Synthesis of Gold-(I) and -(III) Complexes with Carbonyl-stabilized Phosphorus Ylides. Crystal Structure of $[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Et\}]ClO_4$ †

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Phosphonium salts $(Ph_3PCH_2CO_2R)ClO_4$ (R = Me or Et) react with [Au(acac)L′] (acac = acetylacetonate, L′ = PPh_3 or $AsPh_3$), displacing acac as acetylacetone and yielding cationic complexes of the corresponding phosphorus ylides L (L = Ph_3PCHCO_2Me, L′ = PPh_3; L = Ph_3PCHCO_2Et, L′ = PPh_3 or $AsPh_3$). These complexes react with [Au(acac)L′] to give dinuclear species $[(AuL')_2\{\mu\text{-}C(PPh_3)CO_2R\}]ClO_4$ (R = Et, L′ = PPh_3 or $AsPh_3$; R = Me, L′ = PPh_3). The displacement of the ligand tetrahydrothiophene (tht) in [AuCl(tht)] by the ylides Ph_3PCHCO_2R (R = Me or Et) forms complexes [AuCl(L)], which react (*i*) with chlorine to give $[AuCl_3L]$ or (*ii*) with L in the presence of $NaClO_4$ to give complexes $[AuL_2]ClO_4$, which also react with chlorine to form gold(III) complexes $[AuCl_2L_2]ClO_4$. The crystal structure of the complex $[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Et\}]ClO_4$ has been determined: space group $P2_1/c$, with a = 18.666(6), b = 17.490(5), c = 16.413(5) Å, β = 95.10(3) °, and R = 0.055. A short Au ··· Au contact of 2.892(2) Å is observed.

Gold(I) complexes with phosphorus ylides have attracted interest because of possible applications in the treatment of arthritis and in catalysis.[1] Unlike other ylides, carbonyl-stabilized phosphorus ylides are poor donor ligands; thus we have observed that $[AuCl(PPh_3)]$ does not react with Ph_3PCHCO_2Et, although it is known to react with ylides (L) such as Ph_3PCH_2 or Ph_3PCHCH_3 to give $[AuL(PPh_3)]^+$ or $[AuL_2]^+$.[2] Few complexes with such ligands have been reported, despite their ease of handling because of thermal and chemical stability. The only reported gold(I) complexes containing a carbonyl-stabilized phosphorane[3] are $[Au\{CH(PPh_3)COPh\}(PPh_3)]NO_3$ and $[Au\{CH(PPh_3)COPh\}_2][AuCl_4]$,[4] and no gold(III) complex has been reported so far.

We report here two novel syntheses for the gold(I) complexes $[AuL(L')]^+$ and [AuCl(L)], where L = Ph_3PCHCO_2R (R = Me or Et) and L′ = PPh_3 or $AsPh_3$. The last type of complex is otherwise represented only by the recently reported $[AuCl\{C(PPh_3)_2\}]$.[5]

Starting from [AuCl(L)] we describe the preparation of complexes $[AuCl_3L]$ [a new type of gold(III) ylide complex],[3] $[AuL_2]^+$, and $[AuCl_2L_2]^+$. Finally we report the synthesis of dinuclear gold(I) complexes that contain the bridging carbene-type ylide $RO_2C(Ph_3P)C^-$, representing an unusual[6] mode of ylide co-ordination.[7]

Results and Discussion

Synthesis.—Addition of phosphonium salts $(Ph_3PCH_2CO_2R)ClO_4$ to solutions of [Au(acac)L′] leads to the formation of complexes $[Au\{CH(PPh_3)CO_2R\}L']ClO_4$ [L′ = PPh_3, R = Me (**1**) or Et (**2**); L′ = $AsPh_3$, R = Et (**3**); acac = acetylacetonate] (see Scheme 1 and Table 1). These complexes (**1**)—(**3**) cannot be synthesized by the usual reaction[3] of ylides with the corresponding [AuCl(L)] complexes.

The low nucleophilicity of alkylidenephosphoranes containing a carbonyl group attached to the α-carbon atom is due to the increased contribution of resonance form (c) compared with the usual ylide (a) and ylene (b) forms (Scheme 2), as can be observed by the markedly lower C=O stretching frequency of the ylides with respect to the corresponding phosphonium salts [*e.g.* $(Ph_3PCH_2CO_2Et)Br$, 1 725 cm^{-1}; Ph_3PCHCO_2Et, 1 610 cm^{-1}]. The decrease in basic character of these ylides is obviously connected with an increase in acidic character of their conjugate acids, the phosphonium salts. We have taken advantage of this fact to prepare complexes (**1**)—(**3**). As far as we know this method has never been used to synthesize ylide complexes.

The methine proton of the co-ordinated ylides in complexes (**1**)—(**3**) retains acid character, since these complexes react with [Au(acac)L′] to give dinuclear complexes of the type $[(AuL')_2\{\mu\text{-}C(PPh_3)CO_2R\}]^+$ [R = Et, L′ = PPh_3 (**4**) or $AsPh_3$ (**5**); R = Me, L′ = PPh_3 (**6**)]. Complexes (**4**)—(**6**) can also be prepared by direct reaction of the phosphonium salts and [Au(acac)L′] complexes in molar ratio 1:2.

The few reported complexes containing a bridging carbene-type ylide[7] have been synthesized by methods that do not seem to be general. We intend to explore the utility of our synthetic approach in the preparation of other homo- and hetero-dinuclear ylide-bridged complexes.

Gold complexes of the easily replaceable ligand tetrahydrothiophene (tht) have been used to prepare other complexes.[8] The reactions of [AuCl(tht)] with the ylides Ph_3PCHCO_2R lead to complexes $[AuCl\{CH(PPh_3)CO_2R\}]$ [R = Me (**7**) or Et (**8**)]. The only similar reported chlorogold(I) complex $[AuCl\{C(PPh_3)_2\}]$ has been prepared recently[5] by treating [AuCl(CO)] with the double ylide $Ph_3P{=}C{=}PPh_3$.

The reaction of complex (**7**) or (**8**) with chlorine leads to the novel gold(III) complexes $[AuCl_3\{CH(PPh_3)CO_2R\}]$ [R = Me (**9**) or Et (**10**)]. Attempts to synthesize these complexes by other methods proved unsuccessful; by treating Ph_3PCHCO_2Et with $[AuCl_3(tht)]$ or $[NMe_4][AuCl_4]$ a solid was obtained with the same analytical data as (**10**) but having a different i.r. spectrum, being colourless instead of pale yellow, and being a 1:1 electrolyte in acetone solution. By comparing its i.r. spectrum with

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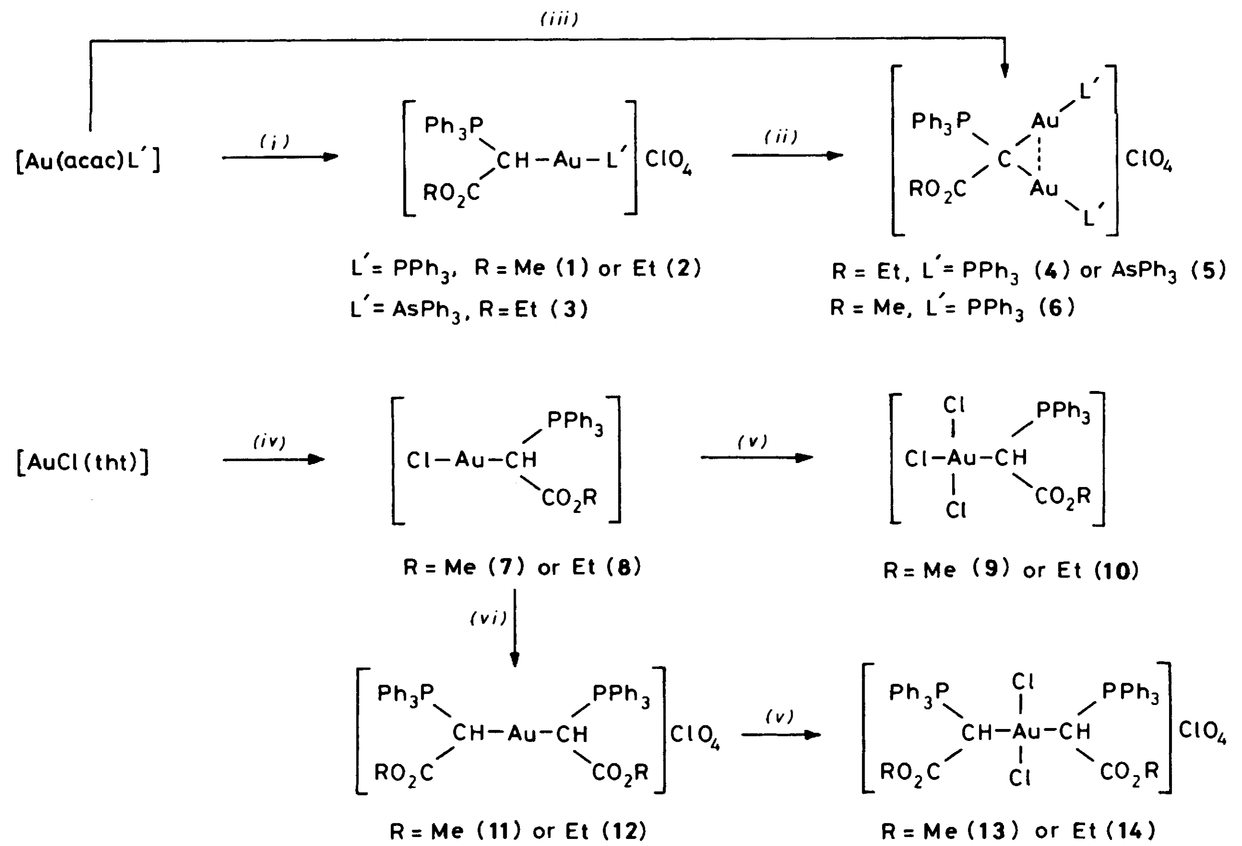
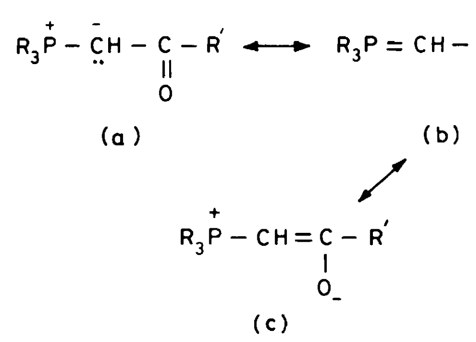
† μ-Ethoxycarbonyl(triphenylphosphoranylidene)methyl-bis(triphenylphosphinegold) (*Au–Au*) perchlorate.



Scheme 1. Syntheses of gold-(I) and -(III) ylide complexes: (*i*) $+(\mathrm{Ph_3PCH_2CO_2R})\mathrm{ClO_4}$, −Hacac; (*ii*) +[Au(acac)L′], −Hacac; (*iii*) +[Au(acac)L′], $+(\mathrm{Ph_3PCH_2CO_2R})\mathrm{ClO_4}$, −2 Hacac; (*iv*) $+\mathrm{Ph_3PCHCO_2R}$, −tht; (*v*) $+\mathrm{Cl_2}$; (*vi*) $+\mathrm{Ph_3PCHCO_2R}$, $+\mathrm{NaClO_4}$, −NaCl



Scheme 2.

those of $(\mathrm{Ph_3PCHClCO_2Et})\mathrm{Cl}$ (prepared from $\mathrm{Ph_3PCHCO_2Et}$ and chlorine) and of $[\mathrm{Ph_3PCH_2Ph}][\mathrm{AuCl_2}]$, we believe this product to be mainly $[\mathrm{Ph_3PCHClCO_2Et}][\mathrm{AuCl_2}]$. This is not unexpected in view of the ease with which such ylides react with other oxidizing agents such as chlorine, iodobenzene dichloride, and t-butyl hypochlorite[9] giving phosphonium salts [*e.g.* $(\mathrm{Ph_3PCHClCO_2Et})\mathrm{Cl}$].

The reaction between $\mathrm{HAuCl_4{\cdot}4H_2O}$ and $\mathrm{Ph_3PCHCOPh}$ has been reported[4] to give the colourless complex $[\mathrm{Au\{CH(PPh_3)COPh\}_2}][\mathrm{AuCl_4}]$. As Schmidbaur[3] points out, the formula is probably incorrect since all $[\mathrm{AuCl_4}]^-$ salts are yellow. It is probable that a redox process leads instead to a gold(I) complex.

Complexes of the type $[\mathrm{AuL_2}]^+$ are well known[1,2,10] only for the most basic ylides and are prepared from [AuCl(L′)] (L′ = $\mathrm{PPh_3}$ or $\mathrm{AsPh_3}$) and two equivalents of ylide. This method is unsuccessful with less basic (*e.g.* carbonyl-stabilized) ylides. Nevertheless the reaction of $[\mathrm{AuCl\{CH(PPh_3)CO_2R\}}]$ with the corresponding ylide in the presence of $\mathrm{NaClO_4}$ leads to complexes $[\mathrm{Au\{CH(PPh_3)CO_2R\}_2}]\mathrm{ClO_4}$ [R = Me (**11**) or Et (**12**)]. In the absence of $\mathrm{NaClO_4}$ this substitution does not occur. The oxidation of (**11**) or (**12**) with chlorine leads to gold(III) complexes $[\mathrm{AuCl_2\{CH(PPh_3)CO_2R\}_2}]\mathrm{ClO_4}$ [R = Me (**13**) or Et (**14**)]. The same method has been used to prepare other $[\mathrm{AuX_2L_2}]^+$ complexes.[3,10]

The use of carbonyl-stabilized phosphorus ylides allows the preparation of new types of stable gold complexes without taking special precautions against oxygen or moisture; this is not the case with more basic ylides.

I.r. and N.M.R. Spectra.— The substitution of a hydrogen atom in the phosphonium cations by the groups AuL′ (**1**)—(**3**), $\mathrm{AuCl^-}$ (**7**), (**8**), or AuL (**11**), (**12**) promotes a decrease in the ν(CO) stretching frequencies from 1 715 (R = Me), 1 720 (R = Et) to 1 680—1 690 cm^{-1} (see Table 2). The replacement of both hydrogen atoms by two AuL′ groups leads, as expected, to even lower ν(CO) frequencies for the dinuclear complexes (1 630—1 640 cm^{-1}). The above mentioned gold(I) groups thus cause appreciable donation of electron density into the CO antibonding orbitals. When the substituent is a gold(III) group $\mathrm{AuCl_3}$ or $\mathrm{AuCl_2L}$ the ν(CO) stretching frequencies are similar to those of the phosphonium salts [1 720, 1 710, 1 705, and 1 710 cm^{-1} for complexes (**9**), (**10**), (**13**), and (**14**) respectively]. This increase in ν(CO) frequencies from gold(I) to gold(III) substituents is an obvious consequence of the increase in oxidation state, which is also reflected in the downfield shift (*ca.* 1 p.p.m.) of the methine resonance in the ^{1}H n.m.r. spectra observed when going from the gold(I) to the gold(III) complexes.

The chlorogold(I) complexes (**7**) and (**8**) show a strong band at 325 and 330 cm^{-1}, respectively. Both $[\mathrm{AuCl_3L}]$ complexes show

Table 1. Physical and analytical data for complexes (**1**)—(**14**)

	Complex	M.p. (°C)	Λ_M[a]/Ω^{-1} cm^2 mol^{-1}	Yield (%)	Analysis[b] (%)		
					C	H	Au
(**1**)	$[Au\{CH(PPh_3)CO_2Me\}(PPh_3)]ClO_4$	97	92	85	52.85 (52.45)	3.90 (3.85)	22.35 (22.05)
(**2**)	$[Au\{CH(PPh_3)CO_2Et\}(PPh_3)]ClO_4$	154	130	63	52.90 (52.95)	4.20 (4.00)	21.55 (21.70)
(**3**)	$[Au\{CH(PPh_3)CO_2Et\}(AsPh_3)]ClO_4$	95	128	75	50.30 (50.50)	4.15 (3.80)	20.85 (20.70)
(**4**)	$[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Et\}]ClO_4$	220	108	63	51.30 (51.00)	3.35 (3.70)	28.75 (28.85)
(**5**)	$[\{Au(AsPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Et\}]ClO_4$	165	106	68	48.10 (47.95)	3.60 (3.45)	27.50 (27.10)
(**6**)	$[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Me\}]ClO_4$	105	92	76	50.90 (50.65)	4.00 (3.60)	28.60 (29.15)
(**7**)	$[AuCl\{CH(PPh_3)CO_2Me\}]$[c]	180	0	77	44.65 (44.50)	3.45 (3.40)	34.40 (34.75)
(**8**)	$[AuCl\{CH(PPh_3)CO_2Et\}]$[d]	164	0	82	45.75 (45.50)	3.70 (3.65)	33.20 (33.90)
(**9**)	$[AuCl_3\{CH(PPh_3)CO_2Me\}]$	161	0	94	39.90 (39.55)	3.20 (3.00)	31.00 (30.90)
(**10**)	$[AuCl_3\{CH(PPh_3)CO_2Et\}]$	155	3	80	40.45 (40.55)	3.15 (3.25)	30.55 (30.20)
(**11**)	$[Au\{CH(PPh_3)CO_2Me\}_2]ClO_4$	125	94	76	51.90 (52.25)	4.20 (3.95)	20.80 (20.40)
(**12**)	$[Au\{CH(PPh_3)CO_2Et\}_2]ClO_4$	100	83	67	53.20 (53.20)	4.25 (4.25)	20.35 (19.85)
(**13**)	$[AuCl_2\{CH(PPh_3)CO_2Me\}_2]ClO_4$	150	90	91	48.20 (48.70)	4.15 (3.70)	18.65 (19.00)
(**14**)	$[AuCl_2\{CH(PPh_3)CO_2Et\}_2]ClO_4$	116	79	98	49.95 (49.65)	4.40 (4.00)	19.10 (18.50)

[a] In acetone (*ca.* 10^{-4} mol dm^{-3}). [b] Calculated values are given in parentheses. [c] Molecular weight determined in $CHCl_3$ ($c = 3.07 \times 10^{-2}$ mol kg^{-1}): 585 (567). [d] M ($c = 1.99 \times 10^{-2}$ mol kg^{-1}): 581 (581).

Table 2. N.m.r.[a] (δ/p.p.m., J/Hz) and i.r. data

	Complex	^{1}H N.m.r.[b]	ν(CO)/cm^{-1}
(**1**)	$[Au\{CH(PPh_3)CO_2Me\}(PPh_3)]ClO_4$	3.66 (s, Me), 4.08 [dd, CH, ^3J(P–H) = 4.8, ^2J(P–H) = 9][c]	1 690
(**2**)	$[Au\{CH(PPh_3)CO_2Et\}(PPh_3)]ClO_4$	1.16 ['t', Me, ^3J(H–H) = 7], 4.22 ('q', CH_2), 4.11 [dd, CH, ^3J(P–H) = 4.8, ^2J(P–H) = 9][d,e]	1 685
(**3**)	$[Au\{CH(PPh_3)CO_2Et\}(AsPh_3)]ClO_4$	1.15 ['t', Me, ^3J(H–H) = 7], 4.28 ('q', CH_2), 4.28 [d, CH, ^2J(P–H) = 5][d]	1 680
(**4**)	$[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Et\}]ClO_4$	1.13 ['t', Me, ^3J(H–H) = 7], 4.00 ('q', CH_2)[f,g]	1 630
(**5**)	$[\{Au(AsPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Et\}]ClO_4$	1.20 ['t', Me, ^3J(H–H) = 7], 4.20 ('q', CH_2)[d]	1 635
(**6**)	$[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)CO_2Me\}]ClO_4$	3.60 (s, Me)[c]	1 640
(**7**)	$[AuCl\{CHPPh_3)CO_2Me\}]$	3.70 (s, Me), 4.17 [d, CH, ^2J(P–H) = 4][d]	1 690
(**8**)	$[AuCl\{CHPPh_3)CO_2Et\}]$	1.05 ['t', Me, ^3J(H–H) = 7.2], 3.93, 4.05 (AB, CH_2, J_{AB} = 11.2), 3.96 [d, CH, ^2J(P–H) = 3.3][c]	1 685
(**9**)	$[AuCl_3\{CH(PPh_3)CO_2Me\}]$	*h*	1 720
(**10**)	$[AuCl_3\{CH(PPh_3)CO_2Et\}]$	1.27 ['t', Me, ^3J(H–H) = 7], 4.28 ('q', CH_2), 5.28 [d, CH, ^2J(P–H) = 9][d]	1 710
(**11**)	$[Au\{CH(PPh_3)CO_2Me\}_2]ClO_4$	3.37, 3.45 (s, Me), 3.69, 3.73 [d, CH, ^2J(P–H) = 3.3, 3.2][c]	1 680
(**12**)	$[Au\{CH(PPh_3)CO_2Et\}_2]ClO_4$	0.90, 0.97 ['t', Me, ^3J(H–H) = 7.1], 3.7—4.0 (m, CH_2, CH)[c]	1 680
(**13**)	$[AuCl_2\{CH(PPh_3)CO_2Me\}_2]ClO_4$	3.59, 3.61 (s, Me), 4.69, 4.88 [d, CH, ^2J(P–H) = 13.6, 8.5][c]	1 705
(**14**)	$[AuCl_2\{CH(PPh_3)CO_2Et\}_2]ClO_4$	1.10, 1.21 ['t', Me, ^3J(H–H) = 7], 3.55, 4.18 ('q', CH_2), 5.00 ['d', CH, J(P–H) = 8][d]	1 710

[a] Recorded in $CDCl_3$ unless otherwise specified; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; 'd', 't', or 'q' = apparent doublet, triplet, or quartet (see text). [b] All complexes show a multiplet in the 7—8 p.p.m. region corresponding to Ph groups. [c] At 200 MHz. [d] At 60 MHz. [e] ^{31}P-{^{1}H} n.m.r. referred to H_3PO_4: 29.07 and 15.53 p.p.m. [f] In $(CD_3)_2CO$ at 80 MHz. [g] ^{31}P-{^{1}H} n.m.r. referred to H_3PO_4: 26.88 (P–Au) and 21.55 (P–C) p.p.m. [h] Not soluble.

two strong bands at 315 and 360 cm^{-1} that can be assigned to ν(AuCl) *trans* to the ylides and ν_{asym}(ClAuCl), respectively. A weak band observed at 340 cm^{-1} can be tentatively assigned to ν_{sym}(ClAuCl). The presence of a strong band at 360 cm^{-1} in the $[AuCl_2L_2]^+$ complexes (**13**) and (**14**) allows the assignment of a *trans* geometry.[11,12] A *cis* geometry should give rise to two bands; even if only one could be observed it should appear around 310—320 cm^{-1}, because of the greater *trans* influence of the ylides compared to the chloro-ligand, as seen for the $[AuCl_3L]$ complexes. The reported $[AuX_2L_2]^+$ complexes are also believed to be *trans* although they slowly isomerize in aqueous solutions to the *cis* complexes.[3,10]

The ylide α-carbon atoms are chiral centres when co-ordinated to the gold atom. There is no reason to expect stereospecificity of the co-ordination process, and all complexes [except the dinuclear complexes (**4**)—(**6**)] should be racemic mixtures. The specific optical rotations of samples of complexes (**7**), (**8**), (**12**), and (**13**) were measured and shown to be zero. As n.m.r. spectroscopy cannot distinguish (in the absence of other chiral species that could interact with them) between *R* and *S* enantiomers, the spectra of complexes of the type $[AuL(L')]^+$, $[AuCl(L)]$, or $[AuCl_3L]$ show only one type of ylide. In complexes with two co-ordinated ylides, a mixture of 50% of the *RS*, 25% of the *SS*, and 25% of the *RR* isomers is to be expected. N.m.r. spectra should thus exhibit 50% of each diastereoisomer as observed.

Proton n.m.r. spectra of the complexes with the ligand Ph_3PCHCO_2Me are simple, and show only one Me signal for (**1**), (**6**), and (**7**) and two for the diylide complexes (**11**) and (**13**), in the region 3.30—3.70. The methine proton appears as a doublet (coupling with phosphorus), except for the PPh_3 complexes (**1**) and (**2**) for which doublets of doublets are observed. When the ligand is Ph_3PCHCO_2Et, the Et group is strictly an ABX_3 system because of the chiral centre. However the X_3 component appears as a triplet, presumably because $(J_{AX} - J_{BX})/J_{AB} \approx 0$ The AB component should consist of four AB subspectra (1:3:3:1), additionally complicated in the mononuclear gold(I) complexes by the superposition of the methine doublet. At 60 MHz the ^{1}H n.m.r. spectra in this region show an apparent quartet for the CH_2 group and a doublet for the methine

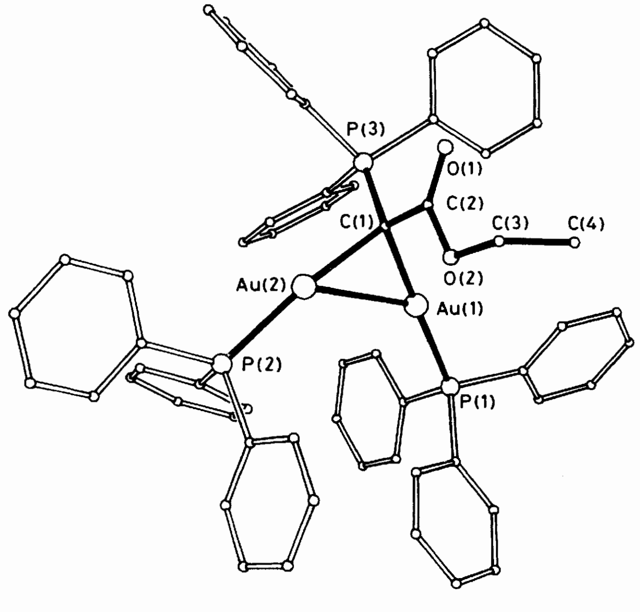
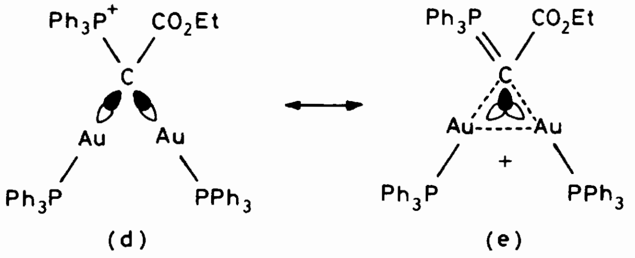


Figure. The cation of complex (4), with H atoms omitted for clarity, showing the atom numbering scheme



Scheme 3.

proton. Irradiation at the Me resonance frequency leads to an apparent singlet for the CH_2 group. Thus, at 60 MHz, the n.m.r. spectra of the Et group are deceptively simple and look like an A_2X_3 system. At 200 MHz the AB component shows its true complexity; a complete analysis for the complex [AuCl{CH(PPh$_3$)CO$_2$Et}] (see Table 2) can be accomplished using irradiation at the Me resonance frequency, whereupon the CH_2 signal collapses to a simple AB pattern, partially overlapped with the CH doublet.

X-Ray Structure Determination of Complex (**4**).—The suggested structure of (**4**) is confirmed by *X*-ray analysis (see below and the Figure). The Au $\cdots$ Au contact [2.892(2) Å, *cf.* 2.6—3.2 Å in gold clusters but formally non-bonded contacts of *ca.* 2.8 Å in gold(I) complexes],[13] the Au(1)–C(1)–Au(2) angle [86.3(4)°], the P(3)–C(1)–C(2) angle [112.3(7)°], and the short P(3)–C(1) distance [1.763(10) Å, *cf.* P–CH_3 single bond lengths of 1.83(3)[14] and 1.84(2) Å,[7a] in two ylide complexes] are consistent with bonding corresponding to the limiting resonance forms (d) and (e) (Scheme 3). The latter represents a closed three-centre two-electron bond, as has been suggested for other complexes containing the Ph$_3$PAuAuPPh$_3$ moiety,[15] and points to a double role of the Ph$_3$PCCO$_2$Et ligand as a ylide[7] and as a bridging carbene. The low ν(CO) frequency of complex (**4**) also suggests partial ylidic nature of the bridging ligand, although C(2)–O(1) is a normal C–O distance.

Experimental

Infrared spectra were recorded in the range 4 000—250 cm^{-1} on Perkin-Elmer 457 and Nicolet MX-1 spectrophotometers using Nujol mulls between polyethylene sheets. Conductivities were measured with a Philips 9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. Carbon and hydrogen analyses were carried out with a Perkin-Elmer 240C microanalyser; Au was determined by ashing the samples with an aqueous solution of hydrazine. Proton n.m.r. spectra were recorded on a Varian EM-360A (60 MHz, ^{1}H), Varian FT-80 (80 MHz, ^{1}H; 32.2 MHz, ^{31}P), and Varian XL-250 (200 MHz, ^{1}H) spectrometers. Molecular weights were determined with a Knauer vapour-pressure osmometer.

All reactions were carried out at room temperature with magnetic stirring and without any special precautions against light, air, or moisture. The gold-(I) and -(III) complexes are colourless and pale yellow respectively.

[Au{CH(PPh$_3$)CO$_2$R}L′]ClO$_4$ [R = Me, L′ = PPh$_3$ (**1**); R = Et, L′ = PPh$_3$ (**2**) *or* AsPh$_3$ (**3**)].—To a solution of [Au(acac)L′][16] (*ca.* 0.1 mmol) in dichloromethane (15 cm^3) an equimolar amount of solid (Ph$_3$PCH$_2$CO$_2$R)ClO$_4$[17] was added. Some time later (6.5, 5, or 22 h, respectively) the reaction mixture was filtered and concentrated to 1 cm^3 and diethyl ether (15 cm^3) was added to precipitate complexes (**1**)—(**3**), which were washed with diethyl ether (3 × 10 cm^3) and recrystallized from dichloromethane–diethyl ether (1:10).

[(AuL′)$_2${μ-C(PPh$_3$)CO$_2$R}]ClO$_4$ [R = Et, L′ = PPh$_3$ (**4**) *or* AsPh$_3$ (**5**); R = Me, L′ = PPh$_3$ (**6**)].—To a solution of [Au(acac)L′] (*ca.* 0.1 mmol) in dichloromethane (10 cm^3), solid (Ph$_3$PCH$_2$CO$_2$R)ClO$_4$ (2:1) was added. Some time later (17, 15, or 14 h, respectively) the reaction mixture was filtered and concentrated to 1 cm^3 and diethyl ether (15 cm^3) was added to precipitate complexes (**4**)—(**6**), which were washed with diethyl ether (3 × 10 cm^3) and recrystallized from dichloromethane–diethyl ether (1:10). These complexes can also be prepared by treating the corresponding mononuclear complexes (**1**)—(**3**) with [Au(acac)L′] (1:1, dichloromethane, 4 h). Single crystals of complex (**4**) were obtained by diffusion of light petroleum ether (b.p. 40—60 °C) into a solution of (**4**) in dichloromethane.

[AuCl{CH(PPh$_3$)CO$_2$R}] [R = Me (**7**) *or* Et (**8**)].—To a solution of [AuCl(tht)] (tht = tetrahydrothiophene) (110 mg, 0.34 mmol) in dichloromethane (5 cm^3) was added an equimolar amount of solid Ph$_3$PCHCO$_2$Me or Ph$_3$PCHCO$_2$Et.[17] After 30 min the solutions were concentrated to 1 cm^3 and diethyl ether (10 cm^3) was added to precipitate complex (**7**) or (**8**), which were crystallized from dichloromethane–diethyl ether (1 : 10).

[AuCl$_3${CH(PPh$_3$)CO$_2$R}] [R = Me (**9**) *or* Et (**10**)].—To a solution of complex (**7**) (100 mg, 0.18 mmol) or (**8**) (100 mg, 0.17 mmol) in dichloromethane (5 cm^3) was added a saturated solution of Cl_2 in CCl_4 (2.7 cm^3). After 30 min the solutions were concentrated to 3 cm^3, and diethyl ether (10 cm^3) was added to precipitate (**9**) or (**10**), which were washed with diethyl ether. Both complexes are only slightly soluble in dichloromethane or acetone.

[Au{CH(PPh$_3$)CO$_2$R}$_2$]ClO$_4$ [R = Me (**11**) *or* Et (**12**)].—To solutions of complex (**7**) (200 mg, 0.35 mmol) or (**8**) (100 mg, 0.17 mmol) in acetone (10 cm^3) were added successively equimolar amounts of solid Ph$_3$PCHCO$_2$Me or Ph$_3$PCHCO$_2$Et and NaClO$_4$. After 1 h the solvent was evaporated, the residues extracted with dichloromethane (10 cm^3), the suspensions filtered off, and the solutions concentrated to 1 cm^3; diethyl ether (15 cm^3) was added to precipitate (**11**) or (**12**), which were recrystallized from dichloromethane–diethyl ether (1:10).

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

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Au(1)	2 192.8(2)	923.1(2)	1 567.9(2)	C(222)	5 311(4)	1 148(4)	2 248(3)
Au(2)	3 144.0(2)	−256.1(2)	1 060.7(2)	C(223)	6 015	922	2 154
P(1)	1 102(1)	902(1)	2 086(2)	C(224)	6 190	622	1 409
P(2)	2 948(1)	−1 529(1)	1 194(1)	C(225)	5 660	547	759
P(3)	3 867(1)	1 356(1)	1 738(1)	C(226)	4 955	773	854
C(1)	3 186(5)	957(4)	1 055(6)	C(221)	4 781	1 073	1 598
C(2)	3 186(5)	1 274(5)	229(6)	C(232)	3 607(4)	1 594(4)	3 373(4)
C(3)	2 580(8)	1 320(7)	−1 101(6)	C(233)	3 542	1 352	4 173
C(4)	2 119(8)	2 037(8)	−1 165(9)	C(234)	3 621	580	4 375
O(1)	3 609(4)	1 738(4)	7(4)	C(235)	3 766	50	3 776
O(2)	2 633(4)	1 019(4)	−275(4)	C(236)	3 831	292	2 976
C(112)	716(3)	−302(3)	1 069(4)	C(231)	3 751	1 064	2 774
C(113)	240	−804	640	C(312)	4 314(4)	−1 956(3)	770(5)
C(114)	−500	−707	660	C(313)	4 816	−2 482	530
C(115)	−764	−110	1 111	C(314)	4 643	−3 258	483
C(116)	−287	392	1 540	C(315)	3 969	−3 508	676
C(111)	453	296	1 519	C(316)	3 467	−2 982	917
C(122)	964(4)	2 430(5)	1 662(4)	C(311)	3 640	−2 206	964
C(123)	700	3 171	1 728	C(322)	2 224(3)	−1 307(4)	2 560(4)
C(124)	193	3 329	2 280	C(323)	2 132	−1 339	3 394
C(125)	−51	2 746	2 765	C(324)	2 619	−1 748	3 922
C(126)	214	2 004	2 699	C(325)	3 198	−2 123	3 615
C(121)	721	1 846	2 147	C(326)	3 289	−2 091	2 782
C(132)	548(3)	141(4)	3 398(4)	C(321)	2 802	−1 682	2 254
C(133)	582	−106	4 209	C(332)	2 029(3)	−1 570(3)	−199(4)
C(134)	1 183	65	4 744	C(333)	1 468	−1 861	−727
C(135)	1 751	483	4 469	C(334)	1 029	−2 438	−462
C(136)	1 717	730	3 658	C(335)	1 151	−2 726	331
C(131)	1 116	559	3 123	C(336)	1 712	−2 435	859
C(212)	3 160(3)	2 746(4)	1 695(4)	C(331)	2 151	−1 857	594
C(213)	3 112	3 542	1 707	Cl	1 886(2)	5 510(2)	2 031(2)
C(214)	3 735	3 985	1 739	O(11)	2 397(5)	5 585(6)	1 448(6)
C(215)	4 407	3 632	1 759	O(12)	1 293(7)	5 941(9)	1 853(9)
C(216)	4 455	2 837	1 746	O(13)	1 650(12)	4 791(7)	2 015(10)
C(211)	3 832	2 394	1 714	O(14)	2 147(7)	5 647(13)	2 785(9)

Table 4. Bond lengths (Å) and angles (°) for complex (**4**)

Au(1) ··· Au(2)	2.892(2)	C(121)–P(1)	1.805(9)	Au(1)–P(1)	2.276(4)	C(131)–P(1)	1.802(8)
Au(1)–C(1)	2.105(10)	C(211)–P(3)	1.816(8)	Au(2)–P(2)	2.271(3)	C(221)–P(3)	1.809(9)
Au(2)–C(1)	2.123(9)	C(231)–P(3)	1.807(7)	C(1)–P(3)	1.763(10)	C(311)–P(2)	1.815(8)
C(1)–C(2)	1.464(14)	C(321)–P(2)	1.805(8)	C(2)–O(1)	1.211(13)	C(331)–P(2)	1.803(8)
C(2)–O(2)	1.341(13)	Cl–O(11)	1.416(12)	C(3)–C(4)	1.520(21)	Cl–O(12)	1.350(16)
C(3)–O(2)	1.448(14)	Cl–O(13)	1.331(15)	C(111)–P(1)	1.804(7)	Cl–O(14)	1.312(15)

P(1)–Au(1)–C(1)	178.2(4)	O(1)–C(2)–O(2)	121.5(9)	P(2)–Au(2)–C(1)	170.7(4)	C(4)–C(3)–O(2)	110.8(11)
Au(1)–P(1)–C(111)	113.5(3)	C(2)–O(2)–C(3)	116.3(10)	Au(1)–P(1)–C(121)	112.0(4)	P(1)–C(111)–C(112)	117.5(3)
C(111)–P(1)–C(121)	108.5(4)	P(1)–C(111)–C(116)	122.5(3)	Au(1)–P(1)–C(131)	114.8(3)	P(1)–C(121)–C(122)	119.2(4)
C(111)–P(1)–C(131)	104.2(4)	P(1)–C(121)–C(126)	120.7(4)	C(121)–P(1)–C(131)	103.0(4)	P(1)–C(131)–C(132)	122.2(3)
Au(2)–P(2)–C(311)	119.7(3)	P(1)–C(131)–C(136)	117.8(3)	Au(2)–P(2)–C(321)	106.1(3)	P(3)–C(211)–C(212)	118.2(3)
C(311)–P(2)–C(321)	106.0(4)	P(3)–C(211)–C(216)	121.7(3)	Au(2)–P(2)–C(331)	113.0(3)	P(3)–C(221)–C(222)	119.3(3)
C(311)–P(2)–C(331)	104.3(4)	P(3)–C(221)–C(226)	120.7(3)	C(321)–P(2)–C(331)	106.9(4)	P(3)–C(231)–C(232)	121.4(3)
C(1)–P(3)–C(211)	111.0(5)	P(3)–C(231)–C(236)	118.5(3)	C(1)–P(3)–C(221)	116.4(5)	P(2)–C(311)–C(312)	121.0(3)
C(211)–P(3)–C(221)	107.6(4)	P(2)–C(311)–C(316)	118.8(3)	C(1)–P(3)–C(231)	110.3(5)	P(2)–C(321)–C(322)	117.7(3)
C(211)–P(3)–C(231)	107.2(4)	P(2)–C(321)–C(326)	121.9(3)	C(221)–P(3)–C(231)	103.6(4)	P(2)–C(331)–C(332)	116.9(3)
Au(1)–C(1)–Au(2)	86.3(4)	P(2)–C(331)–C(336)	122.7(3)	Au(1)–C(1)–P(3)	111.6(6)	O(11)–Cl–O(12)	113.0(9)
Au(2)–C(1)–P(3)	114.7(5)	O(11)–Cl–O(13)	108.4(11)	Au(1)–C(1)–C(2)	117.0(7)	O(12)–Cl–O(13)	105.1(12)
Au(2)–C(1)–C(2)	112.7(7)	O(11)–Cl–O(14)	113.9(9)	P(3)–C(1)–C(2)	112.3(7)	O(12)–Cl–O(14)	109.3(12)
C(1)–C(2)–O(1)	125.9(9)	O(13)–Cl–O(14)	106.6(13)	C(1)–C(2)–O(2)	112.5(9)		

$[AuCl_2\{CH(PPh_3)CO_2R\}_2]ClO_4$[R = Me(**13**)*or*Et(**14**)].—To solutions of complex (**11**) (110 mg, 0.11 mmol) or (**12**) (78 mg, 0.08 mmol) in dichloromethane (3 cm^3) was added a saturated solution of Cl_2 in CCl_4 (1.5 or 2 cm^3 respectively). After 2 h the solutions were concentrated to 1 cm^3 and diethyl ether (15 cm^3) was added to precipitate (**13**) or (**14**), which were washed with diethyl ether (2 × 5 cm^3) and recrystallized from dichloromethane–diethyl ether (1 : 10).

Crystallography.—$C_{58}H_{50}Au_2ClO_6P_3$, (**4**), M = 1 365.3, monoclinic, space group $P2_1/c$, a = 18.666(6), b = 17.490(5), c = 16.413(5) Å, β = 95.10(3)°, U = 5 337 $Å^3$, Mo-K_α radiation (λ = 0.710 69 Å), Z = 4, D_c = 1.70 g cm^{-3}, colourless square plate 0.3 × 0.3 × 0.05 mm with bounding faces ±(011, 0$\bar{1}$1, 100), μ = 5.7 mm^{-1}, F(000) = 2 664.

Data collection and processing. Stoe-Siemens four-circle diffractometer, monochromated Mo-K_α radiation, 9 463 profilefitted[18] reflections measured ($2\theta_{max.}$ 50°, $\pm h + k - l$), 9 367 unique, 7 046 [$F > 4\sigma(F)$] used for all calculations. Absorption correction based on ψ scans; transmissions 0.42—0.99. No crystal decay.

Structure solution and refinement. Gold atoms from the Patterson function, other non-H atoms by difference syntheses. Least-squares refinement on F to R 0.055, R' 0.051 [phenyl rings as isotropic rigid groups with C–C 1.395, C–H 0.96 Å, all angles 120°, $U(H) = 1.2\ U(C)$; other H atoms incorporated using a riding model; other non-H atoms anisotropic; weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,35\ F^2$; 256 parameters]. Program system SHELXTL (written by G. M. S.). Final atomic co-ordinates and derived parameters are given in Tables 3 and 4.*

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* Additional crystallographic material (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. Please quote reference number CSD/51064, the names of the authors, and the title of the paper.

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