Synthesis of Dinuclear Gold-(I), -(II), and -(III) Complexes containing Ylide Ligands $[(RO_2C)CHPPh_2CH(CO_2R)]^-$ (R = Me or Et) and Trinuclear Gold(I) Complexes containing Ylide Ligands $[(RO_2C)CPPh_2CH(CO_2R)]^{2-}$ (R = Me or Et)

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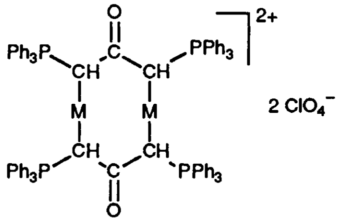
The complexes $[Au_2\{\mu\text{-}[CH(CO_2R)]_2PPh_2\}_2]$ [R = Me, (**1a**); or Et, (**1b**)] can be obtained by treating $[Ag_2\{\mu\text{-}[CH(CO_2R)]_2PPh_2\}_2]$ (R = Me or Et) with [AuCl(tht)] (tht = tetrahydrothiophene) (1 : 2). Complexes (**1a**) and (**1b**) react with Cl_2IPh or I_2 (1 : 1) to give gold(II) complexes $[(AuX)_2\{\mu\text{-}[CH(CO_2R)]_2PPh_2\}_2]$ [X = Cl, R = Me (**2a**) or Et (**2b**); X = I, R = Me (**3a**) or Et (**3b**)]. If an excess of Cl_2 or I_2 (1 : 2) is used gold(III) complexes $[(AuX_2)_2\{\mu\text{-}[CH(CO_2Me)]_2PPh_2\}_2]$ [X = Cl, (**4**) or I, (**5**)] can be obtained. The corresponding derivatives with R = Et could not be prepared under the same conditions because a mixture containing mainly the gold(II) complexes (**2b**) and (**3b**) is obtained. Reaction of (**4**) with $AgClO_4$ (1 : 2) in acetonitrile and, after removal of AgCl and addition of L (1 : 2) gives the first reported cationic gold(II) complexes $[(AuL)_2\{\mu\text{-}[CH(CO_2Me)]_2PPh_2\}_2][ClO_4]_2$ [L = pyridine, (**6**); 3-bromopyridine, (**7**); 4-cyanopyridine, (**8**); 2,4-dimethylpyridine, (**9**); PPh_3, (**10**); or $AsPh_3$, (**11**)]. The phosphonium salts $[PPh_2(CH_2CO_2R)_2]ClO_4$ react with [Au(acac)L] (acac = acetylacetonate) (1 : 4) to give $[(AuL)_2\{\mu\text{-}C(CO_2R)PPh_2CH(AuL)(CO_2R)\}]ClO_4$ [L = PPh_3, R = Me (**12a**) or Et (**12b**); L = PMe_2Ph, R = Me (**13**); L = $P(C_6H_4OMe\text{-}4)_3$, R = Et (**14**)].

Complexes containing anionic ylide ligands $[RCHPR'_2CHR]^-$ (R = H or Ph; R′ = Ph, Me, or CH_2CF_3) are well known.[1,2] Those of gold are the best studied, probably because this type of ligand enables the preparation of interesting complexes such as those of gold(II), A-frame gold(III), and some mixed-valence gold(I)-gold(III) complexes.[3,4] Our interest in both the chemistry of gold[5] and also in complexes containing carbonyl-stabilized ylide ligands[6] stimulated us to explore the ability of ylides derived from the phosphonium salts $[PPh_2(CH_2CO_2R)_2]^+$ (R = Me or Et) to yield gold complexes. The only previously reported complexes with such ylide ligands are $[Ag_2\{\mu\text{-}[CH(CO_2R)]_2PPh_2\}_2]$ (R = Me or Et).[7]

Our interest in extending the chemistry of carbonyl-stabilized phosphorus ylides arose from our results showing (*i*) that they can co-ordinate, in spite of low nucleophilicity, to gold-(I) and -(III), palladium(II), and silver(I) to give stable complexes and (*ii*) that they give new types of ylide complexes.[6,7] On this occasion we wished to confirm these observations with a different type of ylides trying, for example, to prepare polynuclear gold(I) complexes using the parent phosphonium salts and we also had three more objectives. The first was to find a new synthetic procedure because of the unavailability of the corresponding ylides.[1–4] In addition, we have unsuccessfully tried to prepare gold(II) complexes from the gold(I) complex (A) and Cl_2IPh (1 : 1). We justified such behaviour by postulating that, according to its crystal structure, the co-ordination sites for chlorine ligands were too crowded.[8] The dinuclear gold(I) complexes to be prepared on this occasion should give us the opportunity to see whether the presence of the CO_2R substituents at the α-carbon atoms would allow the synthesis of the corresponding gold(II) complexes. Finally, we decided to prepare, if we succeeded in preparing the gold(II) complexes, cationic gold(II) complexes which, to our knowledge, would be the first to be reported.

Results and Discussion

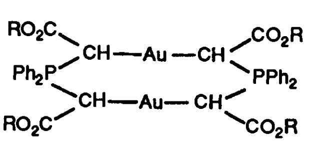
Complex (A) was prepared by treating the corresponding silver complex (B) with [AuCl(tht)] (tht = tetrahydrothiophene) (1 : 2).[8] The same type of reaction, but using $[Ag_2\{\mu\text{-}[CH(CO_2R)]_2PPh_2\}_2]$ (R = Me or Et)[7] leads to $[Au_2\{\mu\text{-}[CH(CO_2R)]_2PPh_2\}_2]$ [R = Me, (**1a**); or Et, (**1b**)]. This reaction involving the transfer of an ylide ligand from one metal centre to another is a new example of the recently reported type of 'ylide-transfer reactions'.[9]



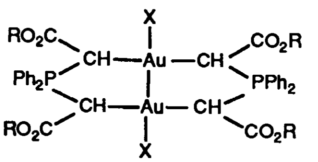
M
(A) Au
(B) Ag

Complexes (**1a**) and (**1b**) react with Cl_2IPh or I_2 (1 : 1) to give gold(II) complexes $[(AuX)_2\{\mu\text{-}[CH(CO_2R)]_2PPh_2\}_2]$ [X = Cl, R = Me (**2a**) or Et (**2b**); X = I, R = Me (**3a**) or Et (**3b**)]. Several attempts to cause (**1b**) to react with $BrCH_2C(O)Ph$ or I_2CH_2 which could give new gold-(II) or -(III) complexes[1–4] were unsuccessful.

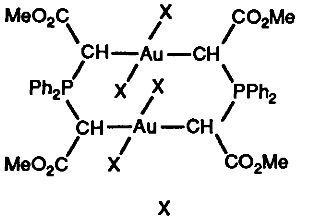
If complex (**1a**) is treated with Cl_2 (excess) or I_2 (1 : 2) gold(III) complexes $[(AuX_2)_2\{\mu\text{-}[CH(CO_2Me)]_2PPh_2\}_2]$ [X = Cl, (**4**); or I, (**5**)] can be obtained. The same reagents give with (**1b**) mixtures which always contain the corresponding gold(II) complexes (**2b**) and (**3b**) and which we were unable to separate. Using Cl_2IPh (1 : 2, 1 : 4, or 1 : 8) the same result was obtained. The chlorogold(III) complex (**4**) decomposes in the solid state, giving mainly the starting complex (**1a**), and also in solution leading to the gold(II) complex (**2a**). The iodogold(III) complex



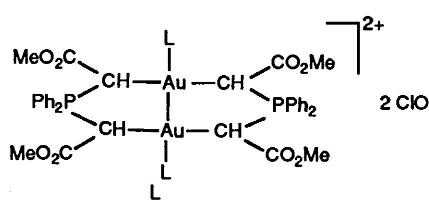
	R
(1a)	Me
(1b)	Et



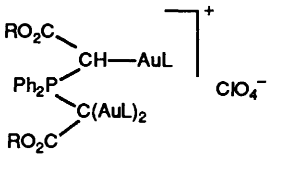
	X	R
(2a)	Cl	Me
(2b)	Cl	Et
(3a)	I	Me
(3b)	I	Et



	X
(4)	Cl
(5)	I



	L
(6)	py
(7)	3 Br-py
(8)	4 NC-py
(9)	2, 4 Me$_2$-py
(10)	PPh$_3$
(11)	AsPh$_3$



	R	L
(12a)	Me	PPh$_3$
(12b)	Et	PPh$_3$
(13)	Me	PMe$_2$Ph
(14)	Et	P(C$_6$H$_4$OMe-4)$_3$

(**5**) is stable in the solid state but decomposes in solution giving mainly metallic gold.

Both the tendency of the chlorogold(III) complexes to decompose to the corresponding gold(II) ones and the different behaviour of the Et and Me derivatives are surprising. Differences in solubility and stability between the silver derivatives [$Ag_2\{\mu$-[CH(CO$_2$R)]$_2$PPh$_2\}_2$] had been observed.[7] Thus, while the complex with R = Me is very insoluble in organic solvents and very stable, that with R = Et is even slightly soluble in diethyl ether and less stable than its methyl homologue. A similar difference in solubility and stability is observed between the corresponding gold(I) complexes (**1a**) and (**1b**). The stability of the gold(III) complexes follows the same rule. Complex (**4**) (R = Me) is insoluble in all common organic solvents except dimethyl sulphoxide. However, the gold(II) complexes (**2a**), (**2b**), (**3a**), and (**3b**) are all equally soluble in organic solvents (even in diethyl ether) and stable in the solid state although the ethyl derivatives are more stable than the methyl ones. In solution they decompose slowly to give metallic gold.

Reaction of complex (**4**) with AgClO$_4$ (1:2) in acetonitrile gives AgCl and a yellow solution. If the solvent is evaporated and the resulting solid mixture extracted with dichloromethane a red solution is obtained. Addition of diethyl ether precipitates a very unstable red solid which we were unable to isolate as an analytically pure compound. However, addition of a neutral ligand L (1:2) to the red dichloromethane solution gives yellow or orange solutions from which the first reported cationic gold(II) complexes[10] [(AuL)$_2\{\mu$-[CH(CO$_2$Me)]$_2$-PPh$_2\}_2$][ClO$_4$]$_2$ [L = pyridine, (**6**); 3-bromopyridine, (**7**); 4-cyanopyridine, (**8**); 2,4-dimethylpyridine, (**9**); PPh$_3$, (**10**); or AsPh$_3$, (**11**)] can be isolated. Several attempts to get single crystals of any of these compounds (which is why we prepared such a large family of derivatives) were fruitless because of instability in solution. However, they are quite stable in the solid state. A parallel study with the ethyl derivative (**2b**) gave also cationic complexes but they were so unstable, even in the solid state, that they could not be properly characterized.

The acidic character of the methylene protons in the carbonylphosphonium salts [Ph$_3$PCH$_2$C(O)R]$^+$ and [(Ph$_3$PCH$_2$)$_2$CO]$^{2+}$ has allowed us to prepare, by reaction with [Au(acac)L] (acac = acetylacetonate), dinuclear [(AuL)$_2\{\mu$-C(PPh$_3$)C(O)R$\}$]$^+$ (L = PPh$_3$ R = OMe, OEt,[11] Me, or Ph;[5] L = AsPh$_3$, R = Me[5]), trinuclear [(AuL)$_2\{\mu$-C(PPh$_3$)C(O)-CH(PPh$_3$)(AuL)$\}$]$^{2+}$ (L = PPh$_3$), or tetranuclear [(AuL)$_4\{\mu$-[C(PPh$_3$)]$_2$CO$\}$]$^{2+}$ (L = PMe$_2$Ph)[8] gold(I) complexes. The synthesis of the tri- or tetra-nuclear complexes depends on the cone angle of the phosphine. The phosphonium salts [PPh$_2$(CH$_2$CO$_2$R)$_2$]ClO$_4$ react with [Au(acac)L] (1:4) to give [(AuL)$_2\{\mu$-C(CO$_2$R)PPh$_2$CH(AuL)(CO$_2$R)$\}$]ClO$_4$ [L = PPh$_3$, R = Me (**12a**) or Et (**12b**); L = PMe$_2$Ph, R = Me (**13**); L = P(C$_6$H$_4$OMe-4)$_3$, R = Et (**14**)]. Therefore, these phosphonium salts do not give tetranuclear complexes as did [(Ph$_3$PCH$_2$)$_2$CO]$^{2+}$. The reasons could be both steric and chemical. The central carbon atom in the latter is *sp*^{2} hybridized and the 2+ charge makes the C–H groups more acidic than those in the present case where the central atom is an *sp*^{3} phosphorus atom. As we have shown the substitution of these methylene hydrogen atoms by AuL$^+$ groups lowers the acidic character of the remaining C–H groups.[11] This lowering could mean that the C–H groups in the trinuclear complexes (**11**)–(**13**) are not acidic enough to react with further [Au(acac)L] to give the corresponding tetranuclear complexes.

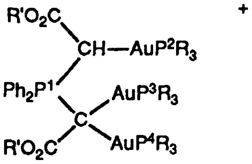
The decrease in acidic character of a phosphonium salt when a hydrogen atom is substituted by a metallic moiety to give an ylide complex can be explained as a consequence of the smaller electron-withdrawing character of such a moiety with respect to that of the hydrogen atom. This can clearly be seen by comparing the band corresponding to the ν(CO) mode in a phosphonium salt and the related ylide complexes. Thus for the phosphonium salts [PPh$_2$(CH$_2$CO$_2$R)$_2$]ClO$_4$ ν(CO) appears at 1 725 (R = Me) and 1 715 and 1 745 cm^{-1} (R = Et). The symmetrical substitution of two hydrogen atoms by two gold(I) centres in complexes (**1a**) and (**1b**) decreases ν(CO) to 1 680 cm^{-1}. As expected, the trinuclear complexes show two ν(CO) bands corresponding to the dinuclear and mononuclear moieties of the complex at 1 645 and 1 690 cm^{-1}, respectively. An increase in the charge of the gold atom shifts ν(CO) to higher energy. Thus the gold(II) complexes show ν(CO) at around 1 700 cm^{-1} while for the chlorogold(III) complex (**4**) it is at 1 710 cm^{-1}.

Complex (**4**) shows a band corresponding to the ν(AuCl) mode at 360 cm^{-1} which indicates a *trans* geometry.[6–8] The chlorogold(II) complexes (**2a**) and (**2b**) show ν(AuCl) at 270 cm^{-1}, in accord with similar values found for related gold(II) complexes.[12] The iodo-complexes have the same i.r. spectra as their homologous chloro-complexes, except for the band assigned to ν(AuCl).

Complexes (**1**)—(**11**) have four chiral carbon atoms, which, even assuming that in solution a rapid chair–boat conversion occurs, makes possible up to three *meso* forms and two pairs of enantiomers. Assuming a planar averaged structure for the PCAuCPCAuC rings, both phosphorus atoms and the protons of the four methyl, methylene, and methyne groups are equivalent for all the stereoisomers, except for the pair of enantiomers which have three protons and one CO_2R group on the same side of the plane which should give one resonance for each of these groups in the molecule.

The $^{31}P-\{^1H\}$ n.m.r. spectra of complexes (**1b**), (**2a**), (**2b**), and (**3a**), (**3b**) show two 1:1 singlets. Therefore, in solution there exist 1:1 mixtures of two of the *meso* forms or one of them and the pair of enantiomers *RRRR* and *SSSS*. This is as observed for the parent silver complexes $[Ag_2\{\mu\text{-}[CH(CO_2R)]_2PPh_2\}_2]$ (R = Me or Et) the structure of one of which (R = Et) shows the eight-membered ring we assume to be present in complexes (**1**)—(**11**).

The $^{31}P-\{^1H\}$ n.m.r. spectra of complexes (**12a**), (**12b**), and (**14**) appear as two AB systems as the result of the coupling of P^1 with P^2 and P^3 with P^4. Although the CH_2CH_3 groups are strictly ABX_3 systems, some ^1H n.m.r. spectra of the (**b**) series are deceptively simple. Thus, those of complexes (**1b**) and (**3b**) show two 1:1 triplets, and a multiplet corresponding to CH_2 and CH protons. For complex (**2b**) both triplets are coincident. However, in the trinuclear complexes (**12b**) and (**13**) the Me, CH_2, and CH protons resonances appear as complex multiplets.



As expected from the $^{31}P-\{^1H\}$ n.m.r. data for (**2a**) and (**3a**), ^1H n.m.r. spectra of these complexes show two 1:1 singlets and two 1:1 doublets corresponding to Me and CH groups respectively of the mixture of isomers, while complex (**12a**) shows two singlets and a multiplet for the same groups, respectively.

The limited solubility of complexes (**1a**) and (**4**) in organic solvents and the instability of (**5**) and the cationic gold(II) complexes prevented us from recording their n.m.r. spectra or assigning the observed resonances, respectively. The molar conductivities of these compounds, measured in *ca.* 10^{-4} mol dm^{-3} solutions in acetone, are according to their proposed formulations. Complex (**4**) behaves in dimethyl sulphoxide as an 1:1 electrolyte (34 Ω^{-1} cm^2 mol^{-1}).

Experimental

Recording of infrared spectra, the C and H analyses, conductance measurements, melting-point determinations, and n.m.r. spectra (at 80 MHz) were performed as described elsewhere.[8] Reactions were carried out at room temperature with magnetic stirring and without special precautions against light or atmospheric moisture, and conductivity was measured in acetone, unless otherwise stated. The ^1H and $^{31}P-\{H\}$ n.m.r. data in $CDCl_3$ (δ in p.p.m.) are referenced to $SiMe_4$ or H_3PO_4, respectively.

$[Au_2\{\mu\text{-}[CH(CO_2R)]_2PPh_2\}_2]$ [R = Me, (**1a**); *or* Et, (**1b**)].—To a light-protected suspension of $[Ag_2\{\mu\text{-}[CH(CO_2Me)]_2PPh_2\}_2]$ (490 mg, 0.56 mmol) or a solution of $[Ag_2\{\mu\text{-}[CH(CO_2Et)]_2PPh_2\}_2]$ (350 mg, 0.38 mmol)[7] in dichloromethane (30 cm^3) was added [AuCl(tht)] (1:2). After 3 h the suspensions were filtered and, in the case of R = Me, the resulting solid was washed with dichloromethane (3 × 20 cm^3) and the extracted solution combined with that obtained from the reaction mixture. The resulting solutions were concentrated (to *ca.* 2 cm^3) and diethyl ether or n-hexane (25 cm^3) added, giving, respectively, complex (**1a**) or (**1b**) as colourless solids: (**1a**), 83%, m.p. 202 °C (decomp.), Λ_M = 1 Ω^{-1} cm^2 mol^{-1} in acetonitrile, $\nu_{asym}(CO_2)$ 1 680vs cm^{-1}, too insoluble for n.m.r. spectrum to be recorded (Found: C, 41.35; H, 3.70; Au, 37.65. $C_{36}H_{36}Au_2O_8P_2$ requires C, 41.10; H, 3.45; Au, 37.45%); (**1b**), 88%, m.p. 188 °C (decomp.), Λ_M = 0 Ω^{-1} cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 680vs cm^{-1}, δ(^1H) 1.02, 1.09 (t, CH_3, $^3J_{HH}$ = 7 Hz), 3.95 (m, CH_2, CH), δ[$^{31}P-\{^1H\}$] 27.45 and 27.54 (s) p.p.m. (Found: C, 44.20; H, 3.85; Au, 35.20. $C_{40}H_{44}Au_2O_8P_2$ requires C, 43.35; H, 4.00; Au, 35.55%).

$[(AuX)_2\{\mu\text{-}[CH(CO_2R)]_2PPh_2\}_2]$ [X = Cl, R = Me (**2a**) *or* Et (**2b**); X = I, R = Me (**3a**) *or* Et (**3b**)].—Equimolecular amounts of Cl_2IPh and complex (**1a**) (300 mg, 0.28 mmol) or (**1b**) (300 mg, 0.27 mmol) or of I_2 and (**1a**) (70 mg, 0.07 mmol) or (**1b**) (100 mg, 0.09 mmol) were stirred in dichloromethane (10 cm^3). After 15 min the solutions were concentrated (2 cm^3) and n-hexane added to precipitate (**2a**), (**2b**) or (**3a**), (**3b**) as dark yellow or red compounds, respectively: (**2a**), 98%, m.p. 156 °C, Λ_M = 3 Ω^{-1} cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 700vs cm^{-1}, δ(^1H) 3.47, 3.51 (s, CH_3), 3.54, 3.91 (d, CH, $^2J_{PH}$ = 8 Hz), δ[$^{31}P-\{^1H\}$], 31.0 and 32.8 (s) p.p.m. (Found: C, 38.95; H, 3.55; Au, 34.70. $C_{36}H_{36}Au_2Cl_2O_8P_2$ requires C, 38.50; H, 3.25; Au, 35.05%); (**2b**), 91%, m.p. 108 °C, Λ_M = 0 Ω^{-1} cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 700vs cm^{-1}, δ(^1H) 1.03 (t, CH_3, $^3J_{HH}$ = 7 Hz) and 4.0 (m, CH_2, CH), δ[$^{31}P-\{^1H\}$], 30.66 and 32.68 (s) p.p.m. (Found: C, 40.80; H, 3.90; Au, 33.85. $C_{40}H_{44}Au_2Cl_2O_8P_2$ requires C, 40.75; H, 3.75; Au, 33.40%); (**3a**), 77%, m.p. 170 °C, Λ_M = 0 Ω^{-1} cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 700vs cm^{-1}, δ(^1H) 3.44, 3.46 (s, CH_3), and 4.42 (apparent triplet = dd, $^2J_{PH}$ = 7 Hz), δ[$^{31}P-\{^1H\}$] 37.8 and 38.1 (s) p.p.m. (Found: C, 32.75; H, 2.65; Au, 30.05. $C_{36}H_{36}Au_2I_2O_8P_2$ requires C, 33.10; H, 2.80; Au, 30.15%); (**3b**), 75%, m.p. 94 °C, Λ_M = 0 Ω^{-1} cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 700vs cm^{-1}, δ(^1H), 1.01, 1.02 (t, CH_3, $^3J_{HH}$ = 7 Hz) and 4.0 (m, CH_2, CH), δ[$^{31}P-\{^1H\}$] 37.94 and 38.03 (s) p.p.m. (Found: C, 35.05; H, 3.75; Au, 28.65. $C_{40}H_{44}Au_2I_2O_8P_2$ requires C, 35.25; H, 3.25; Au, 28.90%).

$[(AuX_2)_2\{\mu\text{-}[CH(CO_2Me)]_2PPh_2\}_2]$ [X = Cl, (**4**) *or* I, (**5**)].—Dichloromethane (5 cm^3) solutions of complex (**1a**) (120 mg, 0.11 mmol) and Cl_2 (2 cm^3 of a 6 mol dm^{-3} solution in CCl_4) or complex (**1a**) (70 mg, 0.07 mmol) and I_2 (37.8 mg, 0.15 mmol) were stirred for 15 min, the resulting solutions concentrated (2 cm^3), and diethyl ether or n-hexane added to precipitate (**4**) or (**5**) as yellow or dark red compounds, respectively: (**4**), 82%, m.p. 173 °C, Λ_M = 34 Ω^{-1} cm^2 mol^{-1}, (in dimethyl sulphoxide), $\nu_{asym}(CO_2)$ 1 710vs cm^{-1}, too insoluble for n.m.r. spectra to be recorded (Found: C, 36.50; H, 3.25; Au, 32.30. $C_{36}H_{36}Au_2Cl_4O_8P_2$ requires C, 36.20; H, 3.05; Au, 33.00%); (**5**), 78%, m.p. 115 °C, Λ_M = 1 Ω^{-1} cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 700vs cm^{-1}; too unstable to assign the observed n.m.r. resonances (Found: C, 28.55; H, 2.70; Au, 25.95. $C_{36}H_{36}Au_2I_4O_8P_2$ requires C, 27.70; H, 2.35; Au, 25.25%).

$[(AuL)_2\{\mu\text{-}[CH(CO_2Me)]_2PPh_2\}_2][ClO_4]_2$ [L = py, (**6**); 3 Br-py, (**7**); 4NC-py, (**8**); 2,4Me$_2$-py, (**9**); PPh_3, (**10**); *or* $AsPh_3$, (**11**)].—To a light-protected solution of $[(AuCl)_2\{\mu\text{-}[CH(CO_2Me)]_2PPh_2\}_2]$ (100 mg, 0.09 mmol) in acetonitrile (4 cm^3) was added $AgClO_4$ (36.9 mg, 0.18 mmol). After 30 min the solvent was evaporated, the residue extracted with dichloromethane, and the resulting suspension filtered. To the red solution the corresponding ligand in a 1:2 molar ratio was added and after a few minutes the yellow (pyridine and their derivatives) or orange (PPh_3 or $AsPh_3$) solutions were filtered, concentrated (to 2 cm^3), and diethyl ether added to precipitate complexes (**6**)—(**11**). All these complexes were too unstable to assign the observed resonances in their n.m.r. spectra: (**6**), 89%, m.p. 165 °C, $\Lambda_M = 197$, Ω^{-1} cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 705vs cm^{-1} (Found: C, 38.70; H, 3.70; Au, 28.30; N, 2.00. $C_{46}H_{46}Au_2Cl_2N_2O_{16}P_2$ requires C, 39.20; H, 3.30; Au, 27.95; N, 2.00%); (**7**), 79%, m.p. 166 °C (decomp.), $\Lambda_M = 165\ \Omega^{-1}$ cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 705vs cm^{-1} (Found: C, 34.70; H, 2.85; Au, 25.95; N, 1.50. $C_{46}H_{44}Au_2Br_2Cl_2N_2O_{16}P_2$ requires C, 35.25; H, 2.90; Au, 25.15; N, 1.80%); (**8**), 81%, m.p. 170 °C (decomp.), $\Lambda_M = 150\ \Omega^{-1}$ cm^2 mol^{-1} $\nu_{asym}(CO_2)$ 1 700vs cm^{-1} (Found: C, 39.35; H, 3.15; Au, 27.45; N, 3.20. $C_{48}H_{44}Au_2Cl_2N_4O_{16}P_2$ requires C, 39.50; H, 3.05; Au, 27.00; N, 3.85%); (**9**), 86%, m.p. 156 °C, $\Lambda_M = 198\ \Omega^{-1}$ cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 705vs cm^{-1} (Found: C, 41.10; H, 3.90; Au, 26.80; N, 2.00. $C_{50}H_{54}Au_2Cl_2N_2O_{16}P_2$ requires C, 40.95; H, 3.70; Au, 26.85; N, 1.90%); (**10**), 67%, m.p. 129 °C, $\Lambda_M = 226\ \Omega^{-1}$ cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 700vs cm^{-1} (Found: C, 48.65; H, 3.90; Au, 22.05. $C_{72}H_{66}Au_2Cl_2O_{16}P_4$ requires C, 48.70; H, 3.75; Au, 22.20%); (**11**), 74%, m.p. 120 °C, $\Lambda_M = 250\ \Omega^{-1}$ cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 690vs cm^{-1} (Found: C, 46.55; H, 3.95; Au, 21.45. $C_{72}H_{66}As_2Au_2Cl_2O_{16}P_2$ requires C, 46.40; H, 3.55; Au, 21.15%).

$[(AuL)_2\{\mu\text{-}C(CO_2R)PPh_2CH(AuL)(CO_2R)\}]ClO_4$ [L = PPh_3, R = Me (**12a**) *or* Et (**12b**); L = PMe_2Ph, R = Me (**13**); L = $P(C_6H_4OMe\text{-}4)_3$, R = Et (**14**)].—To an acetone solution of $[PPh_2(CH_2CO_2R)_2]ClO_4$ (*ca.* 30 mg in 20 cm^3) solid [Au(acac)L] (molar ratio 1:4) was added. After 8 h the suspension was filtered, the resulting solution concentrated (to 2 cm^3), and diethyl ether added to precipitate the corresponding complex as a colourless solid which was recrystallized from acetone–diethyl ether: (**12a**), 73%, m.p. 141 °C, $\Lambda_M = 114\ \Omega^{-1}$ cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 690, 1 654vs cm^{-1}, $\delta(^1H)$ 3.41, 3.56 (s, CH_3), and 4.0 (br m, CH), $\delta[^{31}P\text{-}\{^1H\}]$ 36.72 (A), 37.26 (B) (J_{AB} = 3.8), 36.06 (A′), 38.98 (B′) ($J_{A'B'}$ = 11.5 Hz) (AB = P^3P^4) A′B′ = P^1P^2) (Found: C, 48.00; H, 3.40; Au, 32.70. $C_{72}H_{62}Au_3ClO_8P_4$ requires C, 47.90; H, 3.45; Au, 32.75%); (**12b**), 94%, m.p. 129 °C, $\Lambda_M = 96\ \Omega^{-1}$ cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 680, 1 640vs cm^{-1}, $\delta(^1H)$ 0.90—1.23 (m, CH_3) and 3.84—4.05 (m, CH_2, CH), $\delta[^{31}P\text{-}\{^1H\}]$ 36.78 (A), 37.43 (B) (J_{AB} = 4.0), 35.73 (A′), 39.13 (B′) p.p.m. ($J_{A'B'}$ = 11.8 Hz) (AB = P^3P^4, A′B′ = P^1P^2) (Found: C, 48.15; H, 3.40; Au, 32.60. $C_{74}H_{66}Au_3ClO_8P_4$ requires C, 48.45; H, 3.65; Au, 32.25%); (**13**) 64%, m.p. 85 °C $\Lambda_M = 138\ \Omega^{-1}$ cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 690, 1 640vs cm^{-1} (Found: C, 35.25; H, 3.55; Au, 41.75. $C_{42}H_{50}Au_3ClO_8P_4$ requires C, 35.20; H, 3.50; Au, 41.25%); (**14**), 63%, m.p. 120 °C, $\Lambda_M = 101\ \Omega^{-1}$ cm^2 mol^{-1}, $\nu_{asym}(CO_2)$ 1 680, 1 640vs cm^{-1}, $\delta(^1H)$ 0.96—1.19(m, CH_3), 3.74, 3.76, and 3.79 (s, OMe; the broad multiplets corresponding to CH_2 and CH are obscured by these signals), $\delta[^{31}P\text{-}\{^1H\}]$ 33.62 (A), 32.90 (B) (J_{AB} = 4.0), 35.43 (A′), 34.82 (B′) p.p.m. ($J_{A'B'}$ = 12.5 Hz) (AB = P^3P^4, A′B′ = P^1P^2) (Found: C, 47.85; H, 4.45; Au, 29.80. $C_{83}H_{84}Au_3ClO_{17}P_4$ requires C, 47.40; H, 4.00; Au, 28.10%).

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