å, $\mu = 7.4$ mm^{-1}. Colourless prism, $0.35 \times 0.25 \times 0.25$ mm.

Data collection and reduction. Stoe-Siemens four-circle diffractometer with monochromated Mo-K_α radiation. 7 322 Profile-fitted intensities[23] collected to $2\theta_{\text{max.}}$ 50°, 7 121 unique ($R_{\text{int.}}$ 0.033), 3 166 with $F > 4\sigma(F)$ used for all calculations (program system SHELXTL, written by G. M. S.). Absorption correction based on ψ scans, with transmission factors 0.60—0.95.

Structure solution and refinement. Heavy-atom method, followed by cascade least-squares refinement on F. Atoms Au, P, S, and F anisotropic; phenyl (but not C_6F_5) rings as rigid groups with idealized geometry; H atoms included using a riding model. Weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,35F^2$; 240 parameters; final R 0.091, R' 0.072. The poor R values may be attributed to the weakly diffracting nature of the crystal. S 1.55; maximum shift/e.s.d. 0.01; maximum residual electron density 2 e Å^{-3} near Au(1).

Final atomic co-ordinates are given in Table 3, with selected bond lengths and angles in Table 4.

Acknowledgements

We thank the Fonds der Chemischen Industrie and the Comisíon Asesora Investigación Científica y Téchnica (Spain) for financial support.

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Received 27*th September* 1988; *Paper* 8/03812K