Pentakis(methoxycarbonyl)cyclopentadiene Chemistry. Part 5.[1] Preparation and Crystal and Molecular Structures of $[Au\{C_5(CO_2Me)_5\}(PPh_3)]$ and $[Au(PPh_3)_2][C_5(CO_2Me)_5]\cdot MeOH$ †

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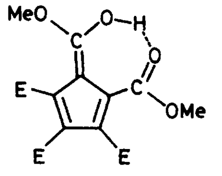
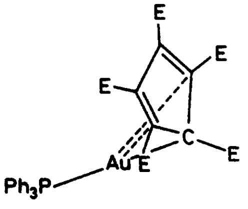
Pentakis(methoxycarbonyl)cyclopentadiene reacts with $[Au(O_2CMe)(PPh_3)]$ to give $[Au\{C_5(CO_2Me)_5\}(PPh_3)]$; an *X*-ray structural study shows that the $Au(PPh_3)$ [Au–P 2.253(1) Å] moiety interacts with three carbons of the C_5 ring [Au–C 2.199(4), 2.705(4), and 2.813(4) Å] such that the co-ordination is intermediate between σ and η^3. The complex reacts with a second molecule of PPh_3 to give $[Au(PPh_3)_2][C_5(CO_2Me)_5]\cdot MeOH$; in the crystal, the gold is bonded to the two PPh_3 ligands [Au–P 2.297(3), 2.300(3) Å; P–Au–P 170.4(2)°], and interacts weakly with an ester carbonyl group of the $C_5(CO_2Me)_5$ anion, and with the oxygen of a methanol solvate molecule.

The previous paper[1] described some silver(I) derivatives of the strong organic acid, pentakis(methoxycarbonyl)cyclopentadiene (1) and the structural characterisation of some of these compounds. For derivatives of the type $[Ag\{C_5(CO_2Me)_5\}L]$ (L = H_2O or PPh_3) we found a weak asymmetric interaction between the silver and a C=C double bond in the $C_5(CO_2Me)_5$ ligand, which was readily broken by addition of a second PPh_3 ligand, or by dissolution in polar solvents. In the latter case, complete ionisation occurs to give the $[C_5(CO_2Me)_5]^-$ anion and a solvated silver cation, which also retains the tertiary phosphine ligand(s) if these are present. A common feature of all the structures is the chelation of silver by the carbonyl oxygens of two adjacent CO_2Me groups. We now describe the gold(I) complexes $[Au\{C_5(CO_2Me)_5\}(PPh_3)]$ and $[Au(PPh_3)_2][C_5(CO_2Me)_5]\cdot MeOH$ which although formally similar to the silver complexes described earlier, prove to have significantly different solid-state structures.



(1) E = CO_2Me



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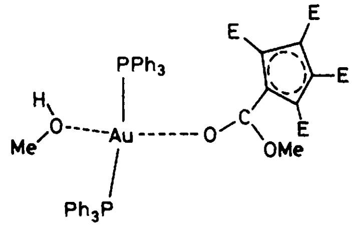

(3) E = CO_2Me

Results and Discussion

As we have noted before, weak organic acids are readily displaced when their salts are reacted with diene (1). This reaction has now been used to convert $[Au(O_2CMe)(PPh_3)]$ to complex (2); the further reaction of (2) with one equivalent of triphenylphosphine afforded (3). Both complexes formed white crystals, which were characterised by elemental microanalyses, spectroscopic methods, and finally by single-crystal *X*-ray studies, which revealed that the latter crystallised from methanol in solvated form. These complexes are soluble in the more polar solvents, such as methanol, ethanol, and acetone. In contrast with the analogous silver(I) complex, (2) is a non-electrolyte in acetone; complex (3), however, resembles its lighter congenor in dissolving as a 1 : 1 electrolyte.

Table 1. Metal atom environments for (2) and (3). Atoms derived from $C_5(CO_2Me)_5$ ligands are italicised. The first column for each entry is the metal–ligand distance (Å); the other entries are the angles (°) subtended at the metal by the ligand atoms in question

(2)	*r*	*C*(1)	(3)	*r*	P(2)
P	2.253(1)	169.7(1)	P(1)	2.300(3)	170.4(2)
C(1)	2.199(4)		P(2)	2.297(3)	

Crystal Structures.—(*a*) $[Au\{C_5(CO_2Me)_5\}(PPh_3)]$ (2). This compound has perhaps the most remarkable structure of those silver and gold complexes that we have studied. The unit-cell contents (see Figure 1) confirm the stoicheiometry, with the monomeric complex comprising the asymmetric unit of the structure. This also distinguishes (2) from the silver analogue, which crystallises as a centrosymmetric dimer.

Initially, the gold atom appears to be essentially linearly two-co-ordinate. One of the bonds is to the triphenylphosphine ligand [Au–P 2.253(1) Å] [*cf.* (3) below] and the other is to one carbon atom of the $[C_5(CO_2Me)_5]^-$ ligand [Au–C(1) 2.199(4) Å] (see Table 1, Figure 2). The P–Au–C angle is 169.7(1) Å. However, bonds from gold to the adjacent ring carbons C(2), C(5) are respectively 2.705(4), 2.813(4) Å; com-

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† *Supplementary data available* (No. SUP 23519, 59 pp.): thermal parameters, structure factors, H-atom parameters, phenyl ring-planes and geometries. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

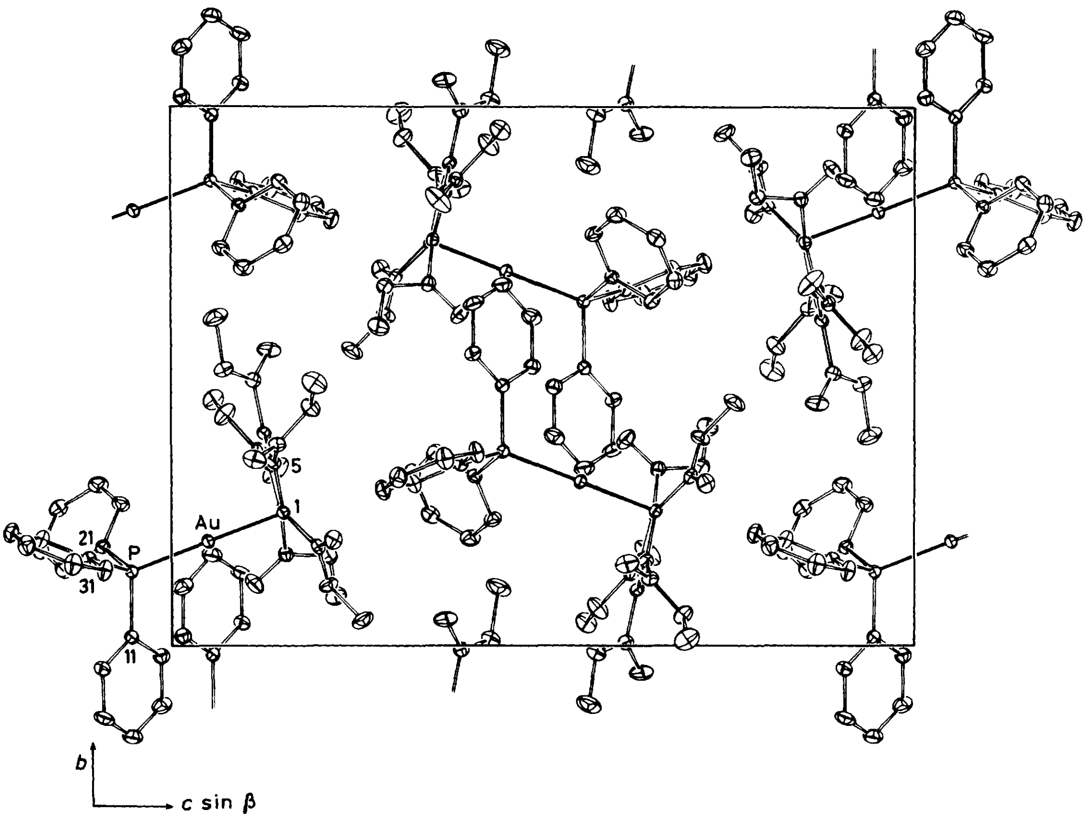

Figure 1. Unit-cell contents of (2) projected down *a*. 20% Thermal ellipsoids are shown, and key-atom labelling is given

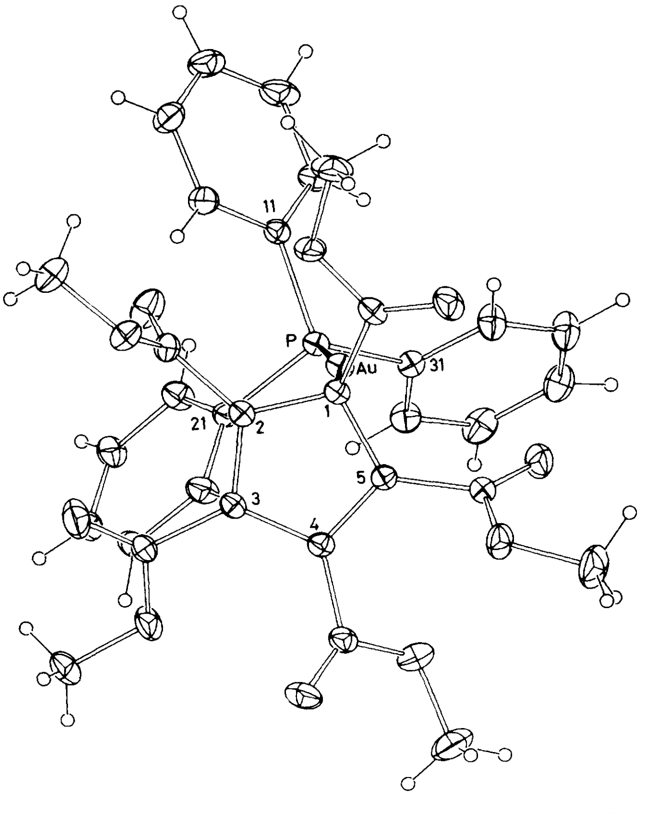

Figure 2. Projection of the ' molecule ' of (2), showing the bonding of the gold atom to the ring system

parison with the recently described complex [Au(C_5HPh_4)(PPh_3)],[2] in which the Au(PPh_3) group is considered to interact with three carbons of the ring at 2.15(1) [Au–C(1)], 2.67, and 2.76(1) Å [Au–C(2,5)], suggests that a similar co-ordination, intermediate between σ and η^3, occurs in complex (2). Other features of the two complexes emphasise the similarity: angles Au–C(1)–C(2) and Au–C(1)–C(5) are respectively 93.3(3) and 98.5(2)°; in the tetraphenylcyclopentadienyl complex, values of 93.4(8) and 97.8(8)° are found. Within the C_5 ring, the bond lengths (Table 2) are characteristic of a 1,3-diene, with C(2)–C(3) and C(4)–C(5) 1.392(6) and 1.379(6) Å respectively; the other three C–C bonds are longer [C(1)–C(2), 1.452(6); C(1)–C(5) 1.458(6); C(3)–C(4), 1.433(6) Å]. The ring remains planar (σ 0.013 Å); however, although substantial seemingly random deviations of the $C_5(CO_2Me)_5$ C(*n*1) atoms have been observed up to *ca.* 0.2 Å in other systems, here C(11) deviates from the ring plane by 0.63(8) Å (see Table 3). However, the gold atom deviation is very much larger [2.19(1) Å], disproportionately so, with regard to the $C_5(CO_2Me)_5$ C(1)–C(11), Au relative distances, suggesting that the bond may have some degree of π-component as well. Within the C_5 ring the angle C(5)–C(1)–C(2) is reduced [105.5(4)°] relative to the other C(*n*)–C(*n* + 1)–C(*n* + 2) angles which are uniformly even [range 108.5(4)—108.8(4)°]. Other features of the $C_5(CO_2Me)_5$ substituent geometry appear ' normal.'

The Au–P distance of 2.253(1) Å is very close to those found in linear Au^I–PPh_3 complexes, *e.g.* 2.235(3) Å in [AuCl(PPh_3)],[3] 2.279(8) Å in [AuMe(PPh_3)],[4] and 2.239(3) Å in [Au(C_5HPh_4)(PPh_3)].[2,*]

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* The gold–ring geometry has been explained in terms of destabilizing interactions of the C_5 $e_1(\pi)$ molecular orbitals with filled d_{xz} and d_{yz}, which are relieved by a ' slip ' distortion (see D. P. Evans and D. M. P. Mingos, *J. Organomet. Chem.*, 1982, **232**, 171).

Table 2. $C_5(CO_2Me)_5$ ligand geometries: distances (Å), angles (°)

	(2)	(3)
C(1)–C(2)	1.452(6)	1.44(1)
C(2)–C(3)	1.392(6)	1.38(2)
C(3)–C(4)	1.433(6)	1.40(2)
C(4)–C(5)	1.379(6)	1.42(2)
C(5)–C(1)	1.458(6)	1.42(2)
C(1)–C(11)	1.501(6)	1.48(2)
C(2)–C(21)	1.498(6)	1.47(2)
C(3)–C(31)	1.487(7)	1.44(2)
C(4)–C(41)	1.477(6)	1.45(2)
C(5)–C(51)	1.483(7)	1.47(1)
C(11)–O(11)	1.202(7)	1.17(1)
C(21)–O(21)	1.190(6)	1.18(1)
C(31)–O(31)	1.185(6)	1.21(1)
C(41)–O(41)	1.197(6)	1.23(1)
C(51)–O(51)	1.187(5)	1.16(2)
C(11)–O(12)	1.320(5)	1.31(1)
C(21)–O(22)	1.330(5)	1.32(2)
C(31)–O(32)	1.318(6)	1.31(1)
C(41)–O(42)	1.340(6)	1.37(1)
C(51)–O(52)	1.348(6)	1.39(2)
O(12)–C(12)	1.431(8)	1.45(2)
O(22)–C(22)	1.443(7)	1.43(2)
O(32)–C(32)	1.446(8)	1.52(2)
O(42)–C(42)	1.454(7)	1.39(2)
O(52)–C(52)	1.452(8)	1.44(2)
C(5)–C(1)–C(2)	105.5(4)	106.8(10)
C(1)–C(2)–C(3)	108.5(4)	108.3(10)
C(2)–C(3)–C(4)	108.5(4)	109.3(10)
C(3)–C(4)–C(5)	108.6(4)	108.5(10)
C(4)–C(5)–C(1)	108.8(4)	107.1(9)
C(5)–C(1)–C(11)	123.0(4)	127.1(10)
C(2)–C(1)–C(11)	121.8(3)	126.0(11)
C(1)–C(2)–C(21)	125.2(4)	122.8(11)
C(3)–C(2)–C(21)	125.9(4)	128.5(10)
C(2)–C(3)–C(31)	122.0(4)	125.5(11)
C(4)–C(3)–C(31)	129.3(4)	124.9(12)
C(3)–C(4)–C(41)	126.9(4)	127.4(11)
C(5)–C(4)–C(41)	124.5(4)	124.0(10)
C(4)–C(5)–C(51)	125.4(4)	122.2(11)
C(1)–C(5)–C(51)	125.6(4)	130.8(10)
C(1)–C(11)–O(11)	124.1(4)	122.2(10)
C(2)–C(21)–O(21)	123.9(4)	124.8(11)
C(3)–C(31)–O(31)	124.4(5)	127.7(13)
C(4)–C(41)–O(41)	125.2(4)	130.7(11)
C(5)–C(51)–O(51)	126.2(5)	127.5(11)
C(1)–C(11)–O(12)	110.7(4)	109.5(9)
C(2)–C(21)–O(22)	112.6(4)	113.2(9)
C(3)–C(31)–O(32)	113.4(4)	113.8(10)
C(4)–C(41)–O(42)	111.1(3)	112.2(10)
C(5)–C(51)–O(52)	109.7(3)	107.8(10)
O(11)–C(11)–O(12)	125.2(4)	128.2(12)
O(21)–C(21)–O(22)	123.5(4)	121.9(12)
O(31)–C(31)–O(32)•	122.2(5)	118.4(12)
O(41)–C(41)–O(42)	123.6(4)	117.1(13)
O(51)–C(51)–O(52)	124.1(5)	124.7(10)
C(11)–O(12)–C(12)	117.6(5)	116.6(10)
C(21)–O(22)–C(22)	115.8(4)	117.6(10)
C(31)–O(32)–C(32)	116.0(4)	118.8(10)
C(41)–O(42)–C(42)	116.5(4)	116.9(11)
C(51)–O(52)–C(52)	115.9(4)	113.4(11)

(*b*) $[Au(PPh_3)_2][C_5(CO_2Me)_5]\cdot MeOH$ (3). The structural determination showed that the stoicheiometry of the material studied, obtained by recrystallisation from methanol, was as indicated; one molecule is the asymmetric unit (Figure 3).

As found in (2), the gold atom is essentially linearly two-co-ordinate, both bonds being to a pair of equidistant triphenylphosphine ligands [Au–P 2.300(3), 2.297(3) Å (Table 1)].

Table 3. Ligand least-squares planes, calculated through the C_5 ring skeleton, given in the form $pX + qY + rZ = s$, where the right hand orthogonal Å frame (X, Y, Z) is defined with X parallel to *a*, Z in the *ac* plane: σ (defining atoms) and atom deviations, δ, are in Å; θ° is the dihedral angle to the C–CO–O carboxyl plane

	(2)	(3)
10^4p	547	−3 101
10^4q	2 227	8 822
10^4r	9 733	−3 545
s	3.903	1.181
σ	0.013	0.009
δC(1)	−0.016	0.011
δC(2)	0.014	−0.011
δC(3)	−0.006	0.007
δC(4)	−0.005	0.001
δC(5)	0.013	−0.007
δC(11)	0.638	0.006
δC(21)	−0.089	−0.203
δC(31)	−0.134	0.163
δC(41)	0.025	0.040
δC(51)	0.136	−0.020
δO(11)	1.021	−0.958
δO(21)	−1.098	−0.894
δO(31)	0.254	0.600
δO(41)	0.666	0.990
δO(51)	−0.609	−0.096
δO(12)	0.708	1.204
δO(22)	1.077	0.466
δO(32)	−0.772	−0.135
δO(42)	−0.744	−1.208
δO(52)	1.233	0.039
δC(12)	1.364	1.348
δC(22)	1.047	0.239
δC(32)	−0.912	0.119
δC(42)	−0.648	−1.284
δC(52)	1.409	0.055
θ(1)	26.3	76.0
θ(2)	78.3	38.8
θ(3)	29.0	20.6
θ(4)	39.1	84.9
θ(5)	57.1	3.4

The P–Au–P angle is 170.4(2)°; this deviation from linearity probably arises as a consequence of long interactions with the methanol solvate molecule [Au · · · O 3.343(17) Å] and the $C_5(CO_2Me)_5$ ligand [Au · · · O(11) 3.370(9) Å].

The $[C_5(CO_2Me)_5]^-$ ligand appears to be the first example described of an essentially free anion; because of decomposition during data collection and the presence of a very heavy metal atom, its precision is the lowest of the $C_5(CO_2Me)_5$ geometries so far determined. It conforms well to the geometries already established in the Group 1 and 2 metal complexes and the discussion already provided for those embraces the present situation fairly satisfactorily.

Conclusions

The solution behaviour of the two gold complexes described above is much more readily explained in terms of their solid-state structures than is the case for the silver(I) compounds. Thus, (2) is a non-electrolyte; in the solid, the C_5 ring is found to interact with the gold in an unusual, asymmetric η^3 mode. The central carbon of the three closest to the metal is almost collinear with the Au–P system; this is the first instance of a strong, σ-type interaction of a metal with the $C_5(CO_2Me)_5$ ligand, although there is an asymmetric, and much weaker, interaction with two carbons in some silver derivatives, including $[\{Ag[C_5(CO_2Me)_5](PPh_3)\}_2]$.[1] In (2), the gold–ring interaction is strong enough to resist cleavage by polar sol-

Table 4. Non-hydrogen atom co-ordinates for $[Au\{C_5(CO_2Me)_5\}(PPh_3)]$ (2)

Atom	*x*	*y*	*z*
Au	0.198 57(2)	0.194 48(1)	0.049 67(1)
Ligand anion			
C(1)	0.268 2(4)	0.248 6(3)	0.151 2(2)
C(11)	0.226 2(4)	0.184 9(3)	0.197 3(2)
O(11)	0.135 3(4)	0.197 6(2)	0.217 9(2)
O(12)	0.301 3(3)	0.113 2(2)	0.210 8(2)
C(12)	0.277 6(7)	0.047 7(4)	0.256 7(3)
C(2)	0.398 8(4)	0.251 9(3)	0.148 1(2)
C(21)	0.484 7(4)	0.171 2(3)	0.153 8(2)
O(21)	0.475 8(4)	0.116 0(3)	0.111 1(2)
O(22)	0.571 1(3)	0.167 1(2)	0.212 4(2)
C(22)	0.659 7(6)	0.092 5(4)	0.220 7(3)
C(3)	0.425 2(4)	0.340 0(3)	0.131 3(2)
C(31)	0.546 9(4)	0.363 8(3)	0.116 8(2)
O(31)	0.644 5(4)	0.326 3(3)	0.140 3(3)
O(32)	0.535 9(3)	0.429 7(3)	0.072 9(2)
C(32)	0.651 5(6)	0.456 9(4)	0.057 4(3)
C(4)	0.314 7(4)	0.395 0(3)	0.125 5(2)
C(41)	0.302 0(5)	0.493 4(3)	0.110 7(2)
O(41)	0.382 0(4)	0.549 4(2)	0.131 9(2)
O(42)	0.186 9(4)	0.513 1(2)	0.071 0(2)
C(42)	0.155 5(8)	0.609 1(4)	0.060 7(4)
C(5)	0.220 9(4)	0.341 4(3)	0.138 4(2)
C(51)	0.095 7(4)	0.374 4(3)	0.143 1(2)
O(51)	−0.004 7(3)	0.346 6(3)	0.112 3(2)
O(52)	0.112 0(3)	0.442 4(2)	0.188 0(2)
C(52)	−0.002 8(6)	0.487 9(5)	0.193 0(4)
Triphenylphosphine ligand			
P	0.164 14(10)	0.138 55(7)	−0.054 11(5)
C(11)	0.186 5(4)	0.016 2(3)	−0.054 6(2)
C(12)	0.298 9(5)	−0.018 8(3)	−0.014 6(3)
C(13)	0.323 5(6)	−0.111 0(4)	−0.015 2(3)
C(14)	0.236 2(7)	−0.169 6(3)	−0.054 8(3)
C(15)	0.124 8(6)	−0.135 7(3)	−0.092 9(3)
C(16)	0.098 5(5)	−0.042 8(3)	−0.094 3(2)
C(21)	0.281 0(4)	0.184 2(3)	−0.092 2(2)
C(22)	0.346 5(5)	0.263 8(3)	−0.067 7(3)
C(23)	0.434 6(5)	0.299 3(3)	−0.098 0(3)
C(24)	0.459 5(5)	0.255 9(4)	−0.151 5(3)
C(25)	0.394 8(5)	0.177 7(3)	−0.176 2(3)
C(26)	0.307 9(5)	0.140 4(3)	−0.146 1(2)
C(31)	0.010 1(4)	0.161 8(3)	−0.110 4(2)
C(32)	−0.005 9(5)	0.197 9(3)	−0.174 3(2)
C(33)	−0.126 8(6)	0.209 8(4)	−0.215 7(3)
C(34)	−0.230 7(5)	0.186 4(4)	−0.195 2(3)
C(35)	−0.216 4(5)	0.151 8(5)	−0.132 4(3)
C(36)	−0.096 5(5)	0.140 0(4)	−0.090 0(2)

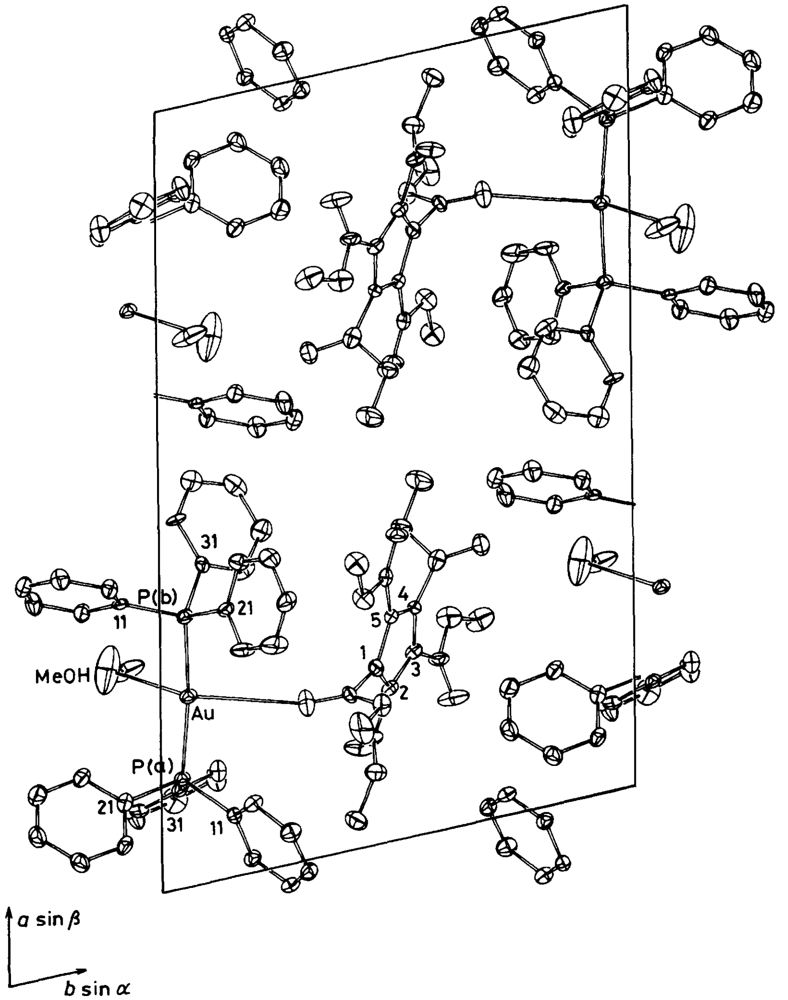

Figure 3. Unit-cell contents of (3) projected down *c*. 20% Thermal ellipsoids are shown for the non-hydrogen atoms and key-atom labelling is given

vents, unlike the silver(I) compounds. However, addition of a strong donor ligand, such as PPh_3, readily generates the $[Au(PPh_3)_2]^+$ cation, releasing the stable $[C_5(CO_2Me)_5]^-$ anion; dissolution in polar solvents is accompanied by complete ionisation.

Finally, we note that in solution, all CO_2Me groups in (2) are magnetically equivalent, presumably as a result of some fluxional process; rapid migration of the $Au(PPh_3)$ group around the C_5 ring has been observed with $[Au(C_5H_4R)(PPh_3)]$ (R = H or Me),[5] whereas the tetraphenylcyclopentadienyl complex is stereochemically rigid.[2]

Experimental

General experimental details have been described in previous papers in this series. All reactions were run under nitrogen, and were protected from light.

Preparation of $[Au\{C_5(CO_2Me)_5\}(PPh_3)]$ (2).—Solid $[Au(O_2CMe)(PPh_3)]$ (330 mg, 0.7 mmol) was added to a solution of $HC_5(CO_2Me)_5$ (250 mg, 0.72 mmol) in methanol (10 cm^3). After 18 h at room temperature, the solution was filtered and evaporated to dryness. The product was extracted with acetone (5 cm^3) and induced to crystallise by adding light petroleum (b.p. 40—60 °C). White prismatic *crystals* of $[Au\{C_5(CO_2Me)_5\}(PPh_3)]$ (2) (404 mg, 71%) were collected, washed with methanol and dried, m.p. 145 °C (Found: C, 48.50; H, 3.50. $C_{33}H_{30}AuO_{10}P$ requires C, 48.65; H, 3.70%). Infrared (Nujol): ν(C=O) 1 710vs, ν(C–O) 1 215s, 1 195s, 1 170s, 1 160s, other bands at 1 510w, 1 435s, 1 398m, 1 365m, 1 338m, 1 225m, 1 100m, 1 060m, 980w, 940w, 865w, 800w, 790w, 783m, 755m, 745m, 710m, 690s, 660m cm^{-1}. ^1H N.m.r.: δ($CDCl_3$) 3.80 (s, 15 H, OMe), 7.48 (m, 15 H, Ph). Conductivity (acetone) 9.1 ohm^{-1} cm^2 mol^{-1}.

Preparation of $[Au(PPh_3)_2][C_5(CO_2Me)_5]\cdot MeOH$ (3).—A similar reaction to the above, with an added equivalent of PPh_3, gave white prismatic *crystals* of $[Au(PPh_3)_2][C_5(CO_2Me)_5]\cdot MeOH$ (3) (313 mg, 41%), m.p. 218—220 °C (Found: C, 56.30; H, 4.40. $C_{51}H_{45}AuO_{10}P_2$ requires C, 56.90; H, 4.2%). Infrared (Nujol): ν(C=O) 1 745m, 1 713vs, 1 685vs, ν(C–O) 1 270s, 1 210s, 1 180s, 1 160s, 1 155s, other bands at 1 440s, 1 395w, 1 105m, 1 098m, 1 068s, 1 015m, 995m, 940m, 785m, 750s, 715m, 695s, 660m cm^{-1}. ^1H N.m.r.: δ($CDCl_3$) 3.68 (s, 15 H, OMe), 7.57 (m, 30 H, Ph). ^{13}C N.m.r.: δ($CDCl_3$) 50.65 (s, OMe), 117.20 (s, ring C), 126.92—133.97 (m, Ph), 167.85 (s, *C*O_2Me). Conductivity (acetone) 87.7 ohm^{-1} cm^2 mol^{-1}.

Crystallography.—General details are given in ref. 6. Atomic co-ordinates for complexes (2) and (3) are shown in Tables 4 and 5 respectively and phosphorus environments for both complexes in Table 6.

Crystal data. $[Au\{C_5(CO_2Me)_5\}(PPh_3)]$ (2), $C_{33}H_{30}AuO_{10}P$,

Table 5. Non-hydrogen atom co-ordinates for $[Au(PPh_3)_2][C_5(CO_2Me)_5]\cdot MeOH$ (3)

Atom	*x*	*y*	*z*
Au	0.245 79(2)	0.059 19(4)	0.301 27(5)
Ligand anion			
C(1)	0.226 9(6)	0.455 6(8)	0.483 7(11)
C(11)	0.200 4(6)	0.399 6(8)	0.382 5(12)
O(11)	0.201 9(6)	0.308 1(6)	0.401 8(10)
O(12)	0.177 7(5)	0.467 7(6)	0.273 5(8)
C(12)	0.154 1(10)	0.424 3(13)	0.159 3(18)
C(2)	0.196 6(6)	0.484 2(8)	0.622 1(11)
C(21)	0.137 5(6)	0.448 5(6)	0.688 1(11)
O(21)	0.129 4(5)	0.417 6(8)	0.810 9(9)
O(22)	0.093 2(4)	0.453 6(7)	0.594 8(9)
C(22)	0.037 2(8)	0.411 0(12)	0.644 7(18)
C(3)	0.236 3(6)	0.535 3(8)	0.682 6(11)
C(31)	0.219 7(6)	0.588 0(10)	0.811 3(13)
O(31)	0.165 7(5)	0.618 1(10)	0.869 0(11)
O(32)	0.269 8(5)	0.610 4(8)	0.863 9(9)
C(32)	0.257 7(8)	0.675 9(14)	0.991 7(17)
C(4)	0.292 3(5)	0.538 3(7)	0.590 7(12)
C(41)	0.346 0(7)	0.586 3(9)	0.611 5(12)
O(41)	0.352 6(5)	0.678 8(6)	0.584 1(10)
O(42)	0.397 7(4)	0.513 0(7)	0.667 8(10)
C(42)	0.451 8(9)	0.551 2(15)	0.693 4(22)
C(5)	0.287 7(5)	0.488 3(7)	0.466 4(11)
C(51)	0.339 5(6)	0.477 9(8)	0.348 0(11)
O(51)	0.389 7(4)	0.502 1(7)	0.343 0(9)
O(52)	0.318 8(5)	0.430 5(7)	0.241 2(9)
C(52)	0.364 8(8)	0.417 2(12)	0.117 3(15)
Triphenylphosphine ligand a			
P	0.141 5(2)	0.045 5(2)	0.387 2(3)
C(11)	0.079 1(6)	0.154 2(8)	0.314 5(11)
C(12)	0.089 1(6)	0.194 4(9)	0.171 7(12)
C(13)	0.041 4(7)	0.272 6(10)	0.106 0(13)
C(14)	−0.015 1(6)	0.310 8(9)	0.180 0(14)
C(15)	−0.026 2(6)	0.270 9(9)	0.323 8(15)
C(16)	0.018 9(6)	0.191 9(8)	0.387 6(12)
C(21)	0.127 1(6)	−0.077 7(8)	0.336 8(10)
C(22)	0.072 0(6)	−0.078 4(8)	0.266 4(12)
C(23)	0.062 6(7)	−0.173 7(10)	0.232 8(15)
C(24)	0.107 9(8)	−0.264 9(10)	0.265 7(16)
C(25)	0.161 6(8)	−0.264 2(11)	0.331 0(18)
C(26)	0.171 5(6)	−0.168 5(9)	0.367 5(13)
C(31)	0.128 1(5)	0.039 5(8)	0.582 8(10)
C(32)	0.112 4(6)	−0.047 2(9)	0.666 7(11)
C(33)	0.105 0(7)	−0.054 3(9)	0.811 5(12)
C(34)	0.115 8(8)	0.028 3(12)	0.874 3(13)
C(35)	0.132 3(8)	0.117 1(10)	0.800 0(13)
C(36)	0.140 7(7)	0.121 1(9)	0.646 7(12)
Triphenylphosphine ligand b			
P	0.348 3(2)	0.053 4(2)	0.188 9(3)
C(11)	0.383 1(5)	−0.082 9(8)	0.143 6(11)
C(12)	0.382 6(6)	−0.164 5(9)	0.255 5(12)
C(13)	0.408 5(8)	−0.267 6(9)	0.228 2(14)
C(14)	0.433 2(7)	−0.289 1(9)	0.095 9(16)
C(15)	0.431 5(7)	−0.210 6(10)	−0.015 1(13)
C(16)	0.405 3(6)	−0.105 6(8)	0.011 6(11)
C(21)	0.344 9(5)	0.140 9(8)	0.023 0(12)
C(22)	0.401 5(6)	0.168 9(10)	−0.047 0(12)
C(23)	0.397 4(7)	0.233 7(10)	−0.176 0(13)
C(24)	0.337 4(7)	0.269 2(10)	−0.236 1(13)
C(25)	0.285 9(7)	0.241 2(13)	−0.170 1(17)
C(26)	0.288 5(6)	0.174 8(12)	−0.041 5(16)
C(31)	0.409 2(5)	0.091 4(7)	0.288 1(10)
C(32)	0.473 8(5)	0.037 5(9)	0.287 1(10)
C(33)	0.519 1(7)	0.070 2(10)	0.352 2(13)
C(34)	0.499 9(8)	0.162 5(11)	0.418 4(14)
C(35)	0.435 2(7)	0.216 8(11)	0.426 9(14)
C(36)	0.388 8(7)	0.178 5(11)	0.358 4(14)
Solvent			
C	0.295 7(9)	−0.070 2(19)	0.698 8(25)
O	0.302 6(11)	−0.112 0(12)	0.580 9(19)

M = 814.6, Monoclinic, space group $P2_1/c$ (C^5_{2h}, no. 14), a = 10.959(3), b = 14.691(3), c = 20.889(5) Å, β = 105.70(2)°, U = 3 237(2) Å^3, D_m = 1.65(1), Z = 4, D_c = 1.67 g cm^{-3}, F(000) = 1 608, specimen size 0.39 × 0.22 × 0.35 mm, μ(Mo-K_α) = 44.9 cm^{-1}, λ = 0.701 69 Å, 2θ$_{max.}$ = 65°, N = 11 775, N_o = 7 481; R,R',S = 0.038, 0.044, 1.22.

[Au(PPh$_3$)$_2$][C$_5$(CO$_2$Me)$_5$]·MeOH (3), $C_{52}H_{49}AuO_{11}P_2$, M = 1 108.9, Triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 21.04(1), b = 12.936(8), c = 9.376(5) Å, α = 82.85(4), β = 76.95(4), γ = 76.95(4)°, U = 2 461(2) Å^3, Z = 2, D_c = 1.50 g cm^{-3}, F(000) = 1 116, specimen size 0.23 × 0.48 × 0.35 mm, (μMo-K_α) = 30.2 cm^{-1}, λ = 0.701 69 Å, 2θ$_{max.}$ = 50°, N = 7 647, N_o = 5 282: R,R',S = 0.053, 0.070, 1.95

Abnormal features. The specimen of (2) was mounted in a capillary, but nevertheless decomposed considerably during data collection, and data were appropriately scaled. All data for (2) and (3) were corrected for absorption (analytical correction).

In the phosphine ligands, ring carbon atoms are numbered C(*n*1)—C(*n*6) for ring *n*; C(*n*1) is attached to the phosphorus atom. The C$_5$(CO$_2$Me)$_5$ ligand numbering follows that employed previously[1,6] with ring atoms designated C(*n*), *n* = 1—5 and attached carbon and oxygen atoms designated C,O(*n*1, *n*2) in order from the point of attachment. For clarity in presentation of the Figures only the numbering of the C$_5$(CO$_2$Me)$_5$ ring atoms is shown, together with C(*n*1) of the phosphine phenyl rings.

Acknowledgements

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Table 6. Phosphorus environments: distances (Å), angles (°)

Atoms	(2)	(3)/a	(3)/b
P–C(11)	1.815(4)	1.808(10)	1.835(10)
P–C(21)	1.809(5)	1.813(12)	1.804(11)
P–C(31)	1.810(4)	1.823(10)	1.839(12)
Au–P–C(11)	112.3(1)	113.2(4)	108.9(4)
Au–P–C(21)	109.5(1)	108.1(4)	111.2(4)
Au–P–C(31)	116.1(2)	114.0(4)	117.6(3)
C(11)–P–C(21)	104.6(2)	107.9(5)	107.6(5)
C(11)–P–C(31)	106.6(2)	106.6(4)	106.7(5)
C(21)–P–C(31)	106.9(2)	106.7(5)	104.4(5)

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