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Keto-stabilized phosphorus ylide gold(I) and gold(III) complexes

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Abstract

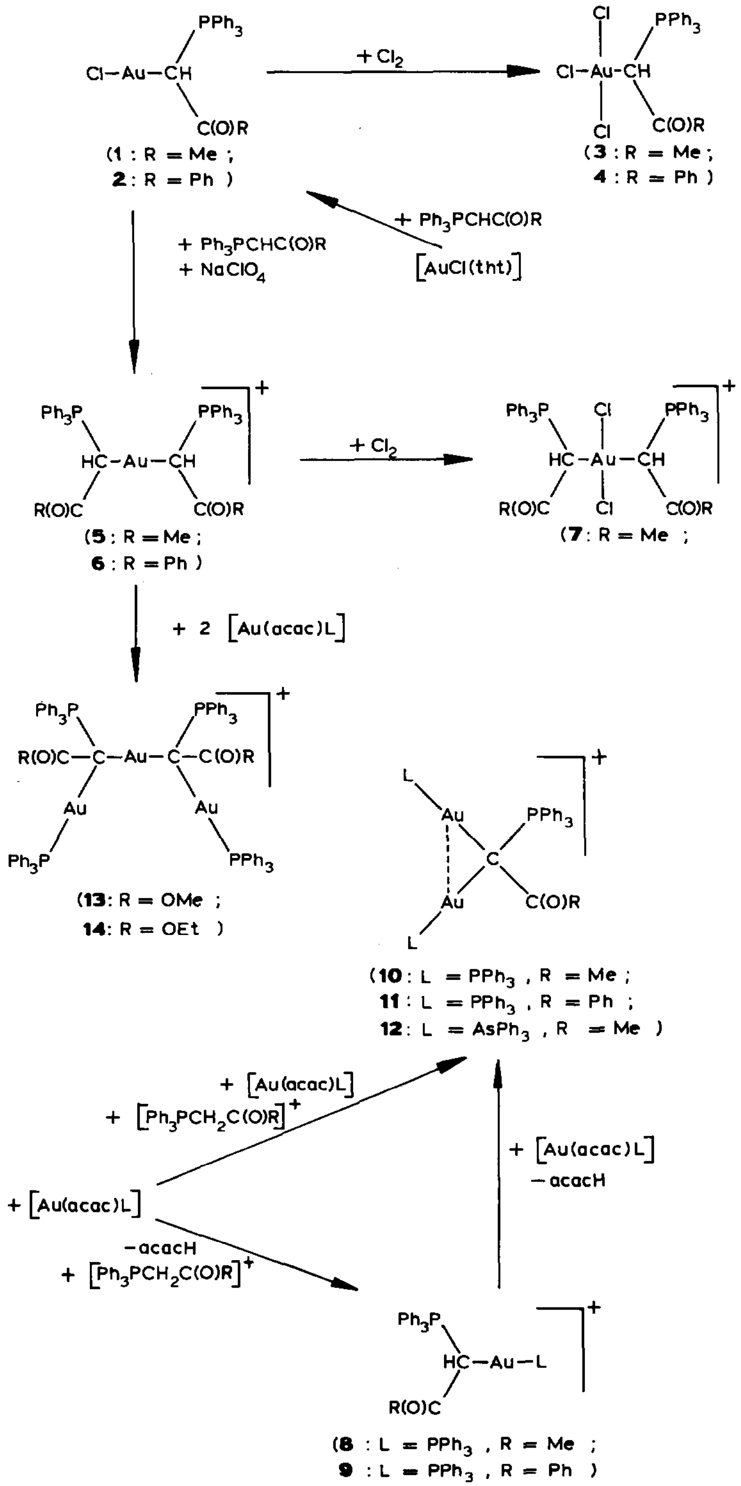
Reactions between [AuCl(tht)] (tht = tetrahydrothiophene) and the ylides $Ph_3PCHC(O)R$ give complexes $[AuCl\{CH(PPh_3)C(O)R\}]$ (R = Me, Ph), which react (1) with chlorine to give $[AuCl_3\{CH(PPh_3)C(O)R\}]$ (R = Me, Ph) and (2) with the same ylide and $NaClO_4$ to form $[Au\{CH(PPh_3)C(O)R\}_2]ClO_4$ (R = Me, Ph). The latter species react with chlorine to give *trans*-$[AuCl_2\{CH(PPh_3)C(O)R\}_2]ClO_4$ (R = Me), and with $[Au(acac)(PPh_3)]$ (molar ratio 1/2) to give $[Au\{C(AuPPh_3)(PPh_3)C(O)R\}_2]ClO_4$ (R = OMe, OEt). The phosphonium salts $[Ph_3PCH_2C(O)R]ClO_4$ react with $[Au(acac)(EPh_3)]$ (acac = acetylacetonate) in 1/1 or 1/2 molar ratio to give, respectively, $[Au\{CH(PPh_3)C(O)R\}(PPh_3)]ClO_4$ (R = Me, Ph) or $[\{Au(EPh_3)\}_2\{\mu\text{-}C(PPh_3)C(O)R\}]ClO_4$ (E = P, R = Me, Ph; E = As, R = Me).

Introduction

Possible applications of gold(I) complexes with phosphorus ylides in the treatment of arthritis and in catalysis have provoked much interest in the synthesis of such species [1]. However, although there is a considerable body of information about gold-ylide complexes [2], the number of such complexes that contain keto-stabilized phosphorus ylides is limited almost to those recently reported by some of us [3] which contain ylides of the type Ph_3PCHCO_2R (R = Me, Et).

These ylides are less basic than the more studied Ph_3PCHR (R = H, alkyl or aryl groups), which for example, react with $[AuCl(PPh_3)]$ to give $[Au\{CH(PPh_3)R\}(PPh_3)]^+$ and, in an excess of the ylide, $[Au\{CH(PPh_3)R\}_2]^+$ [4,5], whereas Ph_3PCHCO_2R and $[AuCl(PPh_3)]$ do not react [3]. However we have described [3] other routes to gold(I) and gold(III) complexes containing this type of ligand and which give types of gold complexes which are unique or scarce, such as $[AuCl_3L]$, or [AuClL] (L = ylide).

In this paper we describe a comparison of the ylides $Ph_3PCHC(O)R$ (R = Me, Ph) with the previously studied [3] (R = OMe, OEt) in order to obtain information



Scheme 1. Synthesis of complexes 1–14.

about (1) the generality of our routes to complexes containing carbonyl-stabilized phosphorus ylides, and (2) the differences between the properties of gold complexes of the same overall structure but differing in the nucleophilic character of the ylides.

Results and discussion

Synthesis

Tetrahydrothiophene (tht) is sufficiently labile in the complex [AuCl(tht)] to permit its replacement by ylides of formula $Ph_3PCHC(O)R$ to give complexes of stoichiometry $AuCl\{CH(PPh_3)C(O)R\}$ (R = Me (**1**), R = Ph (**2**)) in very good yields (see Scheme 1). However, while **1** is soluble in most organic solvents, as are those with R = OMe and OEt [3], **2** is insoluble in dichloromethane, acetone, acetonitrile and toluene.

When a concentrated solution of **1** in acetone reacts with a solution of chlorine in CCl_4 the complex $[AuCl_3\{CH(PPh_3)C(O)CH_3\}]$ (**3**) separates as a yellow solid. However, **2** reacts with chlorine in CCl_4 to give products which depend on the reaction time. Thus after 30 min (in acetonitrile or chloroform) the yellow complex $[AuCl_3\{CH(PPh_3)C(O)Ph\}]$ (**4**) was isolated. However, after 44 h (in chloroform) we isolated only a different (by IR spectroscopy) yellow complex, which conducts in acetone as a 1/1 electrolyte if it is formulated as the isomer of **4**, $[AuCl_2\{CH(PPh_3)C(O)Ph\}_2][AuCl_4]$. However we were unable to obtain any analytically pure sample of this complex.

Complexes **1** and **2** do not react with the corresponding ylides to give complexes of the type $[Au(ylide)_2]^+$ but do react in the presence of $NaClO_4$ to give NaCl and $[Au\{CH(PPh_3)C(O)R\}_2]ClO_4$ (R = Me (**5**), R = Ph (**6**)). Complex **6** can also be obtained by treating [AuCl(tht)] with $[Ag\{CH(PPh_3)C(O)Ph\}_2]ClO_4$ [6]. This transmetallation is one of the few reported in which two metal centres interchange an ylide ligand [7] *.

Complexes **5** and **6** behave differently towards chlorine. Thus **5** reacts to give *trans*-$[AuCl_2\{CH(PPh_3)C(O)CH_3\}_2]ClO_4$ (**7**) while **6** gives a mixture (by IR spectroscopy) of complexes, which we have been unable to separate.

The phosphonium salts, $[Ph_3PCH_2C(O)R]ClO_4$ (R = Me, Ph), are conjugate acids of the weakly basic ylides coordinated in complexes **1**–**7**. We have taken advantage of their acidic characters to prepare complexes of the type $[Au(CH(PPh_3)C(O)R\}(PPh_3)]ClO_4$ (R = Me (**8**), R = Ph (**9**)) by treating them with equimolar amounts of $[Au(acac)(PPh_3)]$. These reactions give acetylacetone as the only by-product. However **9** is always obtained along with unchanged phosphonium salt (by IR spectroscopy), which means that this reaction is an equilibrium process observed only with the less basic ylide (see below). It is for this reason that **9** is better made by treating $[AuCl(PPh_3)]$ with $[Ag\{CH(PPh_3)C(O)Ph\}_2]ClO_4$ [6]. This reaction, when used to prepare **8**, gives a mixture containing the phosphonium perchlorate (see below).

The methine protons in **8** or **9** retain acidic character since these complexes react with $[Au(acac)(PPh_3)]$ to give the dinuclear complexes $[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)C(O)R\}]ClO_4$ (R = Me (**10**), R = Ph (**11**), which can also be prepared

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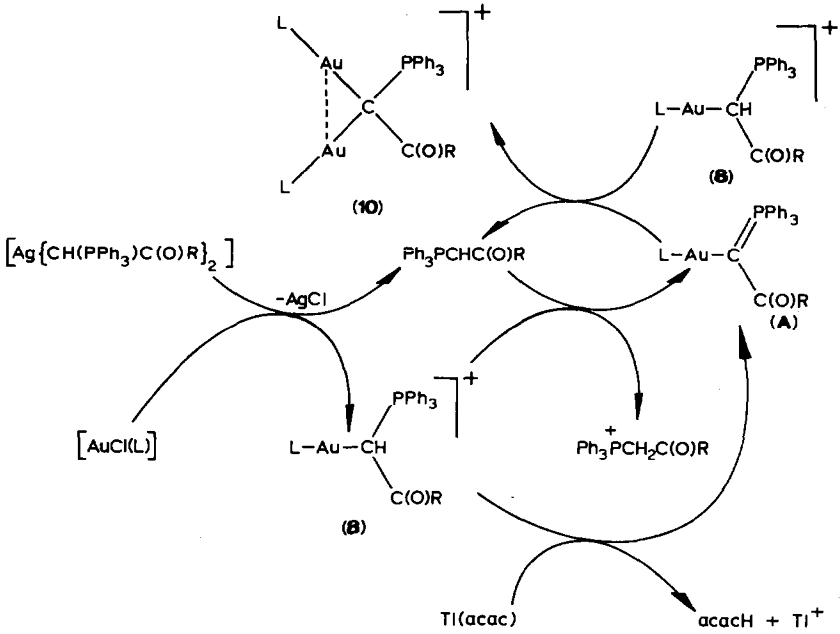
* This and other references marked with asterisks indicate notes occurring in the list of references.



Scheme 2. L = PPh_3, R = Me.

directly by treating $[Au(acac)(PPh_3)]$ with the corresponding phosphonium salt in a 2/1 molar ratio. Again the reaction with the phenacylphosphonium salt is an equilibrium process, and **11** cannot be isolated as a pure compound. However pure **11** is obtained if a > 2/1 molar ratio is used, since the excess of $[Au(acac)(PPh_3)]$ can be readily removed by washing the mixture with diethyl ether. The same type of reaction but with $[Au(acac)(AsPh_3)]$, gives the complex $[\{Au(AsPh_3)\}_2\{\mu\text{-}C(PPh_3)C(O)CH_3\}]$ (**12**). The structures of complexes **10**–**12** are probably the same as that established by X-ray diffraction for the complex $[\{Au(PPh_3)\}_2\{(\mu\text{-}C(PPh_3)CO_2Et\}]$ [3].

The nature of the reaction that gave **10**–**12** from **8** and **9** suggested to us the possibility of preparing trinuclear complexes by treating $[Au(acac)(PPh_3)]$ with $[Au\{CH(PPh_3)C(O)R\}_2]^+$ complexes in a 2/1 molar ratio, and this way we obtained the complexes $[Au\{C(AuPPh_3)(PPh_3)C(O)R\}_2]ClO_4$ (R = OMe (**13**), R = OEt (**14**)).

We tried to prepare the metallated ylide $[Au\{C(PPh_3)C(O)CH_3\}(PPh_3)]$ (**A**) (see Scheme 2) by treating **8** with Tl(acac) but we isolated only the phosphonium salt and complex **10**. It is possible that the deprotonation reaction leading to **A** was slower than the reaction of **A** with **8** to give **10**. This latter reaction may also account for the result obtained on treatment of $[AuCl(PPh_3)]$ and $[Ag\{CH(PPh_3)C(O)CH_3\}_2]$ (see above). In this case the ylide, obtained along with **8**, could be the base responsible for the deprotonation of **8** to give **A**. As can be seen in Scheme 2 the ylide acts as a catalyst in both processes. This means that **8** must decompose to give **10** and the phosphonium salt ($2\ \mathbf{8} \rightarrow \mathbf{10} + [Ph_3PCH_2C(O)R]ClO_4$) if it is not kinetically inert. We have, in fact, obtained this mixture by stirring an acetone solution of **8** for 24 h at room temperature.

Table 1 gives analytical and other data for complexes **1**–**14**.

Table 1

Analytical and other data for complexes **1–14**

Compound	M.p. (°C)	Λ_M [a]	Analytical data (found (calc.) (%))			Yield (%)
			C	H	Au	
$[AuCl\{CH(PPh_3)C(O)CH_3\}]$ (**1**)	154	8	45.67 (45.79)	3.62 (3.48)	35.27 (35.76)	97
$[AuCl\{CH(PPh_3)C(O)Ph\}]$ (**2**)	239	–	50.42 (50.90)	3.82 (3.45)	32.19 (32.16)	90
$[AuCl_3\{CH(PPh_3)C(O)CH_3\}]$ (**3**)	120	1	40.99 (40.57)	3.31 (3.08)	32.05 (31.68)	83
$[AuCl_3\{CH(PPh_3)C(O)Ph\}]$ (**4**)	147	0	45.35 (45.65)	3.11 (3.07)	29.04 (28.81)	90
$[Au\{CH(PPh_3)C(O)CH_3\}_2]ClO_4$ (**5**)	128	104	53.83 (54.06)	4.33 (4.10)	20.93 (21.11)	91
$[Au\{CH(PPh_3)C(O)Ph\}_2]ClO_4$ (**6**)	146	95	58.72 (59.07)	4.14 (4.00)	17.92 (18.63)	79
$[AuCl_2\{CH(PPh_3)C(O)CH_3\}_2]ClO_4$ (**7**)	130	98	49.67 (50.24)	3.80 (3.81)	20.32 (19.62)	73
$[Au\{CH(PPh_3)C(O)CH_3\}(PPh_3)]ClO_4$ (**8**)	125	115	53.77 (53.41)	3.91 (3.91)	22.01 (22.46)	74
$[Au\{CH(PPh_3)C(O)Ph\}(PPh_3)]ClO_4$ (**9**)	129	87	56.87 (56.31)	4.01 (3.84)	21.20 (20.99)	83
$[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)C(O)CH_3\}]ClO_4$ (**10**)	214	97	50.79 (51.27)	3.66 (3.62)	29.29 (29.50)	84
$[\{Au(PPh_3)\}_2\{\mu\text{-}C(PPh_3)C(O)Ph\}]ClO_4$ (**11**)	216	93	53.09 (53.29)	3.79 (3.61)	27.95 (28.19)	85
$[\{Au(AsPh_3)\}_2\{\mu\text{-}\{C(PPh_3)C(O)CH_3\}]ClO_4$ (**12**)	130	109	47.88 (48.10)	3.34 (3.40)	28.19 (27.68)	74
$[Au\{C(PPh_3)(AuPPh_3)C(O)OMe\}_2]ClO_4$ (**13**)	127	141	50.20 (49.80)	3.80 (3.55)	31.85 (31.40)	66
$[Au\{C(PPh_3)(AuPPh_3)C(O)OEt\}_2]ClO_4$ (**14**)	100	97	51.03 (50.30)	4.00 (3.69)	30.79 (30.94)	69

[a] In $\approx 10^{-4}$ M solutions in acetone (Ω^{-1} cm^2 mol^{-1}).

IR and NMR spectra

When the ylides became coordinated in complexes **1–14**, their ν(CO) bands shift between 105 and 170 cm^{-1} to higher wavenumbers. This means that in all the complexes the bonding is through the C atom of the ligand. When the three main resonance forms **a–c** of these ylides are considered, it can be seen that coordination through the oxygen atom would give a negative value of $\Delta\nu$ ($= \nu(CO)_{complex} - \nu(CO)_{ylide}$), while coordination through the C atom should give a $\Delta\nu > 0$, as is observed.

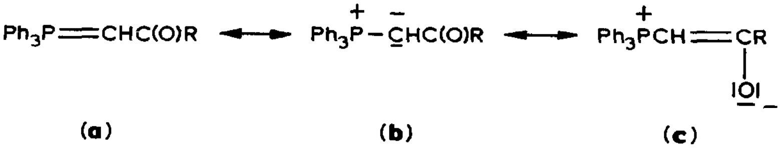


Table 2 shows ν(CO) for complexes **1–10** and their analogues with R^1 = OMe, OEt [3] along with the values for the corresponding ylides {R^2 = O) and phos-

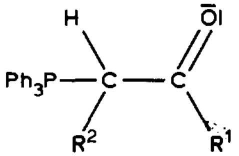
Table 2

ν(CO) (cm^{-1}) for complexes **1–9** and related species

R^1		OMe	OEt	Me	Ph
$\delta(R^1)/\delta_1(0)$ (cm^{-1})		60/−50	55/−60	30/−110	0/−120
$\delta(R^2)$ (cm^{-1})	R^2	ν(CO) (Found (calcd.))			
	Ylides (Y) [a]	1620	1610	1540	1500
	0	(1630)	(1615)	(1540)	(1500)
50	H^+	1720	1715	1710	1665
		(1730)	(1725)	(1700)	(1670)
45	$AuCl_3$	1720	1710	1700	1665
		(1725)	(1720)	(1695)	(1665)
30	$AuCl_2Y^+$	1705	1710	1680	–
		(1710)	(1705)	(1680)	
10	$AuPPh_3{}^+$	1690	1685	1655	1635
		(1690)	(1685)	(1660)	(1630)
5	AuY^+	1680	1680	1650	1630
		(1685)	(1680)	(1655)	(1625)
0	AuCl	1690	1685	1645	1620
		(1680)	(1675)	(1650)	(1620)

[a] Y = ylide.

phonium salts ($R^2 = H^+$). The electron-withdrawing ability of R^1 and R^2 seem to act additively upon ν(CO), and their influence can be represented by $\nu(CO) = \nu_0 + \delta(R^1) + \delta(R^2)$. If δ(Ph) and δ(AuCl) are given in a value of zero, $\delta(R^1)$ and $\delta(R^2)$ measure the increase in ν(CO) due to the greater electron-withdrawing ability of R^1 and R^2 with respect to Ph and AuCl. The values of ν(CO) for the ylides can be calculated in a similar manner by replacing $\delta(R^2)$ by $\delta_1(0)$, which depends on the nature of R^1. As these values are negative they indicate how much of the electron density of the lone pair is transferred to the antibonding CO molecular orbitals, and should be more negative for the less basic ylides. The calculated δ(R) parameters give values of ν(CO) that are within ±10 cm^{-1} of those observed. This enables us to propose sequences for (1) the electron-withdrawing character of the R^2 groups, viz. $H^+ > AuCl_3 > AuCl_2(\text{ylide})^+ > AuPPh_3^+ > Au(\text{ylide})^+ > AuCl$ and (2) the basic character of the ylides $Ph_3PCHC(O)R$, viz. R_i = OMe > OEt > Me > Ph. This last sequence is also that of the ν(CO) frequencies in the ylides. The reverse order for the acidic character of some of these phosphonium salts has been confirmed by measuring their pK_a's (R^1 = OEt ($pK_a = 9.2$), Ph ($pK_a = 6$)) [8].



The formulation of the reported complex $[Au\{CH(PPh_3)C(O)Ph\}_2][AuCl_4]$ [9] has been questioned [2,3]. If the stoichiometry is correct, we think the complex should be reformulated as $[AuCl_2\{CH(PPh_3)C(O)Ph\}_2][AuCl_2]$, since in this case the calculated ν(CO) value (1650 cm^{-1}) is near that observed (1660 cm^{-1}), which is too high for a gold(I)-ylide complex. If the original formulations were correct the value of ν(CO) should be 1630 cm^{-1} as found in complex **6**. Its reported white colour could be due to the *cis* geometry of the cation, because all known *trans*-$[AuCl_2(ylide)_2]^+$ [3], and also **7**, are pale yellow. Such a change in colour on going from a *trans*- to a *cis*-dichlorogold(III) complex has been observed previously [10]. The reported ν(AuCl) absorption at 350 cm^{-1}, which should include the ν(AuCl) absorptions of the anion and the cation is, as expected, lower than those for the *trans* complex **7** (see below).

As the substitution of H^+ by $AuPPh_3{}^+$ leads to a decrease in ν(CO), it is reasonable to expect a further decrease on going from complexes **8**–**9** to the dinuclear complexes **10**–**12** (ν(CO): (**10**), 1605; (**11**), 1550; (**12**), 1604 cm^{-1}), and also from $[Au(ylide)_2]^+$ (1680 cm^{-1}) [3] to the trinuclear **13** and **14** complexes (1630 cm^{-1}).

Complexes **1** and **2** each shows a strong band, at 330 and 340 cm^{-1} respectively, assignable to ν(AuCl), while **3** and **4** each show three bands, at 315(vs), 345(m), 370(vs) cm^{-1} and 310(s), 335(w), 360(s) cm^{-1}, respectively, assignable to ν(AuCl) *trans* to the ylide and ν_{sym}- and ν_{asym}(ClAuCl). The presence in **7** of two medium bands at 350 and 370 cm^{-1} indicates that it has a *trans* geometry.

Because of the insolubility of **2** the only technique available for it was IR spectroscopy, but this did not enable us to propose a structure. Both ν(AuCl) and ν(CO) could correspond to formulations such as [AuCl(L)] or $[AuL_2][AuCl_2]$ ($L = Ph_3PCHC(O)Ph$). The complex reacts with PPh_3 to give $[AuCl(PPh_3)]$, and it can also be prepared by treating $PhCH_2PPh_3[AuCl_2]$ and $[AuL_2]ClO_4$. In both cases metal–metal interactions or halogen bridging could lead to a polymeric structure which could account for its extreme insolubility. However halogen bridging seem to be less likely, because ν(AuCl) appears at a position (340 cm^{-1}) where the absorption due to terminal Au–Cl bond is usually found. It is likely that in **2** an infinite chain is formed through Au...Au interactions, as observed in $[\{Au(tht)_2\}(AuI_2)]_\infty$ [11].

The available ^1H NMR spectra of some of the acetyl derivatives ($R^1 = CH_3$) show signals corresponding to the methine proton in an intermediate position between those corresponding to the free ylide (doublet (d), 3.69 ppm, ^2J(PH) 27 Hz) [12] and the phosphonium salt ((d), 6.14 ppm, ^2J(PH) 11 Hz), as previously observed for the related gold complexes with R^1 = OMe, OEt [3]. However while in **8** the signal is a doublet (5.30 ppm, ^2J(PH) 10 Hz), in **1** (4.45 ppm) and **5** the ^2J(PH) coupling is not observed, as is the case also for $[PdCl(C_6F_5)(tht)\{CH(PPh_3)COCH_3\}]$ [13].

In complex **5** there are two chiral carbon atoms, and so the ^1H NMR spectrum shows signals corresponding to both diastereoisomers (*RR* or *SS*, and *RS*) ($\delta(CH_3)$ 1.82, 2.06 ppm (2/1) and δ(CH) 4.40, 4.48 ppm (1/2)]. With complex **8**, while the ^3J(PH) (CH–Au–PPh_3) coupling is not clearly observed (both signals of the methine doublet are broad), ^4J(PH) (CH_3–CO–CH–PPh_3) coupling is seen (3 Hz); the ^4J value is similar to that for the free ylide (^4J(PH) 1.8 Hz) [9]. Similar behaviour is observed for complexes **10** and **12** ($\delta(CH_3)$ 2.63 ppm, d, ^4J(PH) 3 Hz, for both) while in **1** ^4J(PH) 0 ($\delta(CH_3)$ 2.34 ppm).

Experimental

The procedure for recording NMR and infrared spectra, and carrying out the C, H and N analyses, conductance measurements, melting point determinations and

NMR have been described elsewhere [3]. Reactions were carried out at room temperature with magnetic stirring and without special precautions against light or atmospheric moisture unless otherwise stated.

The numbers in parentheses refer to the compounds to which the solvent, the amount, or the reaction conditions apply.

[AuCl{CH(PPh$_3$)C(O)R}] (R = CH$_3$ (1); R = Ph (2)). To a suspension of [AuCl(tht)] (200 mg, 0.62 mmol **1**; 84 mg, 0.26 mmol **2**) in 10 cm^3 of acetone (**1**) or dichloromethane (**2**) the stoichiometric amount of the ylide [14] was added. After 30 min, in the case of **1** the solution was concentrated (2 cm^3) and diethyl ether (10 cm^3) added to precipitate **1** which was recrystallized from dichloromethane/diethyl ether. In the case of **2** the suspension was filtered after 1 h and the solid obtained was washed with acetone and diethyl ether and shown to be **2**.

[AuCl$_3${CH(PPh$_3$)C(O)R}] (R = CH$_3$ (3); R = Ph (4)). To a suspension of **1** (100 mg, 0.16 mmol) in acetone (3 cm^3) or to a suspension of **2** (100 mg, 0.18 mmol) in acetonitrile (4 cm^3) was added a 3 mol/dm^3 solution (1 cm^3) of Cl_2 in CCl_4. After 15 min diethyl ether (20 cm^3) was added, and the resulting suspension was either cooled (5–10 °C) to give **3**, or, after 30 min was diluted with n-hexane (20 cm^3) to give an oil, which after stirring for 15 min gave **4**, which was washed with diethyl ether. Attempts to recrystallize **4** from acetone-n-hexane or dichloromethane/n-hexane led to decomposition. This complex also decomposes slowly in the presence of atmospheric oxygen and moisture but it can be kept for a long time under nitrogen.

[Au{CH(PPh$_3$)C(O)R}$_2$]ClO$_4$ (R = Me (5), R = Ph (6)). To a suspension of [AuCl(tht)] (100 mg, 0.31 mmol **1**; 84 mg, 0.26 mmol **2**) in acetone (10 cm^3) were added the appropriate ylide, and $NaClO_4 \cdot H_2O$ in the molar ratio 1/2/1. After 3 h the solvent was evaporated and the residue shaken with dichloromethane (10 cm^3); the suspension was filtered and the filtrate concentrated to 2 cm^3. Addition of diethyl ether (15 cm^3) precipitated **5** or **6**.

[AuCl$_2${CH(PPh$_3$)C(O)CH$_3$}$_2$]ClO$_4$ (7). To a solution of **5** (100 mg, 0.11 mmol) in acetone (1 cm^3) was added a 3 mol/dm^3 solution (1 cm^3) of Cl_2 in CCl_4 to produce a yellow crystalline precipitate. After 15 min diethyl ether (20 cm^3) was added, the suspension was filtered and the solid obtained was washed with ethanol (3 × 3 cm^3) and diethyl ether (5 cm^3) to give **7**.

[Au{CH(PPh$_3$)C(O)CH$_3$}(PPh$_3$)]ClO$_4$ (8). To a solution of [Ph$_3$PCH$_2$C(O)CH$_3$]ClO$_4$ (80 mg, 0.19 mmol) in acetone (7 cm^3) was added solid [Au(acac)(PPh$_3$)] (107 mg, 0.19 mmol). After 2 h the suspension was filtered through Celite, and the resulting solution concentrated (to 1 cm^3). Addition of diethyl ether (15 cm^3) gave a suspension, this was filtered and the solid obtained was washed with diethyl ether and recrystallized from acetone/diethyl ether to give **8**.

[Au{CH(PPh$_3$)C(O)Ph}(PPh$_3$)]ClO$_4$ (9). To a suspension of [Ag{CH(PPh$_3$)C(O)Ph}$_2$]ClO$_4$ (100 mg, 0.10 mmol) in acetone (5 cm^3) protected from light, was added solid [AuCl(PPh$_3$)] (51 mg, 0.10 mmol). After 6 h the suspension was filtered and the filtrate concentrated to 1 cm^3; diethyl ether was added to precipitate a solid, which was washed with diethyl ether and recrystallized from dichloromethane/diethyl ether to give **9**.

[{Au(EPh$_3$)}$_2${μ-C(PPh$_3$)C(O)R}]ClO$_4$ (E = P, R = Me (10), E = P, R = Ph (11); E = As, R = Me (12)). To a solution of [Ph$_3$PCH$_2$C(O)R]ClO$_4$ (51 mg, 0.12 mmol **10**); 45 mg, 0.09 mmol **11**; 33 mg, 0.08 mmol **12**) in acetone (20 cm^3) was added

solid [Au(acac)(EPh_3)] (138 mg, 0.25 mmol **10**; 125 mg, 0.22 mmol **11**; 143 mg. 0.24 mmol **12**). After 14 h the suspension was filtered and the filtrate was concentrated (to 1 cm^3); diethyl ether was added (20 cm^3) to precipitate a solid, which was recrystallized from dichloromethane/diethyl ether to give complexes **10–12**.

[Au{C(PPh$_3$)(AuPPh$_3$)C(O)R}$_2$]ClO$_4$ (R = OMe (13), R = OEt (14)). To a solution of [Au{CH(PPh_3)CO_2R}$_2$]ClO_4 (78 mg, 0.08 mmol **13**; 61 mg, 0.06 mmol **14**) in acetone (15 cm^3) was added solid [Au(acac)(PPh_3)] (90 mg, 0.16 mmol **13**; 68 mg, 0.12 mmol **14**). After 1.5 h at −5 °C under a N_2 atmosphere the suspension was filtered, and the filtrate concentrated (to 2 cm^3); diethyl ether (15 cm^3) was added to precipitate a solid, which was recrystallized from acetone/diethyl ether to give **13**, **14**.

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