Synthesis and Structural Characterization of Gold-(I), -(III) and Silver(I) Complexes of the Ylide Ligand $Ph_3P{=}CHC(O)NMe_2$. Crystal Structure of $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)C(O)NMe_2\}]ClO_4$†

José Vicente,*[a] **María-Teresa Chicote,**[a] **María-Cristina Lagunas**[a] **and Peter G. Jones**[b]

[a] *Departamento de Química Inorgánica, Grupo de Química Organometálica, Facultad de Ciencias Químicas, Universidad de Murcia, 30171 Espinardo, Murcia, Spain*

[b] *Institut für Anorganische und Analytische Chemie der Technischen Universität, Hagenring 30, 3300 Braunschweig, Germany*

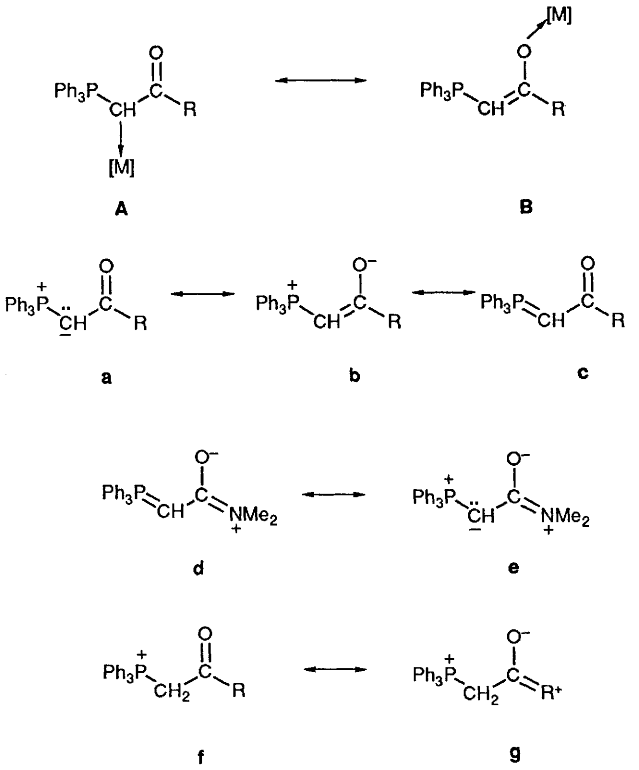
The reaction between [AuCl(tht)] (tht = tetrahydrothiophene) and the ylide $Ph_3P{=}CHC(O)NMe_2$ gives $[AuCl\{CH(PPh_3)C(O)NMe_2\}]$ **1**, which reacts with chlorine to give $[AuCl_3\{CH(PPh_3)C(O)NMe_2\}]$ **2** and with the same ylide and $NaClO_4$ to form $[Au\{CH(PPh_3)C(O)NMe_2\}_2]ClO_4$ **3**. The analogous silver complex $[Ag\{CH(PPh_3)C(O)NMe_2\}_2]ClO_4$ **4** is obtained by the reaction of $AgClO_4$ with the ylide in molar ratio 1:2. The phosphonium salt $[Ph_3PCH_2C(O)NMe_2]ClO_4$ reacts with $[Au(acac)(PPh_3)]$ (acac = acetylacetonate) to give $[Au\{CH(PPh_3)C(O)NMe_2\}(PPh_3)]ClO_4$ **5** or $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)C(O)NMe_2\}]ClO_4$ **6** depending on the reaction conditions. The structure of **6** was confirmed by an X-ray diffraction study at −95 °C [space group $P\bar{1}$, $a = 11.572(3)$, $b = 11.836(3)$, $c = 21.627(7)$ Å, $\alpha = 78.29(2)$, $\beta = 87.19(2)$, $\gamma = 75.65(2)°$, $R = 0.076$]; the Au$\cdots$Au bond length is 2.938(1) Å.

The ylide $Ph_3P{=}CHC(O)NMe_2$ has been found to be a useful intermediate for preparation of morphine and codeine analogues.[1] Carbonyl-stabilized phosphorus ylides are very versatile ligands for three reasons: because of their alternative modes of co-ordination, **A**[2] and **B**;[3] because they give stable complexes in spite of their low nucleophilicity [arising from electron delocalization through resonance forms **a**–**c** (see Scheme 1)]; and finally because they allow the synthesis of unusual types of complexes.[4–6]

In this paper we report the ligand properties of the carbonyl-stabilized ylide $Ph_3P{=}CHC(O)NMe_2$ (of which, as far as we are aware, there was previously no known complex), in terms of the synthesis and structural characterization of some gold(I), gold(III) and silver(I) derivatives, and the X-ray crystal structure of a dinuclear gold(I) complex. This ligand might be expected to display a richer co-ordination chemistry than 'simple' carbonyl ylides because of the lone pair at nitrogen, and also to show a different reactivity associated with the two new resonance forms **d** and **e** (see Scheme 1).

Results and Discussion

Synthesis.—Since carbonyl-stabilized ylides are weak bases they are unable to displace many ligands that are readily substituted by more basic ylides (such as halide, phosphines).[7] However, labile ligands such as tetrahydrothiophene (tht) or ClO_4^- in $[AuCl(tht)]$[7] or $AgClO_4$,[8] respectively, can easily be replaced. Thus, [AuCl(tht)] reacts with $Ph_3P{=}CHC(O)NMe_2$ (1:1) in dichloromethane to give $[AuCl\{CH(PPh_3)C(O)NMe_2\}]$ **1**. The solvent needs to be carefully degassed because



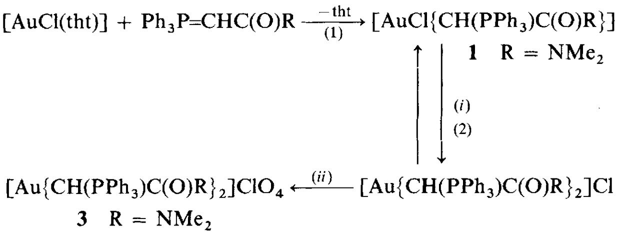
Scheme 1

---

† μ-(Dimethylcarbamoyl)(triphenylphosphoranylidene)methyl-κ^2C-bis[(triphenylphosphine)gold(I)] perchlorate.

Supplementary data available: Further details of the structure determination (H-atom coordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, W-7514 Eggenstein-Leopoldshafen 2, FRG. Any request for this material should quote a full literature citation and the reference number CSD 55310 otherwise trace amounts of HCl, usually present in chlorinated solvents, produce $[Ph_3PCH_2C(O)NMe_2]Cl$, which is difficult to separate from **1**. When a concentrated solution of compound **1** in dichloromethane reacts with excess of chlorine, $[AuCl_3\{CH(PPh_3)C(O)NMe_2\}]$ **2** separates as a yellow solid. The excess of Cl_2 does not affect the complex, in contrast to the ability of unco-ordinated ylides to react with chlorine giving chlorophosphonium salts.[9]

If the reaction between [AuCl(tht)] and $Ph_3P{=}CHC(O)NMe_2$ is carried out in the presence of excess of ylide, partial replacement of the chloride ligand takes place and small amounts of $[Au\{CH(PPh_3)C(O)NMe_2\}_2]Cl$ are obtained along with **1**. This behaviour shows that the ylide is more basic than the carbonyl-stabilized ylides already studied [*viz.* $Ph_3P{=}CHC(O)R$; R = OMe, OEt,[7] Me, or Ph[10]]. Thus, these latter ylides replace tht [equation (1) in Scheme 2] but not chloride from [AuCl(tht)] [equation (2)], even in excess.

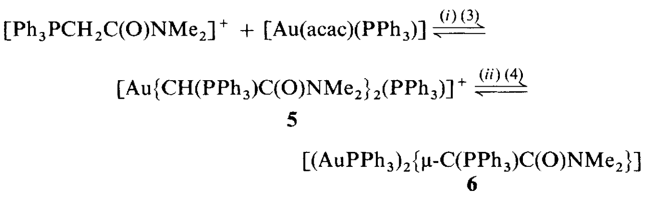


(*i*) $+Ph_3P{=}CHC(O)R$; (*ii*) $+NaClO_4$, $-NaCl$

Scheme 2

The cationic species $[Au\{CH(PPh_3)C(O)NMe_2\}_2]Cl$ is unstable and could not be isolated pure. However, if [AuCl(tht)] and $Ph_3P{=}CHC(O)NMe_2$ react in acetone in molar ratio 1:2, in the presence of $NaClO_4$, the cationic complex $[Au\{CH(PPh_3)C(O)NMe_2\}_2]ClO_4$ **3** is obtained. The analogous silver complex, $[Ag\{CH(PPh_3)C(O)NMe_2\}_2]ClO_4$ **4** is obtained in high yield from the reaction between $AgClO_4$ and the ylide (1:2) in diethyl ether, in which both reagents are soluble but the product insoluble.

The phosphonium salt $[Ph_3PCH_2C(O)NMe_2]ClO_4$ is the conjugate acid of the ylide and can therefore be used in an acid–base reaction to prepare the cationic complex $[Au\{CH(PPh_3)C(O)NMe_2\}(PPh_3)]ClO_4$ **5** by reaction with $[Au(acac)(PPh_3)]$ (acac = acetylacetonate) (Scheme 3). The methine proton in **5**



(*i*) −Hacac; (*ii*) + $[Au(acac)(PPh_3)]$

Scheme 3

is still acidic enough to react further with $[Au(acac)(PPh_3)]$ to give the dinuclear complex $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)C(O)NMe_2\}]ClO_4$ **6**. The extent to which the acid–base equilibria (3) and (4) occur (Scheme 3) also shows that $Ph_3P{=}CHC(O)NMe_2$ is more basic than 'simple' carbonyl ylides. Thus the phosphonium salts corresponding to the simple ylides are more acidic than $[Ph_3PCH_2C(O)NMe_2]^+$ [and their conjugate bases, the ylides, less basic than $Ph_3P{=}CHC(O)NMe_2$] because the former react with $[Au(acac)(PPh_3)]$ in molar ratio 1:1 or 1:2 to give complexes analogous to **5** or **6**, respectively, whereas in the present case the 1:1 reaction gives a mixture of **5** and the reagents. Complex **5** is obtained pure in good yield only when the ratio $[Ph_3PCH_2C(O)NMe_2]^+$:$[Au(acac)(PPh_3)]$ is 1:2, and the synthesis of **6** requires a molar ratio of 1:5. Moreover, Ag_2CO_3 does not react with $[Ph_3PCH_2C(O)NMe_2]^+$, whereas it does react with the more acidic $[Ph_2P(CH_2CO_2R)_2]^+$ (R = Me or Et) to give silver ylide complexes.[11]

Structure, Bonding, and Spectroscopic Data.—The IR spectrum of the phosphonium salt $[Ph_3PCH_2C(O)NMe_2]^+$ shows the ν(CO) band at 1640 cm^{-1}, 15–80 cm^{-1} lower than for other phosphonium salts in which resonance form **g** does not contribute significantly (R = OEt, OMe, Me or Ph). The inequivalence of the Me groups in its ^1H NMR spectrum also points to the importance of the form **g**.

Among the five important resonance forms of the ylide, contributions from **b**, **d** and **e** cause the corresponding ν(CO) band to appear at 1530 cm^{-1}, shifted 110 cm^{-1} from the parent phosphonium salt. Two potential contributions to the electron density of the π* orbitals of the C=O system have to be considered, namely from the Ph_3PCH moiety and from the dimethylamino group. The equivalence of the methyl protons in the ^1H NMR spectrum of the ylide indicates that the π(CN) bond order is small enough to allow rotation of the NMe_2 group, and the main electron donation thus comes from the ylide system. Resonance form **b** thus seems to be the most important.

The above argument indicates the possibility of obtaining complexes of the ylide through the lone pair at nitrogen. In addition, the ylide could co-ordinate to a metal centre through the carbon (of CH) or the oxygen atom. In order to determine the donor atom in complexes **1**–**6** it must be kept in mind that all of them show the ν(CO) mode shifted to higher frequency than that of the ylide and display inequivalent Me groups in their ^1H NMR spectra. If co-ordination were through the oxygen atom, three main resonance forms, derived from the **b**, **d** and **e** forms of the ylide, could be formulated for the metal–ligand system, thus shifting ν(CO) to lower wavenumber. Co-ordination through the nitrogen atom would make both Me groups equivalent. We thus conclude that co-ordination must be through the carbon atom; this has been confirmed for complex **6** by an X-ray diffraction study.

Three other factors support, directly or indirectly, the co-ordination through the carbon atom: (*a*) the great number of stable organogold complexes,[12] whereas those containing N- or O-donor ligands are scarce and of limited stability;[13] (*b*) the position of the ν(AuCl) band, which is very sensitive to the nature of the *trans* ligand [in complexes **1** and **2**, bands assignable to ν(AuCl) (see below) appear at frequencies similar to those of other chloroylide complexes in which co-ordination through the carbon atom is well established];[2,5,7,8] and (*c*) the ^1H NMR spectrum of compound **5** shows a doublet of doublets corresponding to the methyne proton coupled with two different ^{31}P nuclei, whereas its $^{31}P\text{-}\{^1H\}$ NMR spectrum shows an AB system.

The ν(CO) band of the silver complex **4** appears at lower frequency than for the related gold complex **3**, as has previously been observed.[8] However, the expected shift to higher wavenumber (by 30–55 cm^{-1}) of the ν(CO) band on going from complex **1** to **2**, arising from the greater electronegativity of the gold(III) centre in **2**,[10] is not observed (see Table 1). The reason could be the presence of the lone pair on the nitrogen atom, which could act as an electronic buffer on the electron density of the C=O system.

The ν(AuCl) band of complex **1** lies at 310 cm^{-1} whilst **2** shows bands at 310, 335 and 355 cm^{-1}, assignable to ν(AuCl) *trans* to the ylide and ν_{sym} and ν_{asym}(ClAuCl), respectively.[10]

NMR data are presented in Table 2. All the ylidic carbon atoms are chiral; where two such ligands are present the expected double signals are observed. The spectrum of compound **4** is similar of that of its gold analogue but the peaks are wider, as observed for similar silver complexes.[8]

Crystal Structure of Compound **6**.—The structure determination (Fig. 1, Tables 3 and 4) confirms the expected nature of

Table 1 Proton and ^{31}P NMR data

Compound	^{1}H CH	 CH_2	 Me	^{31}P
$Ph_3P{=}CHC(O)NMe_2$	2.96(s)		2.92 (s)	17.2 (s)
$[Ph_3PCH_2C(O)NMe_2]Cl$		5.54 (d, $^2J_{PH}$ = 12.8)	2.69 (s), 3.25 (s)	21.7 (s)
$[Ph_3PCH_2C(O)NMe_2]ClO_4$		4.79 (d, $^2J_{PH}$ = 12.9)	2.82 (s), 3.16 (s)	21.3 (s)
$[AuCl\{CH(PPh_3)C(O)NMe_2\}]$ **1**	3.89 (d, $^2J_{PH}$ = 4.5)		2.80 (s), 3.22 (s)	26.6 (s)
$[AuCl_3\{CH(PPh_3)C(O)NMe_2\}]$ **2**	5.62 (d, $^2J_{PH}$ = 8)		2.91 (s), 3.41 (s)	28.5 (s)
$[Au\{CH(PPh_3)C(O)NMe_2\}_2]ClO_4$ **3**	3.89 (d, $^2J_{PH}$ = 4.2)		2.64 (s), 2.71 (s)	26.4 (d),
	3.67 (d, $^2J_{PH}$ = 4.7)		2.77 (s), 2.83 (s)	27.7 (d)
$[Ag\{CH(PPh_3)C(O)NMe_2\}_2]ClO_4$ **4**	3.78 (br s)		2.72 (s), 2.59 (br s)	25.4 (br s)
$[Au\{CH(PPh_3)C(O)NMe_2\}(PPh_3)]ClO_4$ **5**	4.40 (dd, $^2J_{PH}$ = 8.6, $^3J_{PH}$ = 6)		2.95 (s), 3.43 (s)	27.8 (d), 39.7 (d)
$[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)C(O)NMe_2\}]ClO_4$ **6**			3.36 (br s)	38.1 (t), 31.8 (d) (J_{PP} = 2.4)

In $CDCl_3$, δ, J in Hz. Reference $SiMe_4$. The Ph protons appear for all compounds as multiplets between δ 7 and 8.

Table 2 Analytical and other data for complexes **1**–**6**

Complex	M.p. (°C)	Λ_M[a]	Analysis (%)[b] C	 H	 N	 Au	Yield (%)	ν(CO)/cm^{-1}
1 $[AuCl\{CH(PPh_3)C(O)NMe_2\}]$	194 (decomp)	2	46.3	4.2	2.6	33.8	63	1605
			(45.6)	(3.8)	(2.4)	(33.9)		
2 $[AuCl_3\{CH(PPh_3)C(O)NMe_2\}]$	147	6	40.7	3.2	2.2	29.9	83	1610
			(40.6)	(3.4)	(2.2)	(30.3)		
3 $[Au\{CH(PPh_3)C(O)NMe_2\}_2]ClO_4$	137	133	53.6	4.8	3.1	20.7	61	1600
			(53.3)	(4.5)	(2.8)	(19.8)		
4 $[Ag\{CH(PPh_3)C(O)NMe_2\}_2]ClO_4$	138	133	57.9	5.3	3.0		91	1580
			(58.6)	(4.9)	(3.1)			
5 $[Au\{CH(PPh_3)C(O)NMe_2\}(PPh_3)]ClO_4$	192	108	52.9	4.3	1.8	22.5	82	1600
			(53.0)	(4.1)	(1.5)	(21.7)		
6 $[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)C(O)NMe_2\}]ClO_4$	235 (decomp)	113	51.4	4.1	1.3	28.4	78	1550
			(51.1)	(3.8)	(1.0)	(28.9)		

[a] In Ω^{-1} cm^2 mol^{-1}, on 10^{-4} M acetone solutions. [b] Calculated values in parentheses.

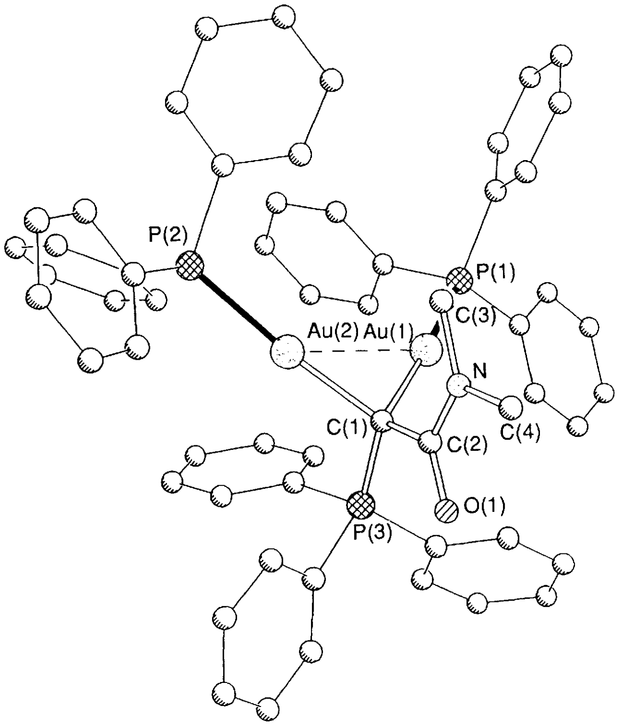


Fig. 1 The cation of complex **6** in the crystal. Radii are arbitrary; H atoms omitted

compound **6**, although the moderate precision precludes detailed discussion of molecular dimensions. The general features of the (ylide)Au_2 centre are similar to those in $[(AuPPh_3)_2\{C(PPh_3)C(O)OEt\}]^+$,[7] for which the values are given in square brackets in the following. The geometry at gold is slightly distorted from linearity, with P–Au–C 173.4(4), 174.9(4)° [178.2, 170.7(4)°], and Au–C bond lengths 2.136(16), 2.077(17) Å [2.105(10), 2.123(9) Å]. The Au(1)$\cdots$Au(2) contact is 2.938(1) Å [2.892(1) Å], a typical value for formally non-bonded contacts in a variety of gold(I) complexes.[14] We previously proposed[7] a three-centre (CAu_2) bonding component for (ylide)Au_2 centres on the basis of the narrow Au(1)–C(1)–Au(2) angle 88.4(7)° [86.3(4)°], the slightly shortened P(3)–C(1) bond {the shortening is less pronounced in **6**, at 1.783(14) Å [1.763(10) Å]}, and the wide P(3)–C(1)–C(2) angle {however the latter is in fact narrower than ideal sp^3 in **6**, at 106.8(12)° [112.3(7)°]}. The geometry at C(2) is essentially planar (sum of angles 360.0°), and the C=O bond is not lengthened [1.23(3) Å] despite the presence of a single bond between C(2) and O(1) in some resonance forms; this was also the case in other (ylide)Au_2 systems.[7] The C(2)–N bond length 1.39(2) Å is normal for amides,[15] in which some contribution from a C=N resonance form is usually postulated.

Experimental

Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets. Conductivities were measured with a Philips PW9501 conductimeter. Melting points were determined on a Reichert apparatus and are uncorrected. The C, H and N analyses were carried out with a Perkin-Elmer 240C microanalyzer; Au was determined by ashing the samples with an aqueous solution of hydrazine. Proton NMR spectra were

Table 3 Atomic coordinates (× 10^4) for compound **6**

Atom	*x*	*y*	*z*
Au(1)	6 440.4(5)	6 600.2(5)	2 121.2(3)
Au(2)	5 344.8(5)	4 832.3(5)	2 924.9(3)
P(1)	6 862(4)	6 914(4)	1 065(2)
P(2)	4 293(4)	3 567(4)	2 689(2)
P(3)	7 603(4)	5 434(4)	3 457(2)
C(1)	6 166(13)	6 101(12)	3 113(8)
C(2)	5 584(15)	7 045(14)	3 461(9)
C(3)	3 737(18)	7 596(17)	2 783(11)
C(4)	3 888(18)	8 653(17)	3 655(11)
N	4 440(12)	7 729(12)	3 299(8)
O(1)	6 066(11)	7 221(10)	3 916(6)
C(11)	7 306(8)	5 467(9)	842(6)
C(12)	8 507	4 886	810
C(13)	8 826	3 738	685
C(14)	7 944	3 172	592
C(15)	6 743	3 753	623
C(16)	6 424	4 901	749
C(21)	5 644(8)	7 744(9)	519(5)
C(22)	5 744	7 704	−122
C(23)	4 848	8 407	−541
C(24)	3 853	9 150	−319
C(25)	3 753	9 190	322
C(26)	4 649	8 487	741
C(31)	8 093(9)	7 620(9)	876(4)
C(32)	8 718	7 774	1 375
C(33)	9 685	8 292	1 254
C(34)	10 027	8 657	632
C(35)	9 402	8 503	133
C(36)	8 435	7 984	255
C(41)	3 319(10)	4 232(7)	1 997(6)
C(42)	2 733	3 604	1 690
C(43)	1 981	4 203	1 180
C(44)	1 815	5 429	978
C(45)	2 400	6 056	1 285
C(46)	3 152	5 458	1 795
C(51)	3 326(12)	3 184(12)	3 330(6)
C(52)	2 313	2 787	3 253
C(53)	1 596	2 513	3 771
C(54)	1 892	2 636	4 368
C(55)	2 905	3 033	4 445
C(56)	3 622	3 306	3 927
C(61)	5 202(8)	2 199(10)	2 483(6)
C(62)	4 760	1 187	2 546
C(63)	5 448	174	2 351
C(64)	6 577	175	2 093
C(65)	7 018	1 187	2 031
C(66)	6 330	2 200	2 225
C(71)	7 581(8)	4 836(11)	4 301(6)
C(72)	8 621	4 568	4 657
C(73)	8 633	4 003	5 290
C(74)	7 605	3 708	5 567
C(75)	6 565	3 977	5 210
C(76)	6 553	4 541	4 577
C(81)	8 251(10)	4 101(8)	3 132(5)
C(82)	8 870	4 147	2 561
C(83)	9 372	3 102	2 342
C(84)	9 254	2 010	2 694
C(85)	8 635	1 964	3 265
C(86)	8 134	3 009	3 484
C(91)	8 705(10)	6 317(7)	3 295(7)
C(92)	9 909	5 774	3 231
C(93)	10 730	6 470	3 059
C(94)	10 347	7 707	2 951
C(95)	9 143	8 250	3 015
C(96)	8 322	7 555	3 187
Cl(1)	1 756(5)	460(4)	1 699(3)
O(2)	1 905(12)	510(14)	2 340(7)
O(3)	2 044(13)	−689(12)	1 596(8)
O(4)	2 449(29)	1 123(20)	1 293(11)
O(5)	540(20)	993(20)	1 520(11)
C(100)	5 480(87)	996(81)	4 036(50)
Cl(2)	6 988(27)	−154(25)	3 994(15)
Cl(3A)	6 199(37)	1 427(38)	4 588(23)
Cl(3B)	5 980(48)	257(52)	5 017(31)

recorded on a Bruker AC-200 spectrometer and phosphorus NMR spectra on a Varian FT-80 spectrometer.

All reactions were carried out at room temperature with magnetic stirring. The gold(I) and silver complexes are colourless and the gold(III) complex is pale yellow.

$[Ph_3PCH_2C(O)NMe_2]Cl$.—A solution of PPh_3 (2.494 g, 9.5 mmol) and $ClCH_2C(O)NMe_2$ (1 cm^3, 9.5 mmol) in chloroform (6 cm^3) was refluxed for 3 h, then concentrated (to 4 cm^3) and poured into diethyl ether (100 cm^3). The product $[Ph_3PCH_2C(O)NMe_2]Cl$ was obtained as an oily material, which was stirred with diethyl ether (2 × 15 cm^3) until it became a white solid in 83% yield, m.p. 218 °C. [Found (Calc.): C, 67.20 (68.85); H, 6.40 (6.05); N, 3.90 (3.65%)].

$[Ph_3PCH_2C(O)NMe_2]ClO_4$.—To a suspension of $[Ph_3PCH_2C(O)NMe_2]Cl$ (100 mg, 0.26 mmol) in acetone (15 cm^3) was added $NaClO_4$ (60 mg, 0.43 mmol). The suspension was stirred for 2 h and the solvent removed under vacuum. The residue was extracted with dichloromethane (2 × 10 cm^3) and filtered. The solution was concentrated (to 1 cm^3) and diethyl ether (20 cm^3) added to give $[Ph_3PCH_2C(O)NMe_2]ClO_4$ as a white solid, 86% yield, m.p. 206 °C, [Found (Calc.): C, 58.65 (59.00); H, 5.55 (5.20); N, 2.85 (3.20%)].

$Ph_3P{=}CHC(O)NMe_2$.—A solution of $[Ph_3PCH_2C(O)NMe_2]Cl$ (500 mg, 1.30 mmol) in dichloromethane (20 cm^3) was treated with NaH (60% suspension in mineral oil, 180 mg) under a nitrogen atmosphere. The resulting suspension was stirred for 30 min and then filtered over Celite. The solution was concentrated (to 1 cm^3) and hexane (10 cm^3) added to give $Ph_3P{=}CHC(O)NMe_2$ as a white solid, which as recrystallized from diethyl ether–hexane (1:10), 76% yield, m.p. 176 °C [Found (Calc.): C, 75.80 (76.05); H, 6.55 (6.40); N, 4.55 (4.05%)].

$[AuCl\{CH(PPh_3)C(O)NMe_2\}]$ **1**.—The stoichiometric amount of $Ph_3P{=}CHC(O)NMe_2$ was added to a solution of [AuCl(tht)] (49.8 mg 0.15 mmol) in dichloromethane (25 cm^3), after 20 min the reaction mixture was filtered through Celite, the filtrate concentrated to 1 cm^3, and diethyl ether (10 cm^3) added to precipitate **1** as a white solid, which was washed with diethyl ether (3 × 3 cm^3) and recrystallized from dichloromethane–diethyl ether.

$[AuCl_3\{CH(PPh_3)C(O)NMe_2\}]$ **2**.—A saturated solution of Cl_2 in CCl_4 (2 cm^3, 0.6 mol dm^{-3}) was added to a solution of complex **1** (141.0 mg, 0.24 mmol) in dichloromethane (5 cm^3). The resulting solution was stirred for 30 min, and a pale yellow solid precipitated. Diethyl ether (20 cm^3) was added to complete the precipitation of compound **2**.

$[Au\{CH(PPh_3)C(O)NMe_2\}_2]ClO_4$ **3**.—To a solution of [AuCl(tht)] (46.1 mg, 0.14 mmol) in dichloromethane (20 cm^3) was added $Ph_2P{=}CHC(O)NMe_2$ (100.0 mg, 0.29 mmol) and $NaClO_4{\cdot}H_2O$ (40.3 mg, 0.29 mmol). After 20 min the resulting suspension was filtered through Celite and the filtrate concentrated (to 1 cm^3). Diethyl ether (10 cm^3) was added to precipitate compound **3** as a white solid, which was washed with diethyl ether and recrystallized from dichloromethane–diethyl ether.

$[Ag\{CH(PPh_3)C(O)NMe_2\}_2]ClO_4$ **4**.—To a solution of

Table 4 Selected bond lengths (Å) and angles (°) for compound **6**

Au(1) • • • Au(2)	2.938(1)	Au(1)–P(1)	2.288(5)
Au(1)–C(1)	2.136(16)	Au(2)–P(2)	2.294(5)
Au(2)–C(1)	2.077(17)	P(1)–C(11)	1.817(12)
P(1)–C(21)	1.830(10)	P(1)–C(31)	1.812(13)
P(2)–C(41)	1.837(13)	P(2)–C(51)	1.796(14)
P(2)–C(61)	1.824(12)	P(3)–C(1)	1.783(14)
P(3)–C(71)	1.819(13)	P(3)–C(81)	1.833(11)
P(3)–C(91)	1.819(12)	C(1)–C(2)	1.479(24)
C(2)–N	1.390(20)	C(2)–O(1)	1.231(25)
C(3)–N	1.468(30)	C(4)–N	1.465(27)
Au(2)–Au(1)–P(1)	131.5(1)	Au(2)–Au(1)–C(1)	45.0(4)
P(1)–Au(1)–C(1)	173.4(4)	Au(1)–Au(2)–P(2)	132.0(1)
Au(1)–Au(2)–C(1)	46.6(4)	P(2)–Au(2)–C(1)	174.9(4)
Au(1)–P(1)–C(11)	107.4(4)	Au(1)–P(1)–C(21)	117.7(4)
C(11)–P(1)–C(21)	103.8(6)	Au(1)–P(1)–C(31)	112.4(4)
C(11)–P(1)–C(31)	107.4(5)	C(21)–P(1)–C(31)	107.3(5)
Au(2)–P(2)–C(41)	112.8(4)	Au(2)–P(2)–C(51)	110.7(6)
C(41)–P(2)–C(51)	105.8(6)	Au(2)–P(2)–C(61)	115.1(4)
C(41)–P(2)–C(61)	103.3(6)	C(51)–P(2)–C(61)	108.6(6)
C(1)–P(3)–C(71)	114.3(6)	C(1)–P(3)–C(81)	108.1(7)
C(71)–P(3)–C(81)	102.6(5)	C(1)–P(3)–C(91)	116.5(6)
C(71)–P(3)–C(91)	109.3(6)	C(81)–P(3)–C(91)	104.7(5)
Au(1)–C(1)–Au(2)	88.4(7)	Au(1)–C(1)–P(3)	106.6(7)
Au(2)–C(1)–P(3)	111.6(7)	Au(1)–C(1)–C(2)	118.2(10)
Au(2)–C(1)–C(2)	123.6(11)	P(3)–C(1)–C(2)	106.8(12)
C(1)–C(2)–N	120.3(17)	C(1)–C(2)–O(1)	121.9(14)
N–C(2)–O(1)	117.8(16)	C(2)–N–C(3)	124.1(16)
C(2)–N–C(4)	118.9(17)	C(3)–N–C(4)	117.0(14)

$AgClO_4$ in diethyl ether was added $Ph_3P{=}CHC(O)NMe_2$ in molar ratio 1:2. The reaction mixture was stirred for 30 min in the dark. The suspension was filtered and the resulting solid **4** washed with diethyl ether.

$[Au\{CH(PPh_3)C(O)NMe_2\}(PPh_3)]ClO_4$ **5**.—To a solution of $[Ph_3PCH_2C(O)NMe_2]ClO_4$ (52.0 mg, 0.12 mmol) in acetone (10 cm^3) was added solid $[Au(acac)(PPh_3)]$ (130.0 mg, 0.23 mmol). The resulting suspension was stirred for 90 min, filtered through $MgSO_4$ and the filtrate was concentrated to 1 cm^3. Diethyl ether (15 cm^3) was added to precipitate complex **5** as a white solid, which was recrystallized from acetone–diethyl ether.

$[(AuPPh_3)_2\{\mu\text{-}C(PPh_3)C(O)NMe_2\}]ClO_4$ **6**.—To a solution of $[Ph_3PCH_2C(O)NMe_2]ClO_4$ (16.3 mg, 0.04 mmol) in acetone (8 cm^3) was added $[Au(acac)(PPh_3)]$ (101.4 mg, 0.18 mmol). The suspension was stirred under N_2 for 16 h, and filtered over Celite. The solution was concentrated (1 cm^3) and diethyl ether (20 cm^3) added to precipitate complex **6** as a white solid, which was recrystallized from dichloromethane–diethyl ether.

X-Ray Structure Determination of Compound **6**.—*Crystal Data.* $C_{58}H_{51}Au_2ClNO_5P_3 \cdot CH_2Cl_2$, $M_r = 1449.2$, triclinic, space group $P\bar{1}$, $a = 11.572(3)$, $b = 11.836(3)$, $c = 21.627(7)$ Å, $\alpha = 78.29(2)$, $\beta = 87.19(2)$, $\gamma = 75.65(2)°$, $U = 2810$ Å^3, $Z = 2$, $D_c = 1.71$ Mg m^{-3}, $F(000) = 1416$, λ(Mo-Kα) = 0.710 69 Å, $\mu = 5.5$ mm^{-1}, $T = 293$ K.

Data collection and reduction. Single crystals of compound **6** in the form of colourless prisms and tablets were obtained by liquid diffusion of hexane into a dichloromethane solution. Despite ready solvent loss in air, samples could be mounted in inert oil and transferred to the cold gas stream of the diffractometer without appreciable loss of crystallinity. However, the reflection shape, even using optically perfect crystals, was always poor (irregular profiles with asymmetric backgrounds). A tablet 0.55 × 0.3 × 0.1 mm was used to collect 10 305 intensities to $2\theta_{max}$ 50° (Siemens R3 diffractometer, monochromated Mo-Kα radiation). An absorption correction based on ψ scans was applied, with transmission factors 0.36–0.99. Merging equivalents gave 9781 unique reflections (R_{int} 0.018), of which 7364 with $F > 4\sigma(F)$ were used for all calculations (program system Siemens SHELXTL PLUS). Cell constants were refined from setting angles of 50 reflections in the range 2θ 20–23°.

Structure solution and refinement. The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement on F; Au, P, Cl and O atoms were refined anisotropically, phenyl rings as idealized hexagons with C–C 1.395, C–H 0.96 Å and all angles 120°. Other H atoms were not included. An ill defined region of residual electron density was interpreted as disordered dichloromethane. Refinement proceeded to R 0.076, R' 0.100 for 239 parameters. The weighting scheme was $w^{-1} = \sigma^2(F) + 0.0004F^2$; S 3.0; maximum Δ/σ 0.11; maximum $\Delta\rho$ 7 e Å^{-3} near the gold atoms.

Final atomic coordinates are given in Table 3, with selected bond lengths and angles in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank the Fonds der Chemischen Industrie, the Deutscher Akademischer Austauschdienst and Dirección General de Investigacion Científica y Técnica (Spain) (PB89–0430) for financial support. M.-C. L. gratefully acknowledges a grant from the Ministerio de Educación y Ciencia.

References

1 M. E. Jung and S. A. Abrecht, *J. Org. Chem.*, 1988, **53**, 423.

2 See, for example, J. Vicente, M. T. Chicote and I. Saura-Llamas, *J. Chem. Soc., Dalton Trans.*, 1990, 1941 and refs. therein.

3 See, for example, R. Usón, J. Forniés, R. Navarro, P. Espinet and C. Mendivil, *J. Organomet. Chem.*, 1985, **290**, 125 and refs. therein.

4 H. Schmidbaur, *Acc. Chem. Res.*, 1980, **52**, 1057; W. C. Kaska, *Coord. Chem. Rev.*, 1983, **48**, 1.

5 See, for example, J. A. Albanese, A. L. Rheingold and J. L. Burmeister, *Inorg. Chim. Acta*, 1988, **150**, 213 and refs. therein.

6 See, for example, J. Vicente, M. T. Chicote, I. Saura-Llamas, P. G. Jones, K. Meyer-Bäse and C. F. Erdbrügger, *Organometallics*, 1988, **7**, 997 and refs. therein.

7 J. Vicente, M. T. Chicote, J. A. Cayuelas, J. Fernández-Baeza, P. G. Jones, G. M. Sheldrick and P. Espinet, *J. Chem. Soc., Dalton Trans.*, 1985, 1163.

8 J. Vicente, M. T. Chicote, J. Fernández-Baeza, J. Martín, I. Saura-Llamas and J. Turpín, *J. Oganomet. Chem.*, 1987, **331**, 409.

9 D. B. Denney and S. T. Ross, *J. Org. Chem.*, 1962, **27**, 998.

10 J. Vicente, M. T. Chicote, I. Saura-Llamas, J. Turpín and J. Fernández-Baeza, *J. Organomet. Chem.*, 1987, **333**, 129.

11 J. Vicente, M. T. Chicote, I. Saura-Llamas and P. G. Jones, *Organometallics*, 1989, **8**, 767.

12 H. Schmidbaur, *Gmelin Handbuch der Anorganischen Chemie, Organogold Compounds*, Springer, Berlin, 1980.

13 R. J. Puddephatt, *The Chemistry of Gold*, Elsevier, Amsterdam, 1978.

14 P. G. Jones, *Gold Bull.*, 1981, **14**, 102, 159; 1983, **16**, 114; 1986, **19**, 46; H. Schmidbaur, *Gold Bull.*, 1990, **23**, 11; Y. Jiang, S. Alvarez and R. Hoffmann, *Inorg. Chem.*, 1985, **24**, 749.

15 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

Received 18*th February* 1991; *Paper* 1/00766A