Synthesis of Mono-, Di-, and Tri-nuclear Gold Complexes containing the (Diphenylphosphino)methyldiphenylphosphoniomethanide Ligand. Crystal Structures of $[Au(C_6F_5)(Ph_2PCHPPh_2Me)]$ and $[(C_6F_5)Au\{Ph_2P\text{-}\overline{CH(PPh_2Me)\}Au}(C_6F_5)]$†

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The precursors $[AuR_m(Ph_2PCH_2PPh_2Me)]ClO_4$ (R_m = one or three uninegative ligands) react with excess of NaH by deprotonation of the methylene group and simultaneous elimination of the ClO_4 anion to give the neutral methanide complexes $[AuR_m(Ph_2PCHPPh_2Me)]$, which are potential C-donor ligands; these react with complexes of Au^I, Au^{III}, or Ag^I to form di- or tri-nuclear derivatives of the types $[R_mAu\{Ph_2PCH(PPh_2Me)\}AuX]$ (X = Cl or C_6F_5), $[\{(C_6F_5)AuPh_2PCH(PPh_2Me)\}_2M]X$ (M = Au or Ag; X = $AuCl_2$ or ClO_4), or $[(C_6F_5)Au\{Ph_2PCH(PPh_2Me)\}Au(C_6F_5)_3]$. The structure of $[Au(C_6F_5)(Ph_2PCHPPh_2Me)]$ has been determined by *X*-ray diffraction [space group $P\bar{1}$, $a = 8.888(2)$, $b = 13.053(3)$, $c = 14.230(4)$ Å, $\alpha = 103.15(2)$, $\beta = 107.22(2)$, $\gamma = 102.28(2)°$, $R = 0.026$ for 4 806 reflections], as has that of $[(C_6F_5)Au\{Ph_2P\overline{CH(PPh_2Me)\}Au}(C_6F_5)]$ [space group $P2_1/n$, $a = 12.127(3)$, $b = 22.758(6)$, $c = 13.433(3)$ Å, $\beta = 98.97(2)°$, $R = 0.051$ for 4 798 reflections]. In the methanide moieties the P–C bond lengths are much longer, and the P–C–P angles much smaller, in the latter compound, reflecting the reduced electron delocalisation in the P–C–P system when the methanide C functions as a donor ligand.

Few complexes containing the bis(diphenylphosphino)-methanide ligand C-bonded to a metal centre have been reported.[1–4] We have recently published[5] the synthesis of di- or tri-nuclear gold complexes in which the methanide complex $[Au(C_6F_5)_2(Ph_2PCHPPh_2)]$ itself functions as a C-donor ligand. Here we describe the preparation of mononuclear gold(I) and gold(III) complexes $[Au(C_6F_5)(Ph_2PCHPPh_2Me)]$, $[Au(C_6F_5)_3(Ph_2PCHPPh_2Me)]$, and $[Au(C_6F_5)_2Cl(Ph_2PCHPPh_2Me)]$ that contain the (diphenylphosphino)methyldiphenylphosphoniomethanide ligand, and their use as C-donor ligands in the synthesis of novel di- and tri-nuclear complexes.

Results and Discussion

(Diphenylphosphinomethyl)methyldiphenylphosphonium perchlorate can use its phosphino-phosphorus atom to displace weakly co-ordinating ligands (*e.g.* tetrahydrothiophen, tht) from neutral gold(I) and gold(III) complexes, forming cationic complexes [equation (1)]. If the neutral dinuclear $[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]$ is used, the cationic mononuclear (**3**) is obtained [equation (2)].

$$[Au(C_6F_5)_m(tht)] + [Ph_2PCH_2PPh_2Me]ClO_4 \longrightarrow tht + [Au(C_6F_5)_m(Ph_2PCH_2PPh_2Me)]ClO_4 \quad (1)$$
$$m = 1\ (\mathbf{1a}),\ 3\ (\mathbf{2})$$

$$[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2] + 2\,[Ph_2PCH_2PPh_2Me]ClO_4 \longrightarrow 2[Au(C_6F_5)_2Cl(Ph_2PCH_2PPh_2Me)]ClO_4 \quad (2)$$
$$(\mathbf{3})$$

Complexes (**1a**), (**2**), and (**3**) (see Table 1) are white, air- and moisture-stable solids that behave as 1 : 1 electrolytes in acetone solution. Their i.r. spectra show bands at 1 100s, br and 625m cm^{-1} due[6] to the ClO_4^- anion (T_d). The spectrum of complex (**1a**) also shows two bands at 950vs and 795s cm^{-1}, assignable[7–9] to the C_6F_5 group linked to Au^I. The spectrum of complex (**2**) shows the higher-energy absorption shifted to 965vs cm^{-1}, consistent[10,11] with the presence of C_6F_5 groups linked to a gold(III) centre, whilst the second band appears as a double band at 805s and 795s, br cm^{-1}, in agreement with previous observations[10] on tris(pentafluorophenyl)gold(III) complexes. Bands in the spectrum of complex (**3**) at 965vs, 808m, and 784m cm^{-1} confirm[12] the *cis* disposition of the two C_6F_5 groups. A band at 325m cm^{-1} is assigned[13] to ν(Au–Cl).

In the ^1H n.m.r. spectra of complexes (**1a**) and (**3**) the resonance of the methyl group is a doublet at $\delta = 2.61$ [$J(PH) = 13.6$] and $\delta = 2.51$ p.p.m. [$J(PH) = 13.3$ Hz] respectively whilst the signals from the methylene group (the X_2 part of a ABX_2 system) are at $\delta = 4.50$ [$J(P_AH) + J(P_BH) = 25.0$] and $\delta = 4.95$ p.p.m. [$J(P_AH) + J(P_BH) = 29.5$ Hz] respectively.

Complexes (**1a**) and (**3**) react with NaH by deprotonation of the methylene group and ClO_4^- abstraction, leading to neutral methanide complexes [equation (3)]. Complexes (**4**) and (**5**) are

$$[AuR_m(Ph_2PCH_2PPh_2Me)]ClO_4 + NaH \longrightarrow NaClO_4 + H_2 + [AuR_m(Ph_2PCHPPh_2Me)] \quad (3)$$
$$R_m = C_6F_5\ (\mathbf{4}),\ (C_6F_5)_3\ (\mathbf{5}),\ (C_6F_5)_2Cl\ (\mathbf{6})$$

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† [(Diphenylphosphino)methyldiphenylphosphoniomethanide-*P*]-pentafluorophenylgold(I) and μ-[(diphenylphosphino)methyldiphenylphosphoniomethanide-*C*(Au^1)*P*(Au^2)]-bis[pentafluorophenylgold(I)].

Supplementary data available: complete bond lengths and angles, structure factors, H-atom co-ordinates, thermal parameters can be ordered from the Fachinformationszentrum Energie Physik Mathematik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany, quoting reference number CSD/51474 and a full literature citation.

Table 1. Analytical and physical data for complexes (1)—(15)

Complex	Yield (%)	Analysis[a] (%)			Λ_M/ohm^{-1} cm^2 mol^{-1}	M[a,b]	M.p. (°C)
		C	H	Au			
(1a) $[Au(C_6F_5)(Ph_2PCH_2PPh_2Me)]ClO_4$	94	44.8 (44.55)	3.5 (2.9)	22.75 (22.85)	122[c]	—	178 (decomp.)
(1b) $[Au(C_6F_5)(Ph_2PCH_2PPh_2Me)]Cl$	75	48.0 (48.1)	3.25 (3.15)	25.5 (24.65)	74[d]	—	150 (decomp.)
(1c) $[Au(C_6F_5)(Ph_2PCH_2PPh_2Me)]BF_4$	77	45.2 (45.2)	2.7 (2.95)	24.15 (23.15)	100[c]	—	153 (decomp.)
(2) $[Au(C_6F_5)_3(Ph_2PCH_2PPh_2Me)]ClO_4$	75	44.1 (44.15)	2.2 (2.1)	16.55 (16.45)	108[c]	—	217
(3) $[Au(C_6F_5)_2Cl(Ph_2PCH_2PPh_2Me)]ClO_4$	82	42.8 (42.85)	2.5 (2.35)	18.6 (18.5)	124[c]	—	155 (decomp.)
(4) $[Au(C_6F_5)(Ph_2PCHPPh_2Me)]$	85	50.35 (50.4)	3.75 (3.15)	26.1 (25.85)	2[c]	716 (762)	132
(5) $[Au(C_6F_5)_3(Ph_2PCHPPh_2Me)]$	90	48.35 (48.2)	2.9 (2.2)	17.35 (17.95)	6[c]	1 039 (1 096)	165
(6) $[Au(C_6F_5)_2Cl(Ph_2PCHPPh_2Me)]$	95	47.0 (47.3)	2.3 (2.5)	20.45 (20.4)	23[c] 45[d]	932 (965)	119
(7) $[(C_6F_5)Au\{Ph_2PCH(PPh_2Me)\}Au(C_6F_5)]$	76	40.2 (40.5)	2.1 (2.15)	35.8 (34.95)	1[c]	1 286 (1 126)	202 (decomp.)
(8) $[(C_6F_5)_3Au\{Ph_2PCH(PPh_2Me)\}AuCl]$	75	39.85 (39.75)	2.15 (1.8)	30.45 (29.65)	12[c]	1 405 (1 329)	132
(9) $[(C_6F_5)_3Au\{Ph_2PCH(PPh_2Me)\}Au(C_6F_5)]$	82	41.05 (41.1)	1.95 (1.65)	26.25 (26.95)	17[c]	*e*	185 (decomp.)
(10) $[Cl(C_6F_5)_2Au\{Ph_2PCH(PPh_2Me)\}AuCl]$	83	38.0 (38.1)	1.9 (2.0)	33.55 (32.9)	12[c]	1 174 (1 197)	165 (decomp.)
(11) $[Cl(C_6F_5)_2Au\{Ph_2PCH(PPh_2Me)\}Au(C_6F_5)]$	87	39.65 (39.75)	1.8 (1.8)	30.5 (29.65)	6[c]	1 259 (1 329)	153 (decomp.)
(12) $[\{(C_6F_5)AuPh_2PCH(PPh_2Me)\}_2Au][AuCl_2]$	73	38.05 (38.65)	2.6 (2.45)	39.6 (39.6)	96[d]	—	130 (decomp.)
(13) $[\{(C_6F_5)AuPh_2PCH(PPh_2Me)\}_2Au]ClO_4$	56	42.75 (42.2)	3.2 (2.65)	32.9 (32.45)	121[c]	—	125 (decomp.)
(14) $[\{(C_6F_5)AuPh_2PCH(PPh_2Me)\}_2Ag]ClO_4$	94	44.4 (44.4)	2.9 (2.8)	29.6[f] (29.0)	126[c]	—	180 (decomp.)
(15) $[(C_6F_5)Au\{Ph_2PCH(PPh_2Me)\}Au(C_6F_5)_3]$	64	41.7 (41.1)	2.2 (1.65)	27.6 (27.0)	13[c]	1 389 (1 460)	146

[a] Calculated values in parentheses. [b] In chloroform. [c] In acetone. [d] In nitromethane. [e] Insoluble. [f] Au + Ag.

white solids, **(6)** is a yellow solid. At room temperature they are stable for months. They are monomeric in chloroform solution (see Table 1). In acetone or nitromethane solution, complex **(6)** gives conducting species whose concentration slowly increases; after 4—5 h the conductivity reaches the value characteristic for a 1:1 electrolyte, remaining constant thereafter.

The i.r. spectra of complexes **(4)**—**(6)** show no band from the ClO_4^- anion, but a new band (not present in the starting perchlorato-complexes) at 380m, 380m, and 375m, respectively. We consider this band characteristic for the methanide system.

In the ^1H n.m.r. spectra the methyl group resonates as a doublet at $\delta = 2.40$ [J(PH) = 12.7] for complex **(4)**, 1.36 [J(PH) = 12.7] for **(5)**, and 2.32 p.p.m. [J(PH) = 13.1 Hz] for **(6)**, and the PCHP group shows a signal at $\delta = 1.57$(s) for **(4)**, 1.62(s) for **(5)**, and 1.43 p.p.m. [part X of an ABX system, $J(P_AH) + J(P_BH) = 10.9$ Hz] for **(6)**. The ^{31}P n.m.r. spectra show two signals (AB system): the P atom co-ordinated to gold gives a multiplet (coupling with the fluorine nuclei) at $\delta = 25.02$ for **(4)** and 23.09 p.p.m. for **(6)** and the other P atom a signal at $\delta = 17.51$ for **(4)** and 17.06 p.p.m. for **(6)** [J(PP) = 70.9 **(4)** and 27.1 Hz **(6)**].

Single crystals of complex **(4)** were obtained by slow diffusion of n-hexane into a diethyl ether solution and the structure was determined by *X*-ray crystallography (Figure 1). The gold(I) centre has an approximately linear co-ordination with P(1)–Au–C(11) 174.8(2)°. The P–C(1) distances, 1.729(5) and 1.692(5) Å, and the P(1)–C(1)–P(2) angle, 126.0(4)°, are similar to those found in complexes containing the bidentate (P,P-bonded) bis(diphenylphosphino)methanide ligand (1.62 and 1.74 Å, 129° in $[\{Au[(PPh_2)_2CH]\}_2]$;[14] 1.71 and 1.77 Å, 123.5° in $Bu^t_2P(CH_2AuPPh_2)_2CH$[15]). These distances are significantly shorter than those found in $[Au(C_6F_5)_2(Ph_2PCH_2PPh_2)]ClO_4$[16] (1.845 Å) and thus indicate appreciable electron delocalisation in the P–C–P system.

The methanide complexes can be easily protonated with acids HX. Thus complex **(4)** reacts with HCl or HBF_4 to give cationic complexes $[Au(C_6F_5)(Ph_2PCH_2PPh_2Me)]X$ [X = Cl **(1b)** or BF_4 **(1c)**], which behave similarly to the perchlorate **(1a)**.

The presence of excess of electron density on the methanide carbon of complexes **(4)**—**(6)** causes them to act as C-donor nucleophiles, forming binuclear complexes. They can, for instance, displace the neutral ligand in [AuX(tht)] (X = Cl or C_6F_5) [equation (4)]. Complexes **(7)**—**(11)** are white solids, air- and moisture-stable both as solids and in solution. Their molecular weights (isopiestic method, in chloroform solution) are as expected for the binuclear formulations; their acetone solutions are non-conducting. Their i.r. spectra show no band at 380 cm^{-1} whilst a new band appears in the 595—575m cm^{-1} region, assigned[17,18] to v(Au–C). Complexes **(8)**, **(10)**, and **(11)** show v(Au–Cl) at 330m, 325s,br, and 330m cm^{-1}, the broadening of this band in complex **(10)** being due to the overlapping of v(Au^{III}–Cl) and v(Au^{I}–Cl).

As a consequence of the donation of electron density to the gold(I) centre, the proton in the P–CH–P system is less shielded

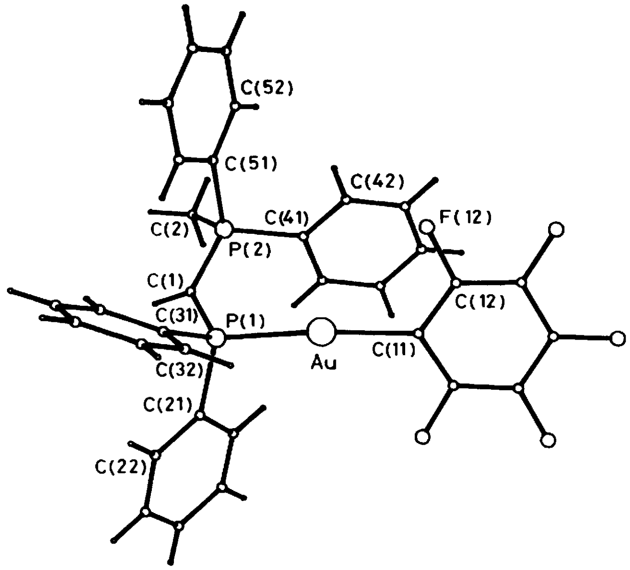


Figure 1. The molecule of complex (**4**) in the crystal, showing the atom numbering scheme. Radii arbitrary

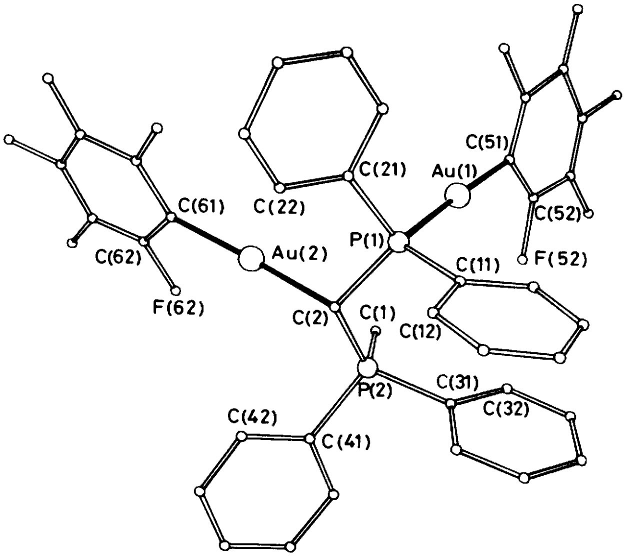


Figure 2. The molecule of complex (**7**) in the crystal, showing the atom numbering scheme. Radii arbitrary

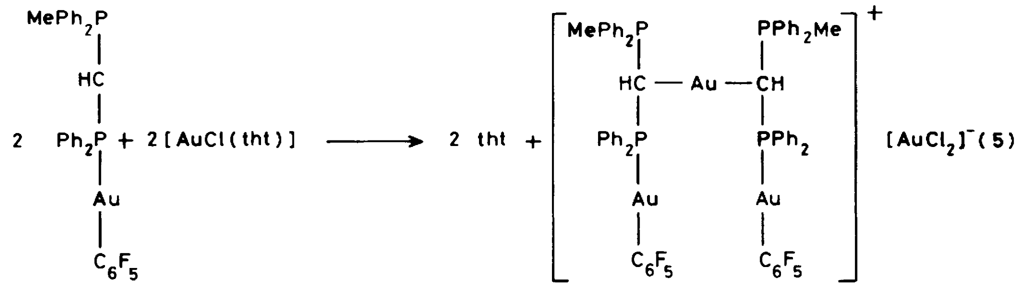
$$[\mathrm{AuR}_m(\mathrm{Ph_2PCHPPh_2Me})] + [\mathrm{AuX(tht)}] \longrightarrow \mathrm{R}_m\mathrm{AuPPh_2}\underset{}{\overset{\mathrm{PPh_2Me}}{\mathrm{CH}}}\mathrm{-AuX} + \mathrm{tht} \quad (4)$$

$\mathrm{R}_m = \mathrm{C_6F_5}$, X = $\mathrm{C_6F_5}$ (**7**); $\mathrm{R}_m = (\mathrm{C_6F_5})_3$, X = Cl (**8**) or $\mathrm{C_6F_5}$ (**9**);
$\mathrm{R}_m = (\mathrm{C_6F_5})_2\mathrm{Cl}$, X = Cl (**10**) or $\mathrm{C_6F_5}$ (**11**)

than in the starting complexes. The ^{1}H n.m.r. resonance (part X of an ABX system) thus appears at δ = 3.27 [$J(\mathrm{P_AH}) + J(\mathrm{P_BH}) = 25.8$] for complex (**7**), 3.28 [$J(\mathrm{P_AH}) + J(\mathrm{P_BH}) = 23.6$ Hz] for (**8**), 2.99 [$J(\mathrm{P_AH}) + J(\mathrm{P_BH}) = 22.2$] for (**9**), and 4.18 p.p.m. [$J(\mathrm{P_AH}) + J(\mathrm{P_BH}) = 28.9$ Hz] for (**11**). The methyl group gives a doublet at δ = 2.85 [J(PH) = 12.7] for (**7**), 2.32 [J(PH) = 12.3] for (**8**), 2.13 [J(PH) = 12.5] for (**9**), and 2.52 p.p.m. [J(PH) = 12.4 Hz] for (**11**). The ^{31}P n.m.r. spectra for complexes (**7**) and (**11**) correspond to an AB system with δ_A = 23.71 [J(AB) = 24.0] and 22.81 p.p.m. [J(AB) = 11.8 Hz] (P–Me) and δ_B = 32.54 and 29.33 p.p.m. (multiplet, coupling with the F nuclei) (P–Au), respectively.

Single crystals of complex (**7**) were obtained by liquid diffusion of n-hexane into a dichloromethane solution and its structure was determined by *X*-ray methods (Figure 2). The gold centres again attain the expected linear geometry (*ca.* 177° in both cases). The geometry of the bidentate (P,C-bonded) methanide ligand in complex (**7**) differs significantly from that in (**4**); in the methanide moiety the P–C bonds are much longer [1.790(10), 1.801(11) Å] and the P–C–P angle much smaller [114.9(6)°]. This is consistent with reduced electron delocalisation over the methanide ligand as a consequence of electron donation to Au(2). Similar P–C bond lengths are observed[5] in the bis(diphenylphosphino)methanide ligand when acting as a C-donor [1.815(6); 1.787(20), 1.826(19) Å in two different complexes; the P–C–P angles in these complexes are not comparable because they are part of four-membered rings]. The Au–C(methanide) bond lengths also reflect the similarity of bonding patterns: 2.090(10) Å in (**7**), 2.094(7), 2.127(29), and 2.098(28) Å in ref. 5.

The reaction between complex (**4**) and [AuCl(tht)] does not follow the normal pattern [equation (4)]: not only is the neutral ligand (tht) displaced but a ligand rearrangement takes place [equation (5)]. Complex (**12**) is an air- and moisture-stable

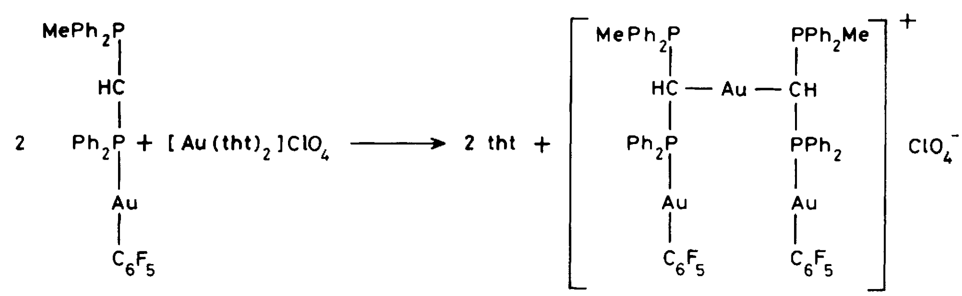


$$2\ \begin{array}{c}\mathrm{MePh_2P}\\ |\\ \mathrm{HC}\\ |\\ \mathrm{Ph_2P}\\ |\\ \mathrm{Au}\\ |\\ \mathrm{C_6F_5}\end{array} + 2\,[\mathrm{AuCl(tht)}] \longrightarrow 2\ \mathrm{tht} + \left[\begin{array}{ccccc}\mathrm{MePh_2P} & & & & \mathrm{PPh_2Me}\\ | & & & & |\\ \mathrm{HC} & - & \mathrm{Au} & - & \mathrm{CH}\\ | & & & & |\\ \mathrm{Ph_2P} & & & & \mathrm{PPh_2}\\ | & & & & |\\ \mathrm{Au} & & & & \mathrm{Au}\\ | & & & & |\\ \mathrm{C_6F_5} & & & & \mathrm{C_6F_5}\end{array}\right]^+ [\mathrm{AuCl_2}]^- \quad (5)$$

(**12**)

white solid, which in nitromethane solution behaves as a 1:1 electrolyte (slope $B = 291$ in the Onsager equation $\Lambda_e = \Lambda_0 - B\sqrt{c}$)[19] (where Λ_e = equivalent conductivity, Λ_0 = conductivity at infinite dilution, and c = equivalent concentration). Its i.r. spectrum shows ν(Au–C) at 580m cm^{-1} and ν(Au–Cl) at 330m cm^{-1}.

The same trinuclear cation is obtained by the reaction between complex (**4**) and $[Au(tht)_2]ClO_4$ [equation (6)].

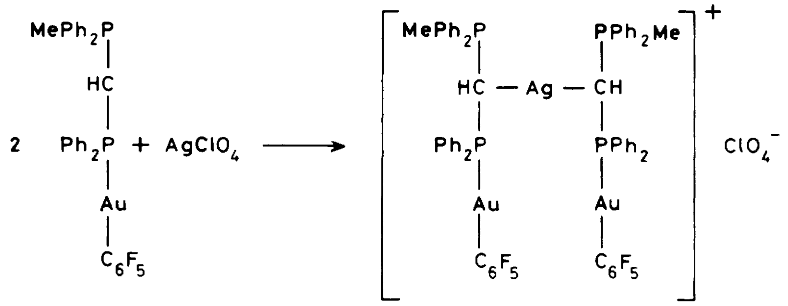


(6)

(13)

Complex (**13**) also behaves as a 1:1 electrolyte in acetone solution ($B = 369$). Its i.r. spectrum shows bands at 580m cm^{-1} [ν(Au–C)] and at 1 100s, br and 620m cm^{-1} (ClO_4^- anion).

A similar trinuclear heterometallic cationic complex (**14**) can be prepared by reaction of complex (**4**) with silver perchlorate [equation (7)]. The white solid (**14**) is air- and moisture-stable, but light-sensitive. It is conducting (1:1 electrolyte) in acetone solution and its i.r. spectrum shows a band at 545m cm^{-1}, assignable to ν(Ag–C).

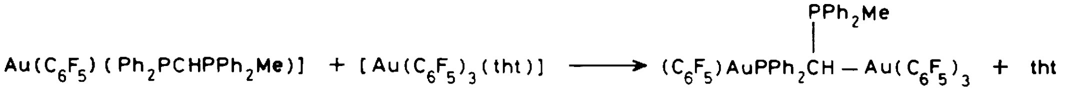


(7)

(14)

The reactions of the gold(III) complexes (**5**) and (**6**) with either $[Au(tht)_2]ClO_4$ or $AgClO_4$ lead to mixtures of unidentifiable products.

Finally, complex (**4**) reacts with $[Au(C_6F_5)_3(tht)]$ to give a neutral mixed-valence complex [equation (8)] which is an air- and moisture-stable pale yellow solid, molecular weight (isopiestic method, in chloroform solution) as expected. Its acetone solutions are non-conducting. A band at 586m cm^{-1} is assigned to ν(Au–C).



$$[Au(C_6F_5)(Ph_2PCHPPh_2Me)] + [Au(C_6F_5)_3(tht)] \longrightarrow (C_6F_5)AuPPh_2\underset{}{\overset{\overset{\displaystyle PPh_2Me}{|}}{C}}H-Au(C_6F_5)_3 + tht \quad (8)$$

(15)

Experimental

Instrumentation and general experimental techniques were as described earlier.[5] Nuclear magnetic resonance spectra were recorded on a Varian XL 200 spectrometer in $CDCl_3$. Chemical shifts are quoted relative to $SiMe_4$ (^1H) and 85% H_3PO_4 (external) (^{31}P). The yields, melting points, and C, H, and Au analyses are listed in Table 1. All reactions were carried out in a dry nitrogen atmosphere.

$[Ph_2PCH_2PPh_2Me]ClO_4$. To a dichloromethane solution (25 cm^3) of $[Ph_2PCH_2PPh_2Me]I$[20] (1.00 g, 1.9 mmol) was added $AgClO_4$ (0.39 g, 1.9 mmol) and the mixture was stirred at room temperature for 60 min. After filtering off the precipitated AgI, the solution was evaporated to *ca.* 5 cm^3. Addition of diethyl ether (15 cm^3) and vigorous stirring gave a white solid (81% yield).

Preparation of the Complexes.—$[AuR_m(Ph_2PCH_2PPh_2Me)]ClO_4$ [$R_m = C_6F_5$ (**1a**), $(C_6F_5)_3$ (**2**), *or* $(C_6F_5)_2Cl$ (**3**)]. To a dichloromethane or chloroform solution (25 cm^3) of $[Ph_2PCH_2PPh_2Me]ClO_4$ (0.251 g, 0.5 mmol) were added, respectively, $[Au(C_6F_5)(tht)]$[21] (0.250 g, 0.5 mmol), $[Au(C_6F_5)_3(tht)]$[10] (0.393 g, 0.5 mmol), or $[\{Au(\mu\text{-}Cl)(C_6F_5)_2\}_2]$[22] (0.283 g, 0.25 mmol) and the mixtures were stirred at room temperature [$R_m = C_6F_5$ and $(C_6F_5)_2Cl$] or at reflux temperature [$R_m = (C_6F_5)_3$] for 2 h. A light turbidity was removed by filtering the solution through a layer (1 cm) of diatomaceous earth. The solutions were evaporated to *ca.* 5 cm^3 and diethyl ether (15 cm^3) was added. The complexes (**1a**)—(**3**) separated as white solids.

$[AuR_m(Ph_2PCHPPh_2Me)]$ [$R_m = C_6F_5$ (**4**), $(C_6F_5)_3$ (**5**), *or* $(C_6F_5)_2Cl$ (**6**)]. A diethyl ether (20 cm^3) suspension of NaH (0.8 g, 33.3 mmol) and complex (**1a**) (0.259 g, 0.3 mmol), (**2**) (0.375 g, 0.3 mmol), or (**3**) (0.319 g, 0.3 mmol) was stirred at room temperature for 2 h. The excess of NaH and the precipitated

Table 2. Atom co-ordinates (× 10^4) for complex (**4**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Au	6 533.3(2)	2 310.0(1)	2 623.2(1)
P(1)	5 902(1)	1 354(1)	3 688(1)
P(2)	2 425(1)	1 577(1)	3 077(1)
C(1)	3 846(4)	966(3)	3 556(3)
C(2)	412(5)	642(4)	2 800(4)
C(11)	7 118(5)	3 039(3)	1 587(3)
C(12)	6 933(5)	4 043(3)	1 514(3)
C(13)	7 225(6)	4 502(4)	791(3)
C(14)	7 777(6)	3 960(4)	88(3)
C(15)	7 988(6)	2 953(5)	111(3)
C(16)	7 664(5)	2 526(4)	854(3)
F(12)	6 405(4)	4 642(2)	2 201(2)
F(13)	7 002(5)	5 491(2)	768(2)
F(14)	8 079(5)	4 377(3)	−642(2)
F(15)	8 505(4)	2 389(3)	−590(2)
F(16)	7 896(4)	1 531(3)	841(2)
C(21)	6 401(4)	58(3)	3 378(3)
C(22)	7 457(5)	−275(3)	4 087(3)
C(23)	7 727(6)	−1 291(4)	3 797(4)
C(24)	6 930(6)	−1 979(4)	2 801(4)
C(25)	5 896(6)	−1 651(4)	2 081(4)
C(26)	5 637(5)	−637(4)	2 361(3)
C(31)	7 225(4)	2 014(3)	5 047(3)
C(32)	8 807(5)	2 706(3)	5 319(3)
C(33)	9 803(5)	3 202(4)	6 348(4)
C(34)	9 264(6)	3 005(4)	7 109(4)
C(35)	7 713(6)	2 313(5)	6 855(3)
C(36)	6 677(5)	1 823(4)	5 824(3)
C(41)	2 447(4)	1 836(3)	1 890(3)
C(42)	2 659(5)	2 865(3)	1 756(3)
C(43)	2 608(6)	3 002(4)	824(4)
C(44)	2 371(7)	2 130(5)	8(4)
C(45)	2 206(7)	1 097(5)	124(4)
C(46)	2 245(6)	949(4)	1 060(3)
C(51)	2 479(4)	2 860(3)	3 915(3)
C(52)	1 288(5)	3 392(4)	3 613(4)
C(53)	1 368(7)	4 376(4)	4 272(4)
C(54)	2 596(7)	4 834(4)	5 235(4)
C(55)	3 761(7)	4 315(4)	5 549(4)
C(56)	3 710(5)	3 339(3)	4 893(3)

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

Au–C(11)	2.057(6)	P(1)–C(1)–P(2)	126.0(4)
C(1)–P(2)	1.692(5)	P(1)–Au–C(11)	174.8(2)
Au–P(1)	2.287(2)	Au–P(1)–C(21)	108.1(3)
C(1)–P(1)	1.729(5)	Au–P(1)–C(31)	113.4(2)
C(2)–P(2)	1.811(5)	C(21)–P(1)–C(31)	102.3(3)
C(21)–P(1)	1.830(5)	C(1)–P(2)–C(41)	113.5(3)
C(31)–P(1)	1.825(4)	C(1)–P(2)–C(51)	117.4(3)
C(41)–P(2)	1.801(5)	C(41)–P(2)–C(51)	105.9(3)
C(51)–P(2)	1.804(5)	Au–P(1)–C(1)	116.1(3)
		C(1)–P(1)–C(21)	104.9(3)
		C(1)–P(1)–C(31)	110.7(3)
		C(1)–P(2)–C(2)	107.2(3)
		C(2)–P(2)–C(41)	107.5(3)
		C(2)–P(2)–C(51)	104.7(3)

$NaClO_4$ were filtered off, the solutions were evaporated to *ca.* 2 cm^3 and n-hexane (15 cm^3) was added to precipitate a white (**4**) or (**5**) or yellow solid (**6**).

$[Au(C_6F_5)(Ph_2PCH_2PPh_2Me)]X$ [X = Cl (**1b**) *or* BF_4 (**1c**)]. To a diethyl ether solution (20 cm^3) of complex (**4**) (0.152 g, 0.2 mmol) was added a diethyl ether solution containing HX (0.2 mmol) (X = Cl, 4.33 cm^3, 0.046 mol dm^{-3}; X = BF_4, 0.43 cm^3, 0.469 mol dm^{-3}). After stirring at room temperature for 30 min the white (**1b**) or (**1c**) was filtered off.

$[R_mAu\{Ph_2PCH(PPh_2Me)\}AuX]$ [$R_m = C_6F_5$, X = C_6F_5 (**7**); $R_m = (C_6F_5)_3$; X = Cl (**8**) *or* C_6F_5 (**9**); $R_m = (C_6F_5)_2Cl$, X = Cl (**10**) *or* C_6F_5 (**11**)]. To a diethyl ether solution (20 cm^3) of complex (**4**) (0.152 g, 0.2 mmol), (**5**) (0.219 g, 0.2 mmol), or (**6**) (0.193 g, 0.2 mmol) were added [AuX(tht)][21] [X = Cl (0.064 g, 0.2 mmol) or C_6F_5 (0.090 g, 0.2 mmol)]. The mixtures were stirred at room temperature for 3 h, whereby complex (**7**), (**10**), or (**11**) partially precipitated as a white solid (additional quantities were obtained by evaporating the filtrates). For complex (**8**) or (**9**), the solution was concentrated to *ca.* 5 cm^3; addition of hexane (15 cm^3) precipitated the complexes as white solids.

$[\{(C_6F_5)AuPh_2PCH(PPh_2Me)\}_2Au]X$ [X = $AuCl_2$ (**12**) *or* ClO_4 (**13**)]. To a dichloromethane solution (20 cm^3) of complex (**4**) (0.152 g, 0.2 mmol) was added [AuCl(tht)][21] (0.064 g, 0.2 mmol) or $[Au(tht)_2]ClO_4$[5] (0.050 g, 0.1 mmol). After stirring for 2 h at room temperature the solutions were evaporated to *ca.* 5 cm^3. Addition of diethyl ether precipitated (**12**) or (**13**) as a white solid.

$[\{(C_6F_5)AuPh_2PCH(PPh_2Me)\}_2Ag]ClO_4$ (**14**). To a diethyl ether solution (25 cm^3) of complex (**4**) (0.228 g, 0.3 mmol) was added $AgClO_4$ (0.031 g, 0.15 mmol) and the mixture was stirred at room temperature for 30 min. Complex (**14**) precipitated as a white solid, which was filtered off.

$[(C_6F_5)Au\{Ph_2PCH(PPh_2Me)\}Au(C_6F_5)_3]$ (**15**). To a dichloromethane solution (25 cm^3) of complex (**4**) (0.137 g, 0.18 mmol) was added $[Au(C_6F_5)_3(tht)]$[10] (0.141 g, 0.18 mmol) and the mixture was stirred at room temperature for 4 h. A light turbidity was removed by filtering through a layer (1 cm) of diatomaceous earth. The filtrate was concentrated to *ca.* 5 cm^3 and n-hexane (20 cm^3) was added to precipitate (**15**) as a white solid.

X-*Ray Structure Determination of Complex* (**4**).—*Crystal data.* $C_{32}H_{24}AuF_5P_2$, *M* = 762.45, triclinic, *a* = 8.888(2), *b* = 13.053(3), *c* = 14.230(4) Å, α = 103.15(2), β = 107.22(2), γ = 102.28(2)°, *U* = 1 464.3 $Å^3$ (by refinement of 2θ values for 30 reflections in the range 20—23°), space group $P\bar{1}$, *Z* = 2, D_c = 1.73 g cm^{-3}, *F*(000) = 740, colourless tablet, 0.45 × 0.35 × 0.15 mm, μ(Mo-K_α) = 5.2 mm^{-1}.

Data collection and processing. Stoe–Siemens four-circle diffractometer, monochromated Mo-K_α radiation (λ = 0.710 69 Å); 5 162 profile-fitted[23] reflections ($2\theta_{max.}$ 50°, $-h \pm k \pm l$), 5 148 unique, 4 806 with $F > 4\sigma(F)$ used for all calculations. Absorption correction (ψ scans) with transmissions 0.56—0.94; three check reflections, no decay.

Structure analysis and refinement. Heavy-atom method. Refinement on *F* to *R* 0.026, *R′* 0.026 {all non-H atoms anisotropic; H atoms [all but H(36) located in difference syntheses] included with riding model [C–H 0.96 Å, H–C–H 109.5°, *U*(H) = 1.2 U_{eq}(C)]; weighting scheme $w^{-1} = \sigma^2(F) + 0.0002\ F^2$; 364 parameters}. Program system SHELXTL (written by G. M. S.). Final atomic co-ordinates and derived parameters are given in Tables 2 and 3.

X-*Ray Structure Determination of Complex* (**7**).—*Crystal data.* $C_{38}H_{24}Au_2F_{10}P_2$, *M* = 1 126.5, monoclinic, *a* = 12.127(3), *b* = 22.758(6), *c* = 13.433(3) Å, β = 98.97(2)°, *U* = 3 662 $Å^3$ (by refinement of 2θ values of 46 reflections in the range 20—23°), space group $P2_1/n$, *Z* = 4, D_c = 2.04 g cm^{-3},

Table 4. Atom co-ordinates ($\times 10^4$) for complex (7)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Au(1)	3 696.5(4)	2 049.4(2)	2 254.8(3)	C(45)	−910(9)	4 497(6)	1 488(10)
Au(2)	3 756.1(3)	3 800.7(2)	1 201.6(3)	C(46)	−281(9)	3 997(6)	1 739(8)
P(1)	3 945(2)	2 930(1)	3 078(2)	C(1)	1 454(9)	2 909(5)	982(7)
P(2)	1 669(2)	3 359(1)	2 102(2)	C(2)	3 115(7)	3 526(4)	2 482(6)
C(11)	3 689(7)	2 869(5)	4 370(7)	C(51)	3 420(13)	1 250(6)	1 552(10)
C(12)	3 860(10)	3 346(7)	5 006(8)	C(52)	2 392(14)	1 042(6)	1 199(10)
C(13)	3 600(12)	3 303(9)	5 967(9)	C(53)	2 176(13)	476(7)	792(10)
C(14)	3 159(13)	2 820(10)	6 318(11)	C(54)	3 019(16)	145(6)	735(11)
C(15)	2 997(11)	2 354(9)	5 697(11)	C(55)	4 163(16)	288(7)	1 078(10)
C(16)	3 252(8)	2 367(6)	4 717(9)	C(56)	4 241(14)	880(7)	1 475(10)
C(21)	5 378(8)	3 187(5)	3 250(7)	F(52)	1 490(7)	1 367(4)	1 245(6)
C(22)	5 695(9)	3 768(6)	3 244(8)	F(53)	1 148(9)	303(4)	438(7)
C(23)	6 784(11)	3 921(7)	3 430(9)	F(54)	2 868(12)	−423(4)	335(7)
C(24)	7 611(11)	3 495(11)	3 622(10)	F(55)	5 004(11)	−57(5)	1 041(7)
C(25)	7 310(12)	2 930(9)	3 638(11)	F(56)	5 350(7)	1 031(4)	1 816(6)
C(26)	6 201(9)	2 755(7)	3 449(8)	C(61)	4 369(9)	4 105(5)	−6(7)
C(31)	1 041(7)	2 979(4)	3 046(7)	C(62)	3 743(9)	4 269(6)	−891(9)
C(32)	706(9)	2 406(5)	2 948(8)	C(63)	4 100(15)	4 495(6)	−1 721(9)
C(33)	261(9)	2 136(5)	3 707(8)	C(64)	5 241(17)	4 577(6)	−1 651(10)
C(34)	166(8)	2 425(6)	4 582(8)	C(65)	5 939(12)	4 441(6)	−815(12)
C(35)	501(9)	3 001(6)	4 701(8)	C(66)	5 507(10)	4 207(5)	8(8)
C(36)	932(8)	3 288(5)	3 926(7)	F(62)	2 628(6)	4 151(5)	−1 004(6)
C(41)	877(8)	4 029(5)	1 837(7)	F(63)	3 440(9)	4 637(4)	−2 558(5)
C(42)	1 381(9)	4 557(5)	1 655(7)	F(64)	5 673(10)	4 813(4)	−2 437(6)
C(43)	716(9)	5 047(5)	1 404(8)	F(65)	7 035(7)	4 526(5)	−749(7)
C(44)	−413(10)	5 016(6)	1 318(8)	F(66)	6 240(6)	4 077(4)	839(6)

Table 5. Selected bond lengths (Å) and angles (°) for complex (7)

Au(1)–C(51)	2.053(15)	P(1)–Au(1)–C(51)	177.5(6)
Au(2)–C(61)	2.011(11)	Au(1)–P(1)–C(11)	111.5(5)
Au(1)–P(1)	2.286(4)	C(11)–P(1)–C(21)	101.9(5)
Au(2)–C(2)	2.090(10)	C(11)–P(1)–C(2)	108.4(5)
C(11)–P(1)	1.817(11)	C(31)–P(2)–C(41)	105.9(6)
C(21)–P(1)	1.815(11)	C(41)–P(2)–C(1)	108.1(6)
C(31)–P(2)	1.800(11)	C(41)–P(2)–C(2)	110.1(6)
C(41)–P(2)	1.809(12)	C(2)–Au(2)–C(61)	177.2(5)
C(1)–P(2)	1.804(11)	Au(1)–P(1)–C(21)	113.4(5)
C(2)–P(2)	1.790(10)	Au(1)–P(1)–C(2)	115.0(4)
C(2)–P(1)	1.801(11)	C(21)–P(1)–C(2)	105.7(6)
		C(31)–P(2)–C(1)	107.0(6)
		C(31)–P(2)–C(2)	113.9(5)
		C(1)–P(2)–C(2)	111.5(6)
		Au(2)–C(2)–P(1)	109.7(5)
		P(1)–C(2)–P(2)	114.9(6)
		Au(2)–C(2)–P(2)	107.6(5)

$F(000)$ = 2 120, colourless tablet, 0.6 × 0.5 × 0.2 mm, $\mu(\text{Mo-}K_\alpha) = 8.2\ \text{mm}^{-1}$.

Data collection and processing. As for complex (4) with following differences: 7 111 reflections measured ($-h\ -k \pm l$ and some $+h$ equivalents), 6 437 unique, 4 798 with $F > 4\sigma(F)$. Transmissions 0.30—0.99.

Structure analysis and refinement. Heavy-atom method. Refinement on F to R 0.051, R' 0.048 [non-H atoms anisotropic, H atoms as for complex (4); weighting scheme $w^{-1} = \sigma^2(F) + 0.0003\ F^2$; 472 parameters]. Final atom co-ordinates and derived parameters are given in Tables 4 and 5.

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