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Synthesis of heteropolynuclear complexes with 1,1,1-tris(diphenylphosphinomethyl)ethane. Crystal structure of $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}AuCl]$

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Treatment of $[M(CO)_4\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}]$ (M = Mo or W) with neutral or cationic gold-(I) or -(III) derivatives afforded bi- or tri-nuclear complexes containing the triphosphine $(Ph_2PCH_2)_3CMe$ (tdppme) acting as a μ-*P*,*P*′,*P*″ ligand, a co-ordination mode poorly represented thus far. The binuclear derivative $[(OC)_4Mo(tdppme)AuCl]$ further reacts with 1 equivalent of Tl(acac) (acac = acetylacetonate) to afford $[(OC)_4Mo(tdppme)Au(acac)]$. This complex acts as a deprotonating agent in reactions with various starting materials containing phosphines such as $(Ph_2P)_2CH_2$ or $(Ph_2P)_3CH$, leading to the formation of trinuclear methanide complexes. The crystal structure of $[(OC)_4Mo(tdppme)AuCl]$ has been established by X-ray crystallography.

The chemistry of diphosphines such as $(Ph_2P)_2CH_2$[1,2] or its methanide $(Ph_2P)_2CH^-$ (ref. 3) has been extensively developed and some gold complexes have already been described.[3,4] In contrast, the chemistry of triphosphines such as $(Ph_2P)_3CH$ or its methanide derivative $(Ph_2P)_3C^-$ has been far less studied.[5] As part of our studies with triphosphines we have previously reported on the synthesis of heterometallic species where these compounds bridge chromium, molybdenum or tungsten centres and a gold(I) atom.[6]

A small number of transition-metal complexes with the triphosphine $(Ph_2PCH_2)_3CMe$ (tdppme) have been synthesized, and in most cases the co-ordination is as a tridentate-chelating ligand, fixing three co-ordination positions and not affecting the reactivity in the rest of the molecule.[7] Furthermore, the same co-ordination mode appears in the heteropolynuclear clusters described with this tridentate ligand,[7a,8] which contain gold–rhodium, -iridium or -ruthenium bonds suported by bridging hydrides. However, little attention has been paid to the study of other co-ordination modes in heteropolynuclear complexes.

We have recently described gold(I) and/or gold(III) complexes containing tdppme in different co-ordination modes, some of them being unprecedented (μ-*P*,*P*′; μ-*P*,*P*′,*P*″ or *P*).[9] Other co-ordination modes of the phosphine as a μ_3 or *P*,*P*′ ligand are poorly represented.[10] Amongst the latter type of complex the derivatives $[M(CO)_4(tdppme\text{-}P,P')]$ (M = Mo or W)[10b] present a free phosphorus which can act as a ligand towards gold-(I) or -(III) species giving rise to heterometallic derivatives. Here we describe several heteropolynuclear compounds with the triphosphine acting as a μ-*P*,*P*′,*P*″ ligand and the use of one of these derivatives, $[(OC)_4Mo(tdppme)Au(acac)]$ (acac = acetylacetonate), as a deprotonating agent in the synthesis of new methanide complexes.

Results and Discussion

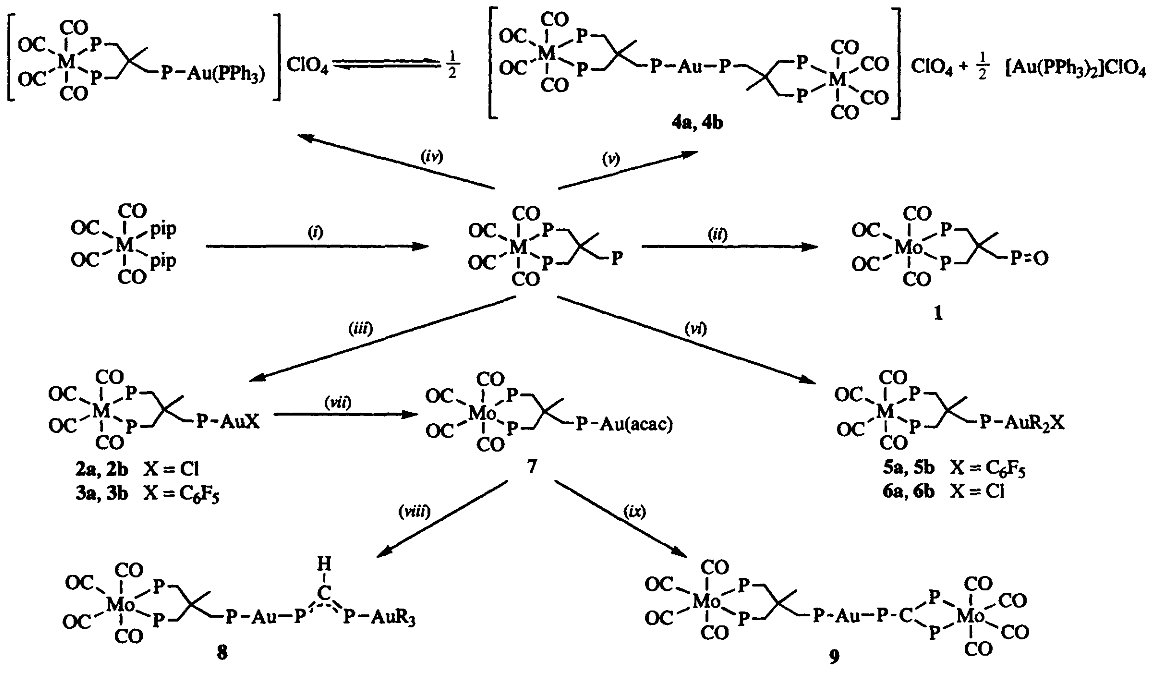
The preparation of the starting materials $[M(CO)_4(tdppme)]$ (M = Mo or W) was as previously described, by reaction of $[M(CO)_6]$ with tdppme in refluxing ethanol.[10b] We have prepared them by an alternative procedure, which consists of the substitution of the piperidine ligands in $[M(CO)_4(pip)_2]$ (M = Mo or W) by the phosphine under mild conditions.

The phosphorus atom of the molybdenum complex can be oxidized by H_2O_2, affording $[Mo(CO)_4\{(Ph_2PCH_2)_2C\text{-}MeCH_2PPh_2(O)\}]$ **1** (Scheme 1, Table 1). [When the same reaction is carried out with the tungsten complex a mixture of the corresponding oxidized derivative and $(OPh_2PCH_2)_3CMe$ is obtained, and their similar solubilities prevent their separation.] Complex **1** is a colourless air-stable solid, soluble in chlorinated solvents and acetone, and slightly soluble in diethyl ether. Its IR spectrum shows three bands for the terminal CO groups, characteristic of *cis*-tetracarbonyl derivatives,[11] and a broad signal at 1149 cm^{-1}, corresponding to the ν(P=O) vibration.[12]

The oxidation of the free phosphorus is easily demonstrated in its $^{31}P\text{-}\{^1H\}$ NMR spectrum (see Table 2), because of the displacement of the resonance (P_A) to low field (Δ ≈ 53 ppm). The phosphorus atoms bonded to the molybdenum centre (P_X) do not show the same effect, because of the length of the hydrocarbon chain, and no coupling between A and X is observed. The ^1H NMR spectrum (Table 2) shows three signals with relative intensity 3 : 2 : 4. The first is a singlet corresponding to the methyl protons; the second, a doublet due to the methylene group bonded to the oxidized phosphorus, and the last signal appears as the AB part of an ABX system (where X is a phosphorus atom). This resonance corresponds to the four methylene protons of the six-membered ring and its simulated spectrum agrees with experiment. In the positive-ion fast atom bombardment (FAB) mass spectrum the parent peak appears protonated at *m*/*z* = 851 (20%) and peaks corresponding to the loss of each carbonyl group are also observed.

Gold(I) phosphine complexes

The tetrahydrothiophene (tht) ligand in $[AuX(tht)]$ (X = Cl or C_6F_5) or $[Au(tht)_2]ClO_4$ can be displaced by the free phosphorus of $[M(CO)_4(tdppme)]$ (M = Mo **a** or W **b**) to give the mixed neutral complexes $[(OC)_4M\{(Ph_2PCH_2)_2CMe\text{-}$



Scheme 1 M = Mo **a** or W **b**; R = C_6F_5. (*i*) $(Ph_2PCH_2)_3CMe$; (*ii*) H_2O_2; (*iii*) [AuX(tht)]; (*iv*) $[Au(PPh_3)(tht)]ClO_4$; (*v*) $\frac{1}{2}[Au(tht)_2]ClO_4$; (*vi*) $[Au(C_6F_5)_3(tht)]$ (**5**) or $\frac{1}{2}[\{Au(C_6F_5)_2(\mu\text{-}Cl)\}_2]$ (**6**); (*vii*) Tl(acac); (*viii*) $[Au(C_6F_5)_3(dppm)]$; (*ix*) $[Mo(CO)_4\{(Ph_2P)_2CHPPh_2\}]$

Table 1 Analytical data and some properties of complexes **1**–**9**

Compound	Yield (%)	Analysis (%)[a] C	H	M.p. (°C)[b]	Λ_M[c]/Ω^{-1} cm^2 mol^{-1}
1 $[Mo(CO)_4\{(Ph_2PCH_2)_2CMeCH_2Ph_2P(O)\}]$	66	64.2 (63.7)	4.85 (4.65)	155 (decomp.)	3
2a $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}AuCl]$	91	50.35 (50.75)	3.7 (3.7)	188 (decomp.)	5
2b $[(OC)_4W\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}AuCl]$	74	46.55 (46.9)	3.35 (3.4)	196	3
3a $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(C_6F_5)]$	68	50.7 (51.2)	3.6 (3.3)	96 (decomp.)	17
3b $[(OC)_4W\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(C_6F_5)]$	56	48.05 (47.7)	3.35 (3.05)	90	21
4a $[\{Mo(CO)_4[(Ph_2PCH_2)_2CMe(CH_2PPh_2)]\}_2Au]ClO_4$	79	54.75 (55.1)	3.9 (4.0)	155 (decomp.)	127
4b $[\{W(CO)_4[(Ph_2PCH_2)_2CMe(CH_2PPh_2)]\}_2Au]ClO_4$	66	50.75 (50.55)	3.95 (3.7)	142	160
5a $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(C_6F_5)_3]$	72	49.6 (49.45)	2.3 (2.55)	152 (decomp.)	28
5b $[(OC)_4W\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(C_6F_5)_3]$	74	46.45 (46.75)	2.8 (2.45)	125 (decomp.)	13
6a $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(C_6F_5)_2Cl]$	55	48.7 (48.95)	3.1 (2.8)	115 (decomp.)	25
6b $[(OC)_4W\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(C_6F_5)_2Cl]$	72	46.55 (46.05)	3.05 (2.65)	116 (decomp.)	43
7 $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(acac)]$	76	53.25 (53.2)	4.0 (4.1)	80	1
8 $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(Ph_2PCHPPh_2)Au(C_6F_5)_3]$	71	50.2 (50.05)	2.75 (2.85)	145	2
9 $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au\{Ph_2PC(PPh_2)_2\}Mo(CO)_4]$	75	57.35 (57.2)	3.1 (3.2)	125	33

[a] Calculated values are given in parentheses. [b] Or decomposition. [c] In acetone.

$(CH_2PPh_2)\}AuX]$ (X = Cl **2a**, **2b** or C_6F_5 **3a**, **3b**) or the trinuclear cationic $[\{M(CO)_4[(Ph_2PCH_2)_2CMe(CH_2PPh_2)]\}_2Au]ClO_4$ **4a**, **4b**. In contrast, when a similar reaction is carried out using $[Au(PPh_3)(tht)]ClO_4$ as starting material, an equimolecular mixture of $[Au(PPh_3)_2]ClO_4$ and **4** is obtained in equilibrium with the expected derivative $[(OC)_4M\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(PPh_3)]ClO_4$. Thus, this complex cannot be isolated as a pure product.

Complexes **2**–**4** are isolated as white or pale yellow solids, air-stable at room temperature. They are soluble in dichloromethane, chloroform, acetone and diethyl ether (**2**, **3**). Their acetone solutions are neutral (**2**, **3**) or show conductivities typical of 1 : 1 electrolytes (**4**). In their IR spectra the same pattern in the CO region is observed, and they also show a band assignable to ν(Au–Cl)[13] at 333 cm^{-1} (**2**), the characteristic pattern of C_6F_5 groups bonded to gold(I) at 1501vs, 955vs and ≈800m cm^{-1} (**3**) or absorptions corresponding to the perchlorate anion[14] at 1100vs (br) and 623m cm^{-1} (**4**).

Table 2 Infrared[a] and ^1H[b] and ^{31}P-{^1H}NMR[c] data for complexes **1**–**9**

		^1H (δ, J/Hz)						^{31}P-{^1H} (δ, J/Hz)	
				2 CH_2P					
Compound	ṽ(CO)/cm^{-1}	CH_3	M–P–CH_2	AB	H_A	H_B	J_{AB}	2 M–P_X	P_A–Au
1	2019s, 1920s, 1900vs	0.86 (s)	2.19 (d, J_{HP} 10.7)	2.65 (ABX)	2.57 (J_{HP} 2.7)	2.73 (J_{HP} 7.2)	13.6	19.6 (s)	25.9 (s)
2a	2020s, 1923s, 1899vs	1.0 (s)	2.37 (d, J_{HP} 11.2)	2.67 (ABX)	2.65 (J_{HP} 0)	2.69 (J_{HP} 2.2)	3.05	20.9 (s)	17.1 (s)
2b	2016s, 1920s, 1889vs	1.01 (s)	2.36 (d, J_{HP} 11.0)	2.78 (m)				1.2 (s)	16.9 (s, J_{PW} 113.8)
3a	2020s, 1922s, 1898vs	1.01 (s)	2.38 (d, J_{HP} 10.7)	2.73 (ABX)	2.68 (J_{HP} 5.3)	2.78 (J_{HP} 5.0)	14.1	20.5 (s)	25.6 (m)
3b	2016s, 1915s, 1891vs	1.0 (s)	2.36 (d, J_{HP} 10.0)	2.81 (m)				0.9 (s)	25.4 (m, J_{PW} 112.1)
4a	2020s, 1924s, 1896vs	0.97 (s)	2.66 (m)	2.41 (m)				20.1 (s)	29.9 (s)
4b	2015s, 1888vs, 1835s	0.99 (s)	2.61 (m)	2.51 (m)				0.5 (s)	29.7 (s, J_{PW} 113.5)
5a	2020s, 1925s, 1893vs	1.64 (s)	2.28 (d, J_{HP} 11.8)	2.15 (ABX)			14.6	22.2 (s)	2.3 (m)
5b	2016s, 1921s, 1885vs	1.65 (s)	2.28 (d, J_{HP} 12.1)	2.28 (ABX)	2.18 (J_{HP} 4.9)	2.38 (J_{HP} 4.2)	14.5	2.0 (s)	1.5 (m, J_{PW} 112.9)
6a	2020s, 1923s, 1896vs	1.33 (s)	2.84 (d, J_{HP} 12.2)	2.50 (ABX)	2.42 (J_{HP} 3.7)	2.58 (J_{HP} 0)	12.3	21.1 (s)	14.0 (m)
6b	2016vs, 1917s, 1885vs	1.38 (s)	2.84 (d, J_{HP} 12.4)	2.61 (ABX)	2.52 (J_{HP} 5.2)	2.70 (J_{HP} 5.2)	15.7	1.5 (s)	13.9 (m, J_{PW} 112.6)
7[d]	2020s, 1924s, 1898vs	1.10 (s)	2.25 (d, J_{HP} 10.9)	2.52 (m)				20.2 (s)	22.6 (s)
8[e]	2020s, 1925s, 1898vs	0.99 (s)	2.35 (d, J_{HP} 11.2)	2.65 (ABX)	2.61 (J_{HP} 5.1)	2.69 (J_{HP} 5.1)	12.3	21.0 (s)	28.5 (s)
9[f]	2020vs, 1895vs, 1847s 2004vs, 1895vs, 1847s	0.74 (s)	1.93 (d, J_{HP} 10.4)	1.79 (m) 3.09 (m)				20.8 (s)	26.6 (s)

[a] In CH_2Cl_2 solutions; v = very, s = strong. [b] In $CDCl_3$ solutions, δ from external $SiMe_4$; s = singlet, m = multiplet, d = doublet. [c] In $CDCl_3$ solutions, δ from external 85% H_3PO_4; t = triplet. [d] The ^1H NMR spectrum also presents resonances corresponding to the acetylacetonate ligand at δ 2.19 (s, $2CH_3$) and 4.51 (m, CH). [e] Au–P_B, δ 33.2 (d, J_{BY} 14.6, J_{AB} 316.5 Hz); P_Y–Mo, δ 16.9 (m). [f] Au–P_B, δ 33.4 (t, J_{BY} 0, J_{AB} 315.8 Hz); P_Y–Mo, δ 19.9 (m).

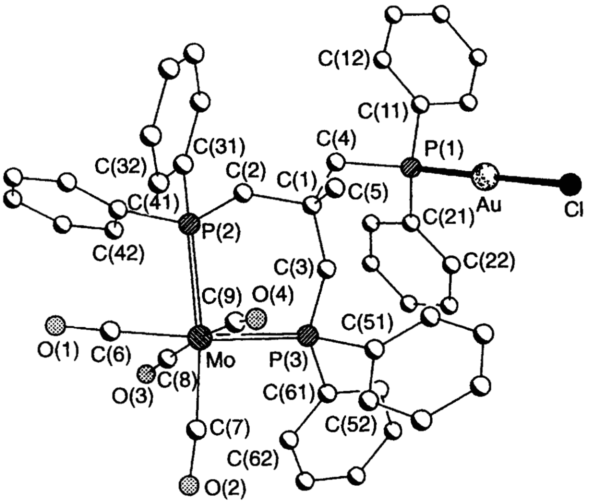


Fig. 1 Molecular structure of complex **2a** showing the atom numbering scheme. Radii are arbitrary; hydrogen atoms are omitted for clarity

The ^{31}P-{^1H} NMR spectra of complexes **2**–**4** show two different phosphorus environments corresponding to an AX_2 system with $J(AX) \approx 0$. For **2b**, **3b** and **4b** the upfield resonance (P_X) displays tungsten satellites with $J(PW)$ = 114, 112 and 113 Hz, respectively. For the pentafluorophenyl derivatives **3** the signal of the phosphorus bonded to gold(I) (P_A) appears as a multiplet because of coupling to the fluorine atoms. The ^1H NMR spectra are very similar to those observed for complex **1**, although in some cases the ABX system is not resolved, and only a multiplet is observed (Table 2). The ^{19}F NMR spectra of **3** display a typical pattern for C_6F_5: two multiplets for the *o*-and *m*- and a triplet for the *p*-fluorine nuclei.

The positive-ion fast atom bombardment (FAB) mass spectra of complexes **2**–**4** show the molecular-ion peaks at m/z = 1069 (**2a**, 52), 1152 (**2b**, 5), 1198 (**3a**, 20) and 1284 (**3b**, 90%) or the molecular cation peaks at m/z = 1863 (**4a**, 20) and 2037 (**4b**, 26%). Some of them also present signals corresponding to loss of carbonyl groups; the peak corresponding to the fragment $[Au(tdppme)]^+$ at m/z = 821 always appears with high intensity.

The crystal structure of complex **2a** has been determined by X-ray crystallography and the molecule is shown in Fig. 1; selected bond lengths and angles are collected in Table 3. The molybdenum atom approaches octahedral co-ordination quite closely, with a maximum deviation from ideal angles of 7.5°. The presence of a six-membered chelate ring causes no distortion arising from the bite angle of the phosphine, with an almost ideal value of 90.14(6)° [P(2)–Mo–P(3)]. There are two slightly different ranges of Mo–CO bond distances; the shortest [1.991(7) and 1.997(8) Å] are to the carbonyl groups *trans* to the phosphorus atoms, whereas the bond lengths to the *cis* carbonyls are 2.029(8) and 2.041(8) Å. The Mo–P distances, 2.509(2) and 2.537(2) Å are very dissimilar but similar values were found in the complex $[Mo(CO)_4\{(Ph_2P)_2CH_2\}]$[15] [2.501(2) and 2.535(3) Å]. The co-ordination at the gold centre is linear, P(1)–Au–Cl 177.47(7)°. The bond lengths at the gold atom, Au–Cl 2.284(2) and Au–P(1) 2.232(2) Å, are of the same order as those found in the complex $[Mo(CO)_4\{(Ph_2P)_2CHPPh_2AuCl\}]$[6] [2.2749(14) and 2.2249(13) Å, respectively]. The intramolecular Au ••• Mo distance is very long, 7.406(2) Å.

Gold(III) phosphine complexes

Mixed gold(III) and molybdenum or tungsten derivatives can be obtained by ligand-displacement or bridge-cleavage reactions. Thus, treatment of $[M(CO)_4(tdppme)]$ (M = Mo **a** or W **b**) with $[Au(C_6F_5)_3(tht)]$ (1:1) or $[\{Au(C_6F_5)_2(\mu\text{-}Cl)\}_2]$ (2:1) leads to the neutral dinuclear products $[(OC)_4M\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(C_6F_5)_2X]$ (X = C_6F_5 **5a**, **5b** or Cl **6a**, **6b**) as white or yellow air-stable solids. They are soluble in chlorinated solvents, acetone and diethyl ether and non-conducting in acetone solutions. Their IR spectra show the same pattern, corresponding to *cis*-tetracarbonyl derivatives in the terminal CO region and with bands at 1507vs, 969vs, ≈805m and 795m cm^{-1} from the C_6F_5 groups bonded to the gold(III) centre; the last two show the characteristic pattern for $Au(C_6F_5)_3$ groups[16] in **5**, and confirming a *cis* disposition[17] in **6**. In the spectra of **6** a ν(Au–Cl) absorption at 336m (**6a**) or 332m cm^{-1} (**6b**) also appears.

The ^{31}P-{^1H} NMR spectra of these complexes show an AX_2 system without coupling between the different phosphorus atoms, and in all cases the resonance corresponding to the phosphorus *trans* to C_6F_5 (P_A) appears as a multiplet caused by the coupling to the ^{19}F nuclei. The signal due to the phosphorus atoms bonded to tungsten (P_X) in **5b** and **6b** shows satellites [$J(PW)$ = 113 Hz]. The ^{19}F NMR spectra confirm the presence of two types of C_6F_5 groups with a relative integration

Table 3 Selected bond lengths (Å) and angles (°) for complex **2a**

Au–P(1)	2.232(2)	Au–Cl	2.284(2)
Mo–C(6)	1.991(7)	Mo–C(7)	1.997(8)
Mo–C(8)	2.029(8)	Mo–C(9)	2.041(8)
Mo–P(2)	2.509(2)	Mo–P(3)	2.537(2)
P(1)–C(21)	1.810(7)	P(1)–C(11)	1.815(7)
P(1)–C(4)	1.838(6)	P(2)–C(41)	1.822(7)
P(2)–C(31)	1.835(7)	P(2)–C(2)	1.834(6)
P(3)–C(51)	1.829(7)	P(3)–C(3)	1.843(7)
P(3)–C(61)	1.851(7)	C(1)–C(5)	1.538(9)
C(1)–C(4)	1.543(9)	C(1)–C(3)	1.544(8)
C(1)–C(2)	1.552(8)	C(6)–O(1)	1.148(8)
C(7)–O(2)	1.146(9)	C(8)–O(3)	1.135(8)
C(9)–O(4)	1.146(9)		
P(1)–Au–Cl	177.47(7)	C(6)–Mo–C(7)	88.7(3)
C(6)–Mo–C(8)	86.4(3)	C(7)–Mo–C(8)	86.9(3)
C(6)–Mo–C(9)	93.1(3)	C(7)–Mo–C(9)	87.8(3)
C(8)–Mo–C(9)	174.8(3)	C(6)–Mo–P(2)	83.8(2)
C(7)–Mo–P(2)	172.5(2)	C(8)–Mo–P(2)	91.9(2)
C(9)–Mo–P(2)	93.2(2)	C(6)–Mo–P(3)	173.4(2)
C(7)–Mo–P(3)	97.3(2)	C(8)–Mo–P(3)	91.1(2)
C(9)–Mo–P(3)	90.0(2)	P(2)–Mo–P(3)	90.14(6)
C(21)–P(1)–C(11)	103.8(3)	C(21)–P(1)–C(4)	106.5(3)
C(11)–P(1)–C(4)	104.5(3)	C(21)–P(1)–Au	112.5(2)
C(11)–P(1)–Au	110.7(2)	C(4)–P(1)–Au	117.7(2)
C(41)–P(2)–C(31)	100.9(3)	C(41)–P(2)–C(2)	100.5(3)
C(31)–P(2)–C(2)	105.5(3)	C(41)–P(2)–Mo	111.4(2)
C(31)–P(2)–Mo	118.3(2)	C(2)–P(2)–Mo	117.7(2)
C(51)–P(3)–C(3)	105.8(3)	C(51)–P(3)–C(61)	97.4(3)
C(3)–P(3)–C(61)	98.3(3)	C(51)–P(3)–Mo	116.3(2)
C(3)–P(3)–Mo	117.2(2)	C(61)–P(3)–Mo	118.7(2)
C(5)–C(1)–C(4)	109.6(5)	C(5)–C(1)–C(3)	112.0(5)
C(4)–C(1)–C(3)	110.2(5)	C(5)–C(1)–C(2)	111.0(5)
C(4)–C(1)–C(2)	102.5(5)	C(3)–C(1)–C(2)	111.2(5)
C(1)–C(2)–P(2)	119.4(5)	C(1)–C(3)–P(3)	121.4(5)
C(1)–C(4)–P(1)	121.7(4)	O(1)–C(6)–Mo	174.5(6)
O(2)–C(7)–Mo	174.5(6)	O(3)–C(8)–Mo	173.5(6)
O(4)–C(9)–Mo	176.5(6)		

of 2:1 for **5** or 1:1 for **6**. The ^1H NMR spectra are very similar to those found for the compounds described above, although for **5a** it is not possible to calculate the values for δ(A), δ(B), *J*(AX) and *J*(BX), because the ABX system and the doublet of the methylene group are superposed.

In all the mass spectra (FAB+) the molecular-ion peaks appear at m/z = 1532 (**5a**, 5), 1618 (**5b**, 8), 1400 (**6a**, 6) and 1486 (**6b**, 13%). There are also peaks corresponding to the loss of CO or C_6F_5 groups, or to the fragments $[M(tdppme)]^+$ (M = Au and Mo **5** or Au and W **6**), in accord with the bridging nature of the ligand.

Methanide complexes

We have previously reported the use of acetylacetonate gold complexes, such as $[Au(acac)(PPh_3)]$, in the synthesis of methanide complexes[6,18] and they are recognized as good deprotonating agents. Taking this fact into account, we have synthesized the acetylacetonate gold(I) derivative $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(acac)]$ **7** by the reaction of equimolecular amounts of **2a** and Tl(acac), in order to use it as a deprotonating reagent. Complex **7** was isolated as an air-stable white solid, non-conducting in acetone solution. Its IR spectrum shows, besides three carbonyl bands, two broad vibrations at 1655vs and 1641vs cm^{-1}, consistent with the presence of the acetylacetonate anion bonded through the C^3 atom.[19]

Its $^{31}P-\{^1H\}$ NMR spectrum is very similar to that of the starting complex **2a**; the signal of the phosphorus bonded to gold(I) (P_A) is displaced to low field (Δ = 5.5 ppm). In its ^1H NMR spectrum the three resonances of the phosphine protons appear as described above, and there are also two new signals corresponding to the acetylacetonate ion at δ 2.19 (s, $2CH_3$) and 4.51 (m, CH). The molecular-ion peak is not present in the mass spectrum (FAB+) of **7**, but some peaks can be assigned to fragments corresponding to loss of the acac or CO groups.

We have recently reported the reaction of $[Au(C_6F_5)_3(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$) and the diauracyclic acetylacetonate complex $[(acac)AuCH(Ph_2PAuPPh_2)_2CHAu(acac)]$ (2:1), which results in deprotonation of the phosphine and co-ordination of the free phosphorus to the gold(I) centre to give the hexanuclear derivative $[(C_6F_5)_3Au(Ph_2PCHPPh_2)AuCH(Ph_2PAuPPh_2)_2CHAu(Ph_2PCHPPh_2)Au(C_6F_5)_3]$.[4d] In contrast, treatment of $[Au(C_6F_5)_3(dppm)]$ with $[Au(acac)(PPh_3)]$ results in an unresolved mixture of $[(C_6F_5)_3Au(Ph_2PCHPPh_2)Au(PPh_3)]$ and $[(C_6F_5)_3Au\{Ph_2PCH(AuPPh_3)PPh_2\}Au(PPh_3)]^+$.[20]

The reaction of $[Au(C_6F_5)_3(dppm)]$ with complex **7** in an equimolecular ratio gives the trinuclear derivative $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(Ph_2PCHPPh_2)Au(C_6F_5)_3]$ **8** as a pure yellow product. It is moderately stable in the solid state, but decomposes in solution. Its IR spectrum presents, besides the pattern of *cis*-$M(CO)_4L_2$ complexes, absorptions corresponding to the $Au(C_6F_5)_3$ fragment. Its $^{31}P-\{^1H\}$ NMR spectrum shows a singlet corresponding to two phosphorus atoms bonded to molybdenum (P_X), a multiplet due to the phosphorus linked to the gold(III) centre (P_Y), and the two phosphorus of the gold(I) environment appear as an AB system (Table 2). Its ^{19}F NMR spectrum presents the typical pattern of the $Au(C_6F_5)_3$ fragment.

Similarly to the last reaction, $[Mo(CO)_4\{(Ph_2P)_2CHPPh_2\}]$ reacts with acetylacetonatogold(I) complexes, giving the expected methanide derivatives.[6] Thus, treatment of $[Mo(CO)_4\{(Ph_2P)_2CHPPh_2\}]$ with an equimolecular amount of complex **7** results in the synthesis of the trinuclear methanide $[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au\{Ph_2PC(PPh_2)_2\}Mo(CO)_4]$ **9** as a pale yellow solid. The IR spectrum presents bands corresponding to two different *cis*-$Mo(CO)_4L_2$ groups, and a new vibration at 879m cm^{-1}, due to the $(PPh_2)_3C^-$ system.[5d] In its $^{31}P-\{^1H\}$ NMR spectrum two signals of the phosphorus atoms of the metallocycles and an AB system corresponding to the P–Au–P unit appear. Its mass spectrum (FAB+) shows the molecular-ion peak at m/z = 1808 (4%).

Experimental

All the reactions were performed at room temperature (except when indicated) and under dry nitrogen for the synthesis of the methanide complexes **8** and **9** and all the solvents were dried by standard methods. Infrared spectra were recorded in the range 4000–200 cm^{-1} on a Perkin-Elmer 883 spectrophotometer using Nujol mulls between polyethylene sheets and in dichloromethane solutions for the CO vibrations. Conductivities were measured in *ca.* 5×10^{-4} mol dm^{-3} solutions with a Jenway 4010 digital conductimeter. The carbon and hydrogen analyses were carried out with a Perkin-Elmer 240C microanalyser. Proton, ^{19}F and $^{31}P-\{^1H\}$ NMR spectra were recorded on Bruker ARX 300 spectrometer in $CDCl_3$ and chemical shifts are cited relative to $SiMe_4$ (external, ^1H), 85% H_3PO_4 (external, ^{31}P) and $CFCl_3$ (external, ^{19}F). Mass spectra were recorded on a VG Autospec instrument, with the FAB technique, using 3-nitrobenzyl alcohol as matrix. Yields, elemental analyses, melting points and conductivities for the new complexes are listed in Table 1. The following compounds were prepared according to the published procedures: *cis*-$[M(CO)_4(pip)_2]$,[11] $[AuCl(tht)]$,[21] $[Au(C_6F_5)(tht)]$,[22] $[Au(PPh_3)(tht)]ClO_4$,[23] $[Au(tht)_2]ClO_4$,[23] $[Au(C_6F_5)_3(tht)]$,[16] $[Au(C_6F_5)_3\{(Ph_2PCH_2)CMe(CH_2PPh_2)_2\}]$,[9] $[\{Au(C_6F_5)_2(\mu-Cl)\}_2]$,[24] $[Au(C_6F_5)_3(dppm)]$[25] and $[Mo(CO)_4\{(Ph_2P)_2CHPPh_2\}]$.[6]

Syntheses

$[M(CO)_4\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}]$ (M = Mo or W). To a suspension of 0.5 mmol of *cis*-$[M(CO)_4(pip)_2]$ (M = Mo, 0.189; or W, 0.233 g) in dichloromethane (40 cm^3) was added $(Ph_2PCH_2)_3CMe$ (0.312 g, 0.5 mmol). After refluxing the mixture for 1 h a small quantity of solid was filtered off through Celite and the solution concentrated *in vacuo*. Addition of hexane gave a white (Mo) or pale yellow (W) solid, which was filtered off and washed with hexane. Yield: 96 (Mo) or 86% (W).

$[Mo(CO)_4\{(Ph_2PCH_2)_2CMeCH_2PPh_2(O)\}]$ 1. To a dichloromethane solution of $[Mo(CO)_4\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}]$ (0.166 g, 0.2 mmol) was added two drops of H_2O_2 (35% in water). The solution was stirred for 15 min, filtered through a 1 cm layer of anhydrous magnesium sulfate and concentrated to *ca.* 5 cm^3. Addition of hexane (20 cm^3) led to precipitation of complex **1** as a white solid.

$[(OC)_4M\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}AuCl]$ (M = Mo 2a or W 2b). To a solution of 0.2 mmol of $[M(CO)_4\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}]$ (M = Mo, 0.166; or W, 0.184 g) in dichloromethane (20 cm^3) was added [AuCl(tht)] (0.064 g, 0.2 mmol). After stirring for 1 h at room temperature the solution was concentrated under reduced pressure and hexane was added (20 cm^3) to precipitate the products as white (**2a**) or yellow (**2b**) solids.

$[(OC)_4M\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(C_6F_5)]$ (M = Mo 3a or W 3b). Addition of $[Au(C_6F_5)(tht)]$ (0.090 g, 0.2 mmol) to 0.2 mmol of $[M(CO)_4\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}]$ (M = Mo, 0.166; or W, 0.184 g) in dichloromethane afforded complex **3a** or **3b** after 1 h of stirring. The solvent was then partially removed *in vacuo*, whereupon the products were obtained by addition of hexane (20 cm^3) as a white (**3a**) or yellow (**3b**) solid. ^{19}F NMR: **3a**, δ −116.0 (m, *o*-F), −155.1 [t, *p*-F, ^3J(FF) 20.0] and −162.2 (m, *m*-F); **3b**, δ −116.0 (m, *o*-F), −155.0 [t, *p*-F, ^3J(FF) 19.8 Hz] and −162.3 (m, *m*-F).

$[\{M(CO)_4[(Ph_2PCH_2)_2CMe(CH_2PPh_2)]\}_2Au]ClO_4$ (M = Mo 4a or W 4b). To a dichloromethane solution containing 0.2 mmol of $[M(CO)_4\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}]$ (M = Mo, 0.166; or W, 0.184 g) was added $[Au(tht)_2]ClO_4$ (0.047 g, 0.1 mmol). The solution was stirred for 1 h and then concentrated to *ca.* 5 cm^3 followed by addition of diethyl ether, which gave **4a** or **4b** as a pale yellow solid.

$[(OC)_4M\{(PPh_2CH_2)_2CMe(CH_2PPh_2)\}Au(C_6F_5)_3]$ (M = Mo 5a or W 5b). *Method 1.* Reaction of $[Au(C_6F_5)_3(tht)]$ (0.157 g, 0.2 mmol) with 0.2 mmol of $[M(CO)_4\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}]$ (M = Mo, 0.166; or W, 0.184 g) in dichloromethane (20 cm^3) produced after 1 h a colourless (**5a**) or yellow (**5b**) solution, which was concentrated under reduced pressure. Addition of hexane (20 cm^3) gave a white (**5a**) or yellow (**5b**) precipitate, which was filtered off and washed with hexane.

Method 2. To a suspension of 0.2 mmol of *cis*-$[M(CO)_4(pip)_2]$ (M = Mo, 0.076; or W, 0.093 g) in dichloromethane (20 cm^3) was added $[Au(C_6F_5)_3\{(Ph_2PCH_2)CMe(CH_2PPh_2)_2\}]$ (0.265 g, 0.2 mmol). After stirring the mixture for 1 h at reflux temperature it was filtered through a 1 cm layer of Celite to remove a small quantity of solid. The solvent was then partially evaporated and hexane (20 cm^3) added to obtain the product as a white (**5a**) or yellow (**5b**) solid. ^{19}F NMR: **5a**, δ −120.0 and −121.8 (m, *o*-F), −156.3 and −157.1 [t, *p*-F, ^3J(FF) 19.9 and 20.0] and −159.8 and −161.2 (m, *m*-F); **5b**, δ −119.8 and −121.6 (m, *o*-F), −156.1 and −156.8 [t, *p*-F, ^3J(FF) 20.1 and 20.0 Hz] and −159.5 and −160.9 (m, *m*-F).

$[(OC)_4M\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(C_6F_5)_2Cl]$ (M = Mo 6a or W 6b). Addition of $[\{Au(C_6F_5)_2(\mu\text{-}Cl)\}_2]$ (0.113 g, 0.1 mmol) to a dichloromethane solution of 0.2 mmol of $[M(CO)_4\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}]$ (M = Mo, 0.166; or W, 0.184 g) afforded complex **6a** or **6b** after 1 h at room temperature. The solution was concentrated *in vacuo* and addition of hexane (20 cm^3) led to precipitation of a white (**6a**) or yellow (**6b**) solid. ^{19}F NMR: **6a**, δ −121.0 and −122.6 (m, *o*-F), −155.4 and −156.2 [t, *p*-F, ^3J(FF) 20.0 and 19.9] and −159.5 and −160.9 (m, *m*-F); **6b**, δ −121.0 and −122.5 (m, *o*-F), −155.4 and −156.2 [t, *p*-F, ^3J(FF) 19.8 and 20.0 Hz] and −159.5 and −160.9 (m, *m*-F).

$[(OC)_4Mo\{(PPh_2CH_2)_2CMe(CH_2PPh_2)\}Au(acac)]$ 7. To a solution of complex **2a** (0.213 g, 0.2 mmol) in dichloromethane (20 cm^3) was added an excess of Tl(acac) (0.121 g, 0.4 mmol). The mixture was stirred for 1 d and TlCl removed by filtration through Celite; the solvent was then evaporated under reduced pressure and hexane was added to precipitate complex **7** as a white solid.

$[(OC)_4M\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au(Ph_2PCHPPh_2)Au(C_6F_5)_3]$ 8. Addition of complex **7** (0.113 g, 0.1 mmol) to a freshly dried diethyl ether solution of $[Au(C_6F_5)_3(dppm)]$ (0.108 g, 0.1 mmol) at room temperature and under nitrogen produced **8** after 3 h as a yellow precipitate, which was filtered off and washed with diethyl ether. ^{19}F NMR: δ −120.3 and −120.7 (m, *o*-F), −159.2 and −160.1 [t, *p*-F, ^3J(FF) 19.4 and 20.2 Hz] and −162.2 and −162.7 (m, *m*-F).

$[(OC)_4Mo\{(Ph_2PCH_2)_2CMe(CH_2PPh_2)\}Au\{Ph_2PC(PPh_2)_2\}Mo(CO)_4]$ 9. To a solution of $[Mo(CO)_4\{(Ph_2P)_2CHPPh_2\}]$ (0.078 g, 0.1 mmol) in freshly dried dichloromethane (20 cm^3) and under a nitrogen atmosphere was added complex **7** (0.113 g, 0.1 mmol). After 1 h of stirring the yellow solution formed was filtered through a 1 cm layer of Celite to remove a small quantity of solid, the solvent was then partially evaporated and hexane (20 cm^3) added, which gave **9** as a yellow solid.

Crystal structure determination of compound 2a·CH_2Cl_2

Crystal data and data-collection parameters. $C_{46}H_{41}AuCl_3MoO_4P_3$, M = 1149.95, monoclinic, space group $P2_1/n$, a = 14.624(5), b = 12.758(4), c = 24.745(6) Å, β = 106.64(3)°, U = 4423(2) Å^3, Z = 4, D_c = 1.727 Mg m^{-3}, $F(000)$ = 2264, λ(Mo-Kα) = 0.710 73 Å, μ = 3.93 mm^{-1}, T = −130 °C.

A crystal 0.60 × 0.30 × 0.20 mm was mounted in inert oil on a Stoe-STADI4 diffractometer, and used to collect 8137 intensities to $2\theta_{max}$ 50° (monochromated Mo-Kα radiation). An absorption correction based on ψ scans was applied, with transmission factors 0.745–0.913. Merging equivalents gave 7793 independent reflections (R_{int} = 0.036). Cell constants were refined from the ±ω angles of 52 reflections in the range 2θ 20–22°. Weighting scheme employed: $w = 1/\sigma^2(F_o^2) + 0.0348P^2 + 19.5659P$, where $P = (F_o^2 + 2F_c^2/3)$.

Structure solution and refinement. The structure was solved by the heavy-atom method and subjected to full-matrix least-squares refinement on F^2 (program system SHELXL 93).[26] All non-hydrogen atoms were refined anisotropically; hydrogen atoms were included using a riding model. Refinement proceeded to $wR(F^2)$ = 0.108, conventional $R(F)$ 0.043, for 518 parameters and 396 restraints (light-atom displacement parameters and ring planarity). S = 1.06; maximum Δρ 1.6 e Å^{-3}.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/174.

Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (PB94-0079) for financial support and the Instituto de Estudios Riojanos for a grant (to E. O.).

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Received 29*th April* 1996; *Paper* 6/02969H