Synthesis of Heterometallic Species with $(Ph_2P)_3CH$ or $(Ph_2P)_3C^-$. Crystal Structures of $[Mo(CO)_4\{(PPh_2)_2CHPPh_2AuCl\}]$, $[Mo(CO)_4\{(PPh_2)_2CHPPh_2Au(C_6F_5)\}]$ and $[NBu_4][Mo(CO)_4\{(PPh_2)_2CPPh_2Au(C_6F_5)\}]$†

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Treatment of $[M(CO)_4\{(PPh_2)_2CHPPh_2\}]$ (M = Cr **a**, Mo **b** or W **c**) with 1 equivalent of [AuX(tht)] or $[Au(tht)(PPh_3)]ClO_4$ (tht = tetrahydrothiophene) afforded the neutral binuclear complexes $[M(CO)_4\{(PPh_2)_2CHPPh_2AuX\}]$ (X = Cl **1a–1c** or C_6F_5 **2a–2c**), or the cationic derivatives $[M(CO)_4\{(PPh_2)_2CHPPh_2Au(PPh_3)\}]ClO_4$ **3a–3c**. Complexes **2** and **3** are readily deprotonated by $[NBu_4][acac]$ (acac = acetylacetonate) to give the tris(diphenylphosphino)methanide species $[NBu_4]$-$[M(CO)_4\{(PPh_2)_2CPPh_2Au(C_6F_5)\}]$ **4a–4c** and $[M(CO)_4\{(PPh_2)_2CPPh_2Au(PPh_3)\}]$ (**5a–5c**). Trinuclear compounds of the type $[NBu_4][\{M(CO)_4[(PPh_2)_2CPPh_2]\}_2Au]$ **6a–6c** were obtained by reaction of $[M(CO)_4\{(PPh_2)_2CHPPh_2\}]$ with $[NBu_4][Au(acac)_2]$ in the ratio 2:1. Single-crystal structure determinations were performed for compounds **1b**, **2b** and **4b**. In the neutral complexes **1b** and **2b** the atoms C(2) (carbonyl), Mo, P(1) (co-ordinated to Au) and Au are essentially coplanar; the principal structural differences between the neutral and anionic (**4b**) complexes are the shorter P–C bonds and a rotation about the C–P(1) bond in the latter complex.

Heterobimetallic complexes have been the subject of much interest in view of their catalytic potential, which is associated with the proximity of the metal atoms even in the absence of any metal–metal bond.[1] Although the tridentate phosphorus compound tris(diphenylphosphino)methane, $(Ph_2P)_3CH$, was originally intended to stabilize triangular arrays of metal atoms, it became clear that it can exhibit a variety of co-ordination modes. Complexes have been described in which $(Ph_2P)_3CH$ acts as a μ_3 bridging,[2] μ-bridging–chelating,[3] chelating[3b,4] and monodentate ligand.[3b] However, the anion $(Ph_2P)_3C^-$ has been studied far less; only a few complexes have been reported.[5] Although tris(diphenylphosphino)methanide is potentially a tetradentate ligand, no examples are known where the carbon uses its lone pair to co-ordinate a metal fragment, in contrast to $(Ph_2P)_2CH^-$ (ref. 6) or $(Ph_2P)_2C^{2-}$ (ref. 7) for which an extensive chemistry has been developed.

We have previously reported gold(I) complexes in which $(Ph_2P)_3C^-$ bridges three metal centres.[5c] This paper deals with the synthesis of heterometallic tris(diphenylphosphino)methane and -methanide complexes containing early and late transition metals.

Results and Discussion

Tris(diphenylphosphino)methane Complexes.—Mixed tris(diphenylphosphino)methane complexes of gold and Group 6 metals have been prepared by ligand-displacement reactions. Treatment of dichloromethane solutions of the complexes $[M(CO)_4\{(PPh_2)_2CHPPh_2\}]$ (M = Cr **a**, Mo **b** or W **c**) with [AuX(tht)] or $[Au(tht)(PPh_3)]ClO_4$ (tht = tetrahydrothiophene) gives neutral $[M(CO)_4\{(PPh_2)_2CHPPh_2AuX\}]$ (X = Cl **1a–1c** or C_6F_5 **2a–2c**) or cationic $[M(CO)_4\{(PPh_2)_2CHPPh_2Au(PPh_3)\}]ClO_4$ **3a–3c** in high yield (see Scheme 1). Complexes **1–3** are colourless or pale yellow air-stable solids. Their IR spectra show three bands for the terminal CO groups, characteristic of tetracarbonyl species and comparing well with those found for a variety of *cis*-$[Mo(CO)_4L_2]$ (L = phosphine or phosphite) complexes.[8] Their acetone solutions are neutral (**1**, **2**) or show conductivities typical of 1 : 1 electrolytes (**3**).

The $^{31}P-\{^1H\}$ NMR spectra (see Table 1) show two different phosphorus environments for complexes **1** and **2**, and an AX_2 system with $J(AX) \approx 0$ is observed. The upfield resonances of complexes **1c** and **2c** possess tungsten satellites with $J(PW)$ 110 and 109 Hz, respectively. In the spectra of compounds **3** an ABX_2 system is present. Coupling between A and X is not observed. However the coupling constants between the A and B nuclei are very high, up to 323.7 Hz, as a consequence of their mutual *trans* disposition; $J(PW)$ is 109 Hz, similar to values found for the other tungsten derivatives. Upon co-ordination of the previously free phosphorus atom (P_A) the resonances are displaced to low field (Δ = 50 ppm) as expected; the same effect is observed for P_2–M (P_X), but the displacement is lower ($\Delta \approx 4$ ppm) than for the complex $[Mo(CO)_4\{(PPh_2)_2CHPPh_2Fe(CO)_4\}]$ (Δ = 26 ppm).[3b]

The ^1H NMR spectra for the complexes show a doublet of

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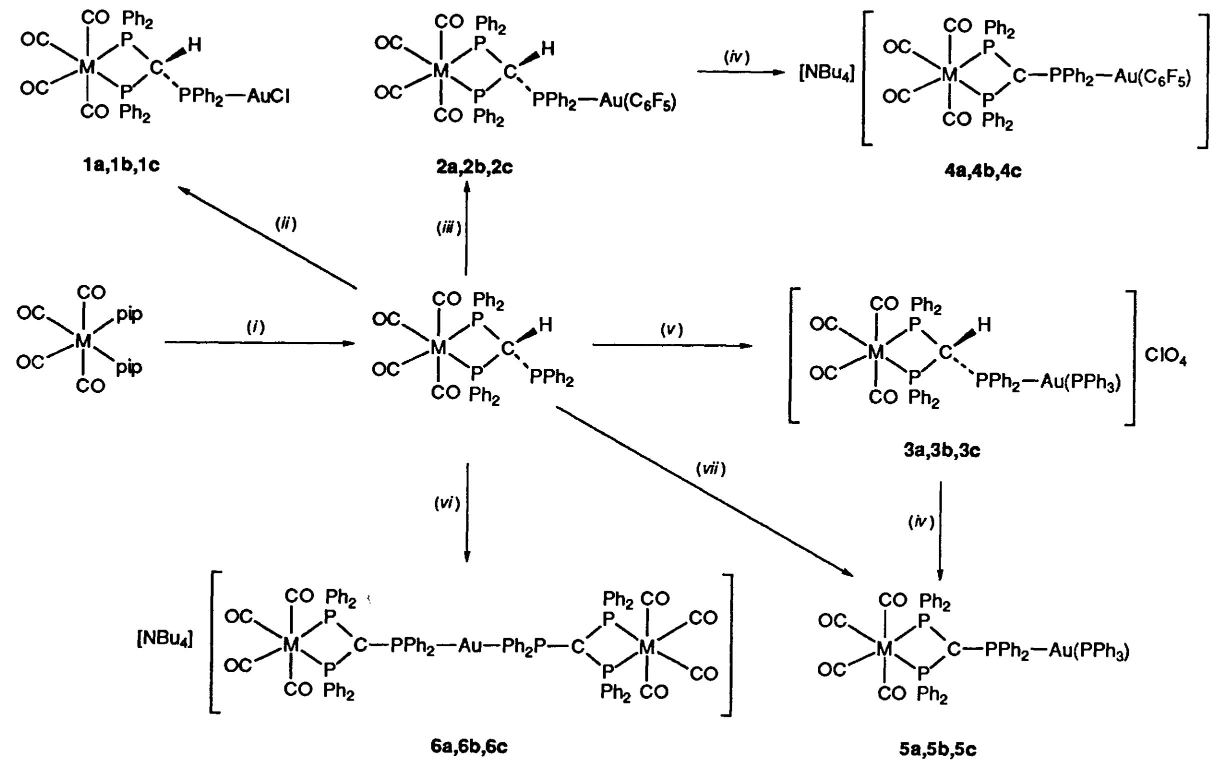
† *Supplementary data available:* Further details of the structure determinations (complete bond lengths and angles, H-atom coordinates, structure factors, thermal parameters) have been deposited at the Fachinformationszentrum Karlsruhe, Gesellschaft für Wissenschaftlich-technische Information mbH, 76344 Eggenstein-Leopoldshafen, Germany. Any request for this material should quote a full literature citation and the reference numbers CSD 400950 (**1b**), 400962 (**2b**) and 400961 (**4b**).



Scheme 1 M = Cr **a**, Mo **b** or W **c**: (*i*) $(Ph_2P)_3CH$, pip = piperidine; (*ii*) [AuCl(tht)]; (*iii*) $[Au(C_6F_5)(tht)]$; (*iv*) $[NBu_4][acac]$; (*v*) $[Au(tht)(PPh_3)]$; (*vi*) $[NBu_4][Au(acac)_2]$; (*vii*) $[Au(acac)(PPh_3)]$

Table 1 Infrared[a] and $^{31}P-\{^1H\}$ NMR[b] data for complexes **1a**–**6c**

		$^{31}P-\{^1H\}$, δ (*J*/Hz)		
Compound	ν(CO)/cm^{-1}	$2P_X$	P_A	P_B
1a $[Cr(CO)_4\{(PPh_2)_2CHPPh_2AuCl\}]$	2010vs, 1928s, 1900vs	50.5(s)	24.4(s)	
1b $[Mo(CO)_4\{(PPh_2)_2CHPPh_2AuCl\}]$	2023vs, 1914vs, 1892s	26.8(s)	26.5(s)	
1c $[W(CO)_4\{(PPh_2)_2CHPPh_2AuCl\}]$	2019s, 1906vs, 1887s	−0.2(s) [J_{PW} 110]	27.0(s)	
2a $[Cr(CO)_4\{(PPh_2)_2CHPPh_2Au(C_6F_5)\}]$	2010vs, 1928s, 1900s	48.7(s)	31.8(m)	
2b $[Mo(CO)_4\{(PPh_2)_2CHPPh_2Au(C_6F_5)\}]$	2023vs, 1914vs, 1892s	25.1(s)	33.4(m)	
2c $[W(CO)_4\{(PPh_2)_2CHPPh_2Au(C_6F_5)\}]$	2019s, 1905vs, 1884s	−1.4(s) [J_{PW} 109]	33.7(m)	
3a $[Cr(CO)_4\{(PPh_2)_2CHPPh_2Au(PPh_3)\}]ClO_4$	2012vs, 1934s, 1896vs	49.7(s)	37.2 [$J(P_AP_B)$ 323.7]	43.7
3b $[Mo(CO)_4\{(PPh_2)_2CHPPh_2Au(PPh_3)\}]ClO_4$	2024vs, 1939s, 1902vs	26.0(s)	39.2 [$J(P_AP_B)$ 323.5]	43.5
3c $[W(CO)_4\{(PPh_2)_2CHPPh_2Au(PPh_3)]ClO_4$	2020vs, 1929s, 1896vs	−1.0(s) [J_{PW} 109)]	40.0 [$J(P_AP_B)$ 323.2]	43.6
4a $[NBu_4]Cr(CO)_4\{(PPh_2)_2CPPh_2Au(C_6F_5)\}]$	1984s, 1883vs, 1830s	33.9(s)	31.8(m)	
4b $[NBu_4][Mo(CO)_4\{(PPh_2)_2CPPh_2Au(C_6F_5)\}]$	2001s, 1893vs, 1835s	14.9(s)	36.7(m)	
4c $[NBu_4][W(CO)_4\{(PPh_2)_2CPPh_2Au(C_6F_5)\}]$	1995s, 1884vs, 1833s	−7.9(s) [J_{PW} 89]	40.7(m)	
5a $[Cr(CO)_4\{(PPh_2)_2CPPh_2Au(PPh_3)\}]$	1989s, 1872vs, 1842s	40.3(d) [$J(P_AP_X)$ 13.0]	29.8 [$J(P_AP_B)$ 320.5]	43.5
5b $[Mo(CO)_4\{(PPh_2)_2CPPh_2Au(PPh_3)\}]$	2004s, 1896vs, 1846s	19.5(d) [$J(P_AP_X)$ 9.8]	34.7 [$J(P_AP_B)$ 319.6]	43.3
5c $[W(CO)_4\{(PPh_2)_2CPPh_2Au(PPh_3)\}]$	2000s, 1887vs, 1840s	−4.4(s) [J_{PW} 89]	39.2 [$J(P_AP_B)$ 319.5]	43.1
6a $[NBu_4][\{Cr(CO)_4[(PPh_2)_2CPPh_2]\}_2Au]$	1985s, 1867vs, 1836s	33.5(s)	27.5(s)	
6b $[NBu_4][\{Mo(CO)_4[(PPh_2)_2CPPh_2]\}_2Au]$	2001s, 1893vs, 1841s	14.6(s)	32.4(s)	
6c $[NBu_4][\{W(CO)_4[(PPh_2)_2CPPh_2]\}_2Au]$	1996s, 1886vs, 1835s	−8.6(s)	36.3(s)	

[a] In CH_2Cl_2 solutions; v = very, s = strong. [b] In $CDCl_3$ solutions, δ from external 85% H_3PO_4; s = singlet, m = multiplet.

triplets for the methine proton at very low field (δ 6–7) with similar values for $J(P_XH)$ and $J(P_AH)$, and thus appear as quartets. For some of the complexes these resonances overlap with the resonances for the phenyl protons. The ^{19}F NMR spectra of complexes **2** display a pattern typical for pentafluorophenyl rings, with two multiplets for the *o*- and *m*- and a triplet for the *p*-fluorine nuclei.

The positive-ion FAB mass spectra of these compounds show molecular-ion peaks at *m*/*z* = 965 (**1a**, 100), 1009 (**1b**, 17), 1097 (**1c**, 32), 1097 (**2a**, 9), 1141 (**2b**, 14) and 1229 (**2c**, 16%), or molecular-cation peaks at *m*/*z* = 1192 (**3a**, 100), 1236 (**3b**, 18) and 1324 (**3c**, 43%). Other fragmentation peaks correspond to loss of CO groups; in particular, the fragments $[M - 2CO]^+$ and $[M - 4CO]^+$ are always present in high intensity.

The crystal structure of complexes **1b** and **2b** have been determined by X-ray crystallography. The molecule of **1b** is shown in Fig. 1, with atomic coordinates in Table 2 and selected bond lengths and angles in Table 3. Fig. 2 shows the molecule of **2b** (corresponding Tables 4 and 5). In both complexes the molybdenum displays approximately octahedral co-ordination, the main distortion arising from the restricted bite of the phosphine, P–Mo–P 67.77(4) **1b** and 67.72(8)° **2b**. This bite angle is smaller than the 72.2(1)° in square-planar $[Pt\{(PPh_2)_2CHPPh_2\}_2][BF_4]_2$,[9] where both ligands chelate

Table 2 Atomic coordinates (× 10^4) for complex **1b**

Atom	*x*	*y*	*z*
Au	5268.8(2)	4049.5(1)	3454.3(1)
Mo	5007.3(4)	1594.5(2)	3281.8(2)
P(1)	3058.0(12)	3765.0(6)	3436.3(5)
P(2)	3151.7(11)	2346.0(6)	2695.9(5)
P(3)	3629.4(11)	2223.6(6)	3946.6(5)
Cl(1)	7523.2(14)	4364.1(8)	3490.6(7)
C(1)	5616(5)	1206(2)	2547(2)
O(1)	5891(4)	1005(2)	2106(2)
C(2)	6648(5)	2256(3)	3352(2)
O(2)	7693(4)	2548(2)	3392(2)
C(3)	6160(5)	1007(3)	3903(2)
O(3)	6764(4)	647(2)	4266(2)
C(4)	3727(5)	747(3)	3243(2)
O(4)	3147(4)	237(2)	3250(2)
C(5)	2663(4)	2828(2)	3361(2)
C(21)	2428(5)	4037(2)	4113(2)
C(22)	1183(5)	3800(3)	4258(2)
C(23)	739(5)	4039(3)	4773(2)
C(24)	1542(6)	4512(3)	5142(2)
C(25)	2754(6)	4758(3)	5001(2)
C(26)	3202(5)	4521(2)	4488(2)
C(31)	1885(5)	4174(2)	2819(2)
C(32)	2422(5)	4608(3)	2426(2)
C(33)	1530(6)	4954(3)	1971(2)
C(34)	128(6)	4858(3)	1910(3)
C(35)	−419(5)	4427(3)	2297(3)
C(36)	453(5)	4083(3)	2756(2)
C(41)	1542(5)	1912(2)	2351(2)
C(42)	219(5)	2166(3)	2371(2)
C(43)	−946(5)	1801(3)	2099(2)
C(44)	−810(6)	1185(3)	1795(3)
C(45)	494(5)	939(3)	1764(2)
C(46)	1662(5)	1294(2)	2040(2)
C(51)	3470(5)	2952(2)	2111(2)
C(52)	2440(5)	3144(3)	1632(2)
C(53)	2752(6)	3583(3)	1186(2)
C(54)	4072(6)	3832(3)	1210(2)
C(55)	5111(6)	3642(3)	1683(2)
C(56)	4814(5)	3196(3)	2126(2)
C(61)	4323(5)	2711(2)	4628(2)
C(62)	3610(5)	2781(3)	5106(2)
C(63)	4186(6)	3153(3)	5614(2)
C(64)	5469(6)	3472(3)	5645(2)
C(65)	6193(6)	3398(3)	5179(2)
C(66)	5631(5)	3013(2)	4675(2)
C(71)	2273(5)	1689(2)	4185(2)
C(72)	861(5)	1818(3)	4037(2)
C(73)	−83(5)	1353(3)	4225(3)
C(74)	372(5)	777(3)	4551(2)
C(75)	1774(5)	643(3)	4705(2)
C(76)	2718(5)	1094(2)	4518(2)
C(6)	8155(15)	3015(8)	795(7)
Cl(2)	9439(2)	2528.2(12)	506.3(11)
Cl(3)	8608(6)	3773(2)	942(2)
Cl(3′)	7539(5)	3738(3)	550(2)

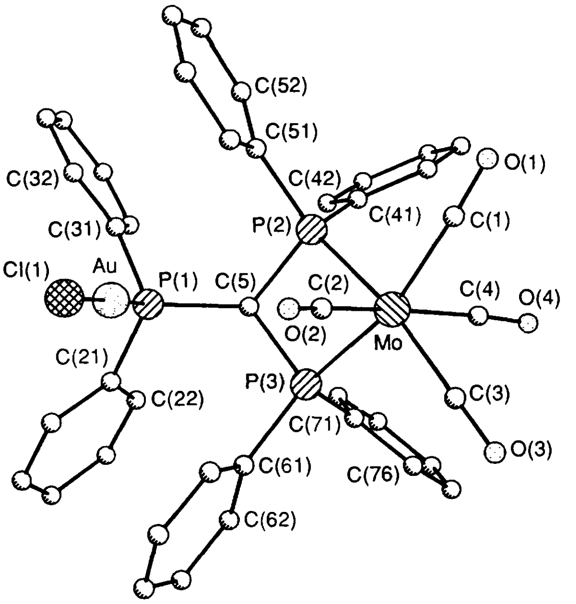


Fig. 1 The molecule of complex **1b** in the crystal, showing the numbering scheme. Hydrogen atoms are omitted for clarity

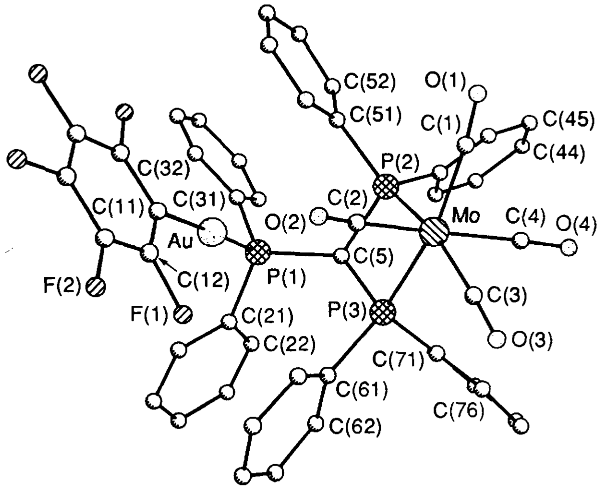


Fig. 2 The molecule of complex **2b** in the crystal, showing the numbering scheme. Hydrogen atoms are omitted for clarity

the metal centre, and is comparable to the smallest values found for complexes containing chelated $Ph_2PCH_2PPh_2$, where the P–M–P angles range from 67 to 74°.[6b] A similar value, 67.3(1)°, is observed in the molybdenum complex $[Mo(CO)_4\{(PPh_2)_2CH_2\}]$.[10] The chelate ring formed by Mo, P(2), P(3) and C(5) is approximately planar, but is folded about the P···P axis by 15.4 (**1b**) and 17.2° (**2b**); the molybdenum atom lies 0.10 (**1b**) and 0.04 Å (**2b**) out of the plane formed by P(2)–P(3)–C(1)–C(3). The strain of the four-membered chelate ring is also reflected in the P(3)–C(5)–P(2) angle of 95.2(2) (**1b**) and 94.1(4)° (**2b**), representing a substantial deviation from ideal tetrahedral geometry at C(5).

The Mo–CO bond distances follow the same pattern in complexes **1b** and **2b**, the shortest being Mo–C *trans* to the phosphorus atoms. However, the differences (maximum 0.06 Å in **1b**, scarcely significant in **2b**) are less pronounced than in the complex $[Mo(CO)_4\{(PPh_2)_2CH_2\}]$[10] with mean distances Mo–CO 2.04 (*cis* P) and 1.93 Å (*trans* P). Presumably the differences in the Mo–C bond lengths arise from differing degrees of π bonding. The Mo–P distances of 2.504(1), 2.494(1) Å in **1b** and 2.496(2), 2.499(3) Å in **2b** are on average slightly shorter than in $[Mo(CO)_4\{(PPh_2)_2CH_2\}]$ [2.535(3) and 2.501(2) Å[10]]. The molybdenum–gold contacts of 4.714 (**1b**) and 4.565 Å (**2b**) are too long to allow any significant bonding interactions.

The co-ordination around the gold atom is essentially linear in both complexes, with P(1)–Au–Cl 178.4(1) (**1a**) and C(11)–Au–P(1) 174.1(3)° (**2b**). The bond lengths at the gold atoms are similar to those found in other gold complexes.[11] The parallel alignment of the linear gold systems with the carbonyl group C(2)–O(2), with torsion angles C(2)–Mo $\cdots$ P(1)–Au 2 (**1b**), 3° (**2b**) [*cf.* P(2)–C(5)–P(1)–Au −56 (**1b**), −55° (**2b**)], allows the Au $\cdots$ C(2) contacts 3.707 and 3.441 Å respectively.

Tris(diphenylphosphino)methanide Complexes.—The reaction of a solution of complexes **2** in dichloromethane with [NBu$_4$][acac] (acac = acetylacetonate) under a nitrogen atmosphere results in deprotonation of the phosphine ligand and formation of the methanide compounds [NBu$_4$][M(CO)$_4${(PPh$_2$)$_2$CPPh$_2$Au(C$_6$F$_5$)}] **4a**–**4c**. The acetylacetonate ligand is displaced as acetylacetone. The reagent [NBu$_4$][acac] is useful because it gives clean reactions and performs both deprotonation and introduction of the cation in one step. In a similar

Table 3 Selected bond lengths (Å) and angles (°) for complex **1b**

Au–P(1)	2.225(1)	Au–Cl(1)	2.275(1)
Mo–C(3)	1.987(5)	Mo–C(1)	2.000(5)
Mo–C(2)	2.029(5)	Mo–C(4)	2.042(5)
Mo–P(3)	2.494(1)	Mo–P(2)	2.504(1)
P(1)–C(31)	1.818(5)	P(1)–C(21)	1.819(5)
P(1)–C(5)	1.835(4)	P(2)–C(51)	1.823(5)
P(2)–C(41)	1.830(5)	P(2)–C(5)	1.891(4)
P(3)–C(61)	1.823(5)	P(3)–C(71)	1.830(4)
P(3)–C(5)	1.881(4)		
P(1)–Au–Cl(1)	178.4(1)	C(3)–Mo–C(1)	99.2(2)
C(3)–Mo–C(2)	87.4(2)	C(1)–Mo–C(2)	87.1(2)
C(3)–Mo–C(4)	81.3(2)	C(1)–Mo–C(4)	86.5(2)
C(2)–Mo–C(4)	166.0(2)	C(3)–Mo–P(3)	98.6(2)
C(1)–Mo–P(3)	161.5(1)	C(2)–Mo–P(3)	99.01(14)
C(4)–Mo–P(3)	90.90(13)	C(3)–Mo–P(2)	165.2(1)
C(1)–Mo–P(2)	94.01(14)	C(2)–Mo–P(2)	100.0(1)
C(4)–Mo–P(2)	92.87(14)	P(3)–Mo–P(2)	67.77(4)
C(31)–P(1)–C(21)	104.9(2)	C(31)–P(1)–C(5)	104.7(2)
C(21)–P(1)–C(5)	105.1(2)	C(31)–P(1)–Au	113.0(2)
C(21)–P(1)–Au	112.7(2)	C(5)–P(1)–Au	115.4(1)
C(51)–P(2)–C(41)	103.0(2)	C(51)–P(2)–C(5)	111.3(2)
C(41)–P(2)–C(5)	103.9(2)	C(51)–P(2)–Mo	123.1(2)
C(41)–P(2)–Mo	117.1(2)	C(5)–P(2)–Mo	97.03(13)
C(61)–P(3)–C(71)	102.7(2)	C(61)–P(3)–C(5)	110.2(2)
C(71)–P(3)–C(5)	104.4(2)	C(61)–P(3)–Mo	126.3(2)
C(71)–P(3)–Mo	113.8(1)	C(5)–P(3)–Mo	97.61(14)
P(1)–C(5)–P(3)	117.5(2)	P(1)–C(5)–P(2)	118.1(2)
P(3)–C(5)–P(2)	95.2(2)		

Table 5 Selected bond lengths (Å) and angles (°) for complex **2b**

Au–C(11)	2.051(10)	Au–P(1)	2.274(2)
Mo–C(3)	1.971(11)	Mo–C(1)	2.027(13)
Mo–C(2)	2.037(12)	Mo–C(4)	2.043(12)
Mo–P(2)	2.496(2)	Mo–P(3)	2.499(3)
P(1)–C(31)	1.805(11)	P(1)–C(21)	1.822(11)
P(1)–C(5)	1.830(10)	P(2)–C(51)	1.823(10)
P(2)–C(41)	1.832(10)	P(2)–C(5)	1.900(10)
P(3)–C(71)	1.817(10)	P(3)–C(61)	1.830(10)
P(3)–C(5)	1.902(9)		
C(11)–Au–P(1)	174.1(3)	C(3)–Mo–C(1)	100.7(5)
C(3)–Mo–C(2)	85.0(5)	C(1)–Mo–C(2)	83.8(5)
C(3)–Mo–C(4)	83.8(5)	C(1)–Mo–C(4)	89.6(5)
C(2)–Mo–C(4)	165.7(4)	C(3)–Mo–P(2)	163.3(4)
C(1)–Mo–P(2)	95.3(4)	C(2)–Mo–P(2)	101.6(3)
C(4)–Mo–P(2)	91.7(3)	C(3)–Mo–P(3)	96.3(4)
C(1)–Mo–P(3)	162.9(4)	C(2)–Mo–P(3)	97.6(3)
C(4)–Mo–P(3)	92.4(3)	P(2)–Mo–P(3)	67.72(8)
C(31)–P(1)–C(21)	104.1(5)	C(31)–P(1)–C(5)	105.3(5)
C(21)–P(1)–C(5)	106.5(4)	C(31)–P(1)–Au	110.6(3)
C(21)–P(1)–Au	111.3(3)	C(5)–P(1)–Au	118.0(3)
C(51)–P(2)–C(41)	102.7(4)	C(51)–P(2)–C(5)	111.5(4)
C(41)–P(2)–C(5)	104.8(4)	C(51)–P(2)–Mo	123.5(3)
C(41)–P(2)–Mo	115.4(3)	C(5)–P(2)–Mo	97.7(3)
C(71)–P(3)–C(61)	101.6(4)	C(71)–P(3)–C(5)	106.5(4)
C(61)–P(3)–C(5)	109.3(4)	C(71)–P(3)–Mo	115.4(4)
C(61)–P(3)–Mo	125.3(3)	C(5)–P(3)–Mo	97.5(3)
P(1)–C(5)–P(2)	115.0(5)	P(1)–C(5)–P(3)	115.4(5)
P(2)–C(5)–P(3)	94.1(4)	C(12)–C(11)–C(16)	114.6(10)

Table 4 Atomic coordinates (× 10^4) for complex **2b**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au	3 017.6(1)	2 226.8(3)	4 995.9(1)	C(31)	4 247(10)	2 444(9)	6 835(6)
Mo	6 863.2(7)	2 883.6(7)	4 213.5(4)	C(32)	3 623(9)	1 392(8)	6 859(6)
P(1)	4 119(2)	3 244(2)	5 949.6(12)	C(33)	3 653(12)	794(10)	7 544(6)
P(2)	6 793(2)	2 449(2)	5 598.2(12)	C(34)	4 289(13)	1 211(10)	8 217(7)
P(3)	5 905(2)	4 481(2)	4 899.5(13)	C(35)	4 934(15)	2 246(10)	8 187(6)
C(1)	7 631(12)	1 356(12)	3 962(7)	C(36)	4 920(13)	2 869(9)	7 517(5)
O(1)	7 989(11)	471(9)	3 879(7)	C(41)	8 253(9)	2 704(8)	6 217(5)
C(2)	5 244(11)	2 146(9)	3 735(6)	C(42)	8 406(10)	3 399(10)	6 857(6)
O(2)	4 431(8)	1 708(8)	3 380(4)	C(43)	9 559(12)	3 520(12)	7 278(7)
C(3)	6 849(12)	3 687(12)	3 225(6)	C(44)	10 583(11)	2 955(11)	7 053(6)
O(3)	6 816(12)	4 238(12)	2 665(5)	C(45)	10 449(11)	2 246(13)	6 420(7)
C(4)	8 616(12)	3 572(11)	4 426(6)	C(46)	9 290(10)	2 136(10)	6 019(6)
O(4)	9 579(9)	3 972(11)	4 492(6)	C(51)	6 264(9)	1 077(8)	5 949(5)
C(5)	5 720(9)	3 672(8)	5 821(5)	C(52)	6 640(10)	678(9)	6 680(6)
C(11)	1 895(10)	1 273(8)	4 215(5)	C(53)	6 271(12)	−412(10)	6 908(7)
C(12)	1 398(10)	1 663(10)	3 515(6)	C(54)	5 512(12)	−1 077(11)	6 402(6)
C(13)	598(12)	1 015(11)	3 008(6)	C(55)	5 128(12)	−693(9)	5 678(7)
C(14)	267(12)	−70(9)	3 201(6)	C(56)	5 515(10)	387(8)	5 440(6)
C(15)	757(12)	−496(10)	3 897(7)	C(61)	4 435(9)	5 210(7)	4 569(5)
C(16)	1 540(10)	173(9)	4 386(6)	C(62)	4 109(9)	6 253(8)	4 883(5)
F(1)	1 652(11)	2 732(7)	3 278(5)	C(63)	3 013(10)	6 789(9)	4 601(6)
F(2)	110(10)	1 460(10)	2 326(4)	C(64)	2 212(12)	6 289(9)	4 019(6)
F(3)	−538(8)	−684(8)	2 730(5)	C(65)	2 528(11)	5 236(10)	3 712(7)
F(4)	417(9)	−1 555(6)	4 106(7)	C(66)	3 655(11)	4 733(10)	3 981(6)
F(5)	1 966(8)	−295(7)	5 074(5)	C(71)	6 931(10)	5 693(8)	5 163(5)
C(21)	3 297(9)	4 554(9)	6 165(5)	C(72)	7 258(11)	6 108(9)	5 891(6)
C(22)	3 808(11)	5 378(8)	6 670(6)	C(73)	8 012(13)	7 080(10)	6 017(8)
C(23)	3 114(12)	6 341(10)	6 841(6)	C(74)	8 417(15)	7 642(11)	5 418(7)
C(24)	1 885(11)	6 455(10)	6 504(7)	C(75)	8 080(17)	7 271(11)	4 686(9)
C(25)	1 373(11)	5 636(10)	5 989(7)	C(76)	7 388(14)	6 259(11)	4 566(7)
C(26)	2 076(12)	4 678(10)	5 833(7)				

Table 6 Atomic coordinates (× 10^4) for complex **4b**

Atom	x	y	z
Au	2835.0(1)	2145.1(1)	1366.1(1)
Mo	922.4(3)	1282.9(3)	3268.5(3)
P(1)	1584.6(8)	2209.2(9)	1142.4(8)
P(2)	1777.5(8)	1238.3(8)	2485.3(8)
P(3)	535.0(8)	2066.8(8)	2166.5(8)
C(1)	1454(4)	654(4)	4078(4)
O(1)	1761(3)	286(3)	4535(3)
C(2)	1521(3)	2100(4)	3835(3)
O(2)	1834(3)	2551(3)	4186(3)
C(3)	139(4)	1543(4)	3683(3)
O(3)	−329(3)	1710(3)	3922(3)
C(4)	288(4)	440(4)	2821(3)
O(4)	−89(3)	−44(3)	2625(3)
C(5)	1311(3)	1902(3)	1871(3)
C(11)	3974(3)	2153(3)	1617(3)
C(12)	4374(3)	2756(3)	1843(3)
C(13)	5137(3)	2776(3)	2093(3)
C(14)	5510(3)	2155(3)	2126(4)
C(15)	5140(3)	1536(4)	1904(4)
C(16)	4378(3)	1551(3)	1645(4)
F(1)	4029(2)	3382(2)	1842(2)
F(2)	5513(2)	3378(2)	2306(2)
F(3)	6259(2)	2155(2)	2388(3)
F(4)	5528(2)	928(2)	1935(3)
F(5)	4037(2)	922(2)	1435(2)
C(21)	1295(3)	3126(3)	955(3)
C(22)	1810(4)	3669(3)	1146(3)
C(23)	1589(4)	4369(4)	1021(4)
C(24)	845(4)	4524(4)	714(4)
C(25)	330(4)	3993(4)	499(4)
C(26)	555(4)	3300(4)	612(3)
C(31)	1073(3)	1797(3)	290(3)
C(32)	1166(4)	2076(4)	−331(3)
C(33)	801(5)	1782(5)	−995(4)
C(34)	346(4)	1205(5)	−1040(4)
C(35)	252(4)	932(4)	−424(4)
C(36)	619(4)	1221(4)	246(4)
C(41)	1848(3)	395(3)	2047(3)
C(42)	2074(4)	348(3)	1435(3)
C(43)	2144(4)	−298(3)	1140(4)
C(44)	2004(4)	−912(3)	1449(3)
C(45)	1782(4)	−878(3)	2052(4)
C(46)	1705(3)	−233(3)	2346(3)
C(51)	2766(3)	1463(3)	2866(3)
C(52)	3321(3)	965(3)	2926(4)
C(53)	4053(3)	1132(4)	3249(4)
C(54)	4250(4)	1792(3)	3543(4)
C(55)	3706(3)	2290(4)	3492(4)
C(56)	2973(3)	2131(3)	3156(3)
C(61)	458(3)	2991(3)	2417(3)
C(62)	−164(3)	3178(3)	2624(4)
C(63)	−222(4)	3838(4)	2891(4)
C(64)	339(4)	4334(4)	2966(4)
C(65)	964(4)	4138(4)	2784(4)
C(66)	1028(4)	3473(3)	2518(3)
C(71)	−335(3)	1929(3)	1442(3)
C(72)	−554(3)	1234(4)	1250(3)
C(73)	−1203(4)	1075(4)	717(4)
C(74)	−1660(4)	1617(4)	365(4)
C(75)	−1456(4)	2308(4)	533(4)
C(76)	−800(3)	2464(3)	1070(3)
N	2850(3)	4918(3)	7911(3)
C(81)	2327(3)	5224(4)	7224(4)
C(82)	2651(4)	5361(4)	6613(4)
C(83)	2061(5)	5666(5)	5989(4)
C(84)	2296(6)	5764(6)	5336(4)
C(85)	2398(4)	4721(4)	8405(4)
C(86)	2034(4)	5328(4)	8674(4)
C(87)	1619(4)	5055(5)	9181(4)
C(88)	987(5)	4585(6)	8828(5)
C(89)	3446(3)	5460(3)	8248(3)
C(90)	3967(4)	5271(4)	8985(4)
C(91)	4557(4)	5841(4)	9259(4)
C(92)	4258(5)	6564(4)	9362(4)
C(93)	3219(3)	4248(3)	7757(4)
C(94)	2717(4)	3677(4)	7331(4)
C(95)	3166(4)	3031(4)	7286(4)
C(96)	2711(4)	2403(4)	6927(5)
C(6)	8361(5)	2212(5)	4728(5)
Cl(1)	7642(2)	2293.5(14)	3915.8(13)
Cl(2)	8399(2)	1362.2(14)	5080.6(13)
C(7)	5638(6)	1540(6)	−244(6)
Cl(3)	4821(2)	1352(3)	−100(2)
Cl(4)	6360(2)	1300(4)	416(3)

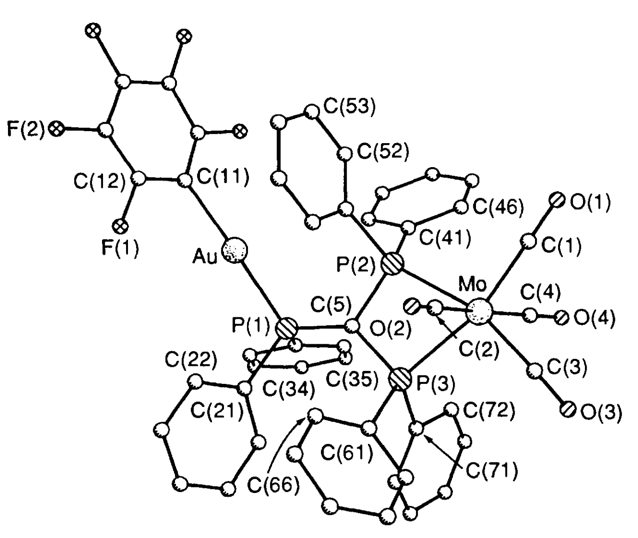


Fig. 3 The anion of complex **4b** in the crystal, showing the numbering scheme. Hydrogen atoms are omitted for clarity

manner, treatment of complexes **3** with [NBu$_4$][acac] affords the neutral methanide derivatives [M(CO)$_4${(PPh$_2$)$_2$CPPh$_2$Au(PPh$_3$)}] **5a**–**5c** along with [NBu$_4$][ClO$_4$]. These compounds can also be obtained from the reaction of the starting material [M(CO)$_4${(PPh$_2$)$_2$CHPPh$_2$}] with [Au(acac)(PPh$_3$)], a reagent that can deprotonate a potential ligand (forming acetylacetone) and allow it to co-ordinate to the remaining Au(PPh$_3$)$^+$ fragment;[7,12] in this case the additional co-ordination could *a priori* occur through the carbon or the phosphorus atom, but, as in bis(diphenylphosphino)methanide complexes,[13] the latter is observed.

Finally, the trinuclear derivatives [NBu$_4$][{Mo(CO)$_4$[(PPh$_2$)$_2$CPPh$_2$]}$_2$Au] **6a**–**6c** are synthesized by reaction of [M(CO)$_4${(PPh$_2$)$_2$CHPPh$_2$}] with [NBu$_4$][Au(acac)$_2$], in the ratio 2:1, in dichloromethane under a nitrogen atmosphere. Complexes **4**–**6** are pale yellow or yellow air-stable solids. Their acetone solutions are neutral (**5**) or show conductivities of 1:1 electrolytes (**4** and **6**). In the IR spectra the same pattern in the CO region is observed, although at lower energy.

The ^{31}P-{^{1}H} NMR spectra of these complexes correspond to AX$_2$ systems for **4** and **6**, without coupling between the different phosphorus atoms (P–Au and P$_2$–M). In the spectra of **5** an ABX$_2$ system is observed, but now small coupling constants of 13.0 and 9.8 Hz are observed between the A and X phosphorus nuclei, for **5a** and **5b**, however J_{AX} must be very small for **5c** and is not observed. Probably, the presence of a methanide carbon which makes the P–C distances smaller leads to a higher coupling constant.

In the positive-ion FAB mass spectra of complexes **4** and **5** the molecular-ion peaks appear at m/z = 1095 (**4a**, 67), 1141 (**4b**, 22), 1227 (**4c**, 57), 1191 (**5a**, 17), 1236 (**5b**, 43) and 1323 (**5c**, 47%). In the negative-ion FAB mass spectra of **6** the molecular-anion peak is also present at m/z = 1660 (**6a**, 100), 1748 (**6b**, 14) and 1924 (**6c**, 48%).

The crystal structure of complex **4b** has been established by X-ray methods. The cation is shown in Fig. 3, with atomic coordinates in Table 6 and selected bond lengths and angles in Table 7. Again the co-ordination of the molybdenum atom, by the two phosphorus atoms of the ligand and the four carbon atoms of the carbonyl groups, deviates from a regular octahedral arrangement. The bite of the phosphine, P(3)–Mo–P(2) 65.14(5)°, is even smaller than those found in complexes **1b** and **2b**. The four-membered ring is more planar than in **1b** and **2b**, with a fold angle of only 6.8° about the P ··· P axis; atoms Mo, P(2), P(3), C(1), C(3) and C(5) are coplanar to within 0.043 Å. The Mo atom lies 0.06 Å out of the plane formed by P(2), P(3), C(1) and C(3).

The P–C(5) bond lengths lie in the range 1.761(6)–1.775(6) Å and are shorter than the P–C distances either in free $(Ph_2P)_3CH$[14] [1.867(1)–1.877(1) Å] or in complexes **1b** and **2b**. This difference can be attributed to a degree of multiple P–C bonding in the methanide ligand. The angles around the central methanide carbon fall in the range 101.2(3)–133.6(3)°. The restricted bite of the ligand is responsible for the distortions from the ideal value of 120° for sp^2 hybridization, the chelating angle P(3)–C(5)–P(2) is the narrowest. Atom C(5) lies 0.04 Å out of the plane formed by the three phosphorus atoms.

The gold atom is almost linearly co-ordinated, with C(11)–Au–P(1) 175.7(2). The molybdenum–gold distance is far longer than in **2b**, 6.172 Å, which is partly a consequence of the increased planarity of the unit MP_2CP but more directly associated with a rotation about the P(1)–C(5) bond; torsion angles P(2)–C(5)–P(1)–Au −30 and C(2)–Mo ··· P(1)–Au 64°.

Table 7 Selected bond lengths (Å) and angles (°) for complex **4b**

Au–C(11)	2.066(6)	Au–P(1)	2.283(2)
Mo–C(3)	1.966(7)	Mo–C(1)	1.991(8)
Mo–C(4)	2.028(7)	Mo–C(2)	2.034(7)
Mo–P(3)	2.534(2)	Mo–P(2)	2.557(2)
P(1)–C(5)	1.761(6)	P(1)–C(21)	1.822(6)
P(1)–C(31)	1.828(6)	P(2)–C(5)	1.775(6)
P(2)–C(41)	1.835(6)	P(2)–C(51)	1.844(6)
P(3)–C(5)	1.771(6)	P(3)–C(61)	1.833(6)
P(3)–C(71)	1.836(6)		
C(11)–Au–P(1)	175.7(2)	C(3)–Mo–C(1)	94.8(3)
C(3)–Mo–C(4)	87.2(3)	C(1)–Mo–C(4)	87.9(3)
C(3)–Mo–C(2)	87.2(3)	C(1)–Mo–C(2)	87.6(3)
C(4)–Mo–C(2)	172.5(3)	C(3)–Mo–P(3)	98.5(2)
C(1)–Mo–P(3)	166.2(2)	C(4)–Mo–P(3)	96.5(2)
C(2)–Mo–P(3)	89.3(2)	C(3)–Mo–P(2)	163.4(2)
C(1)–Mo–P(2)	101.4(2)	C(4)–Mo–P(2)	96.7(2)
C(2)–Mo–P(2)	90.0(2)	P(3)–Mo–P(2)	65.14(5)
C(5)–P(1)–C(21)	109.4(3)	C(5)–P(1)–C(31)	113.1(3)
C(21)–P(1)–C(31)	100.3(3)	C(5)–P(1)–Au	112.1(2)
C(21)–P(1)–Au	108.7(2)	C(31)–P(1)–Au	112.5(2)
C(5)–P(2)–C(41)	113.0(3)	C(5)–P(2)–C(51)	110.1(3)
C(41)–P(2)–C(51)	100.3(3)	C(5)–P(2)–Mo	96.1(2)
C(41)–P(2)–Mo	117.4(2)	C(51)–P(2)–Mo	120.4(2)
C(5)–P(3)–C(61)	113.5(3)	C(5)–P(3)–C(71)	111.4(3)
C(61)–P(3)–C(71)	102.4(3)	C(5)–P(3)–Mo	97.0(2)
C(61)–P(3)–Mo	110.8(2)	C(71)–P(3)–Mo	122.1(2)
P(1)–C(5)–P(3)	133.6(3)	P(1)–C(5)–P(2)	125.0(3)
P(3)–C(5)–P(2)	101.2(3)	C(16)–C(11)–C(12)	115.6(6)

Experimental

All reactions were performed under dry nitrogen, and all solvents were dried by standard methods. Proton, ^{19}F and ^{31}P-{^{1}H} NMR spectra were recorded on a Varian 300 Unity spectrometer in $CDCl_3$, infrared spectra on a Perkin-Elmer 883 spectrophotometer. Conductivities were measured in *ca.* 5×10^{-4} mol dm^{-3} solutions with a Philips 9509 conductimeter. Carbon and H analyses were carried out with a Perkin-Elmer 240C microanalyser. Mass spectra were recorded on a VG Autospec instrument, with the FAB technique, using 3-nitrobenzyl alcohol as matrix. The yields, analyses, melting points and conductivities for the new complexes are listed in Table 8. The compounds $[M(CO)_6]$ and $(Ph_2P)_3CH$ were obtained from commercial suppliers and used without further purification. The following compounds were prepared according to the published procedures: [AuCl(tht)],[15] $[Au(tht)(PPh_3)]ClO_4$,[16] $[Au(acac)(PPh_3)]$,[17] $[NBu_4][Au(acac)_2]$,[7a] and $[M(CO)_4\{(PPh_2)_2CHPPh_2\}]$.[3b,18]

Syntheses.—$[M(CO)_4\{(PPh_2)_2CHPPh_2AuCl\}]$ (M = Cr **1a**, Mo **1b** *or W* **1c**). To a solution of 0.3 mmol of $[M(CO)_4\{(PPh_2)_2CHPPh_2\}]$ (M = Cr, 0.220; Mo, 0.233; or W, 0.259 g) in dichloromethane (20 cm^3) was added [AuCl(tht)] (0.100 g, 0.3 mmol). After stirring for 1 h at room temperature, the solvent was removed *in vacuo* from the solution and diethyl ether was added to give a pale yellow (**1a**, **1c**) or white (**1b**) solid, which was filtered off and washed with diethyl ether.

$[M(CO)_4\{(PPh_2)_2CHPPh_2Au(C_6F_5)\}]$ (M = Cr **2a**, Mo **2b** or W **2c**). To a dichloromethane solution of $[M(CO)_4\{(PPh_2)_2CHPPh_2\}]$ prepared as above was added $[Au(C_6F_5)(tht)]$ (0.136 g, 0.3 mmol). The solution remained pale yellow (**2a**, **2c**) or colourless (**2b**) and after 2 h of stirring, evaporation of the solvent *in vacuo* followed by addition of diethyl ether gave a pale yellow (**2a**, **2c**) or white (**2b**) powder, which was filtered off, washed with diethyl ether and dried *in vacuo*.

$[M(CO)_4\{(PPh_2)_2CHPPh_2Au(PPh_3)\}]ClO_4$ (M = Cr **3a**, Mo **3b** *or* W **3c**). To a dichloromethane solution of $[M(CO)_4\{(PPh_2)_2CHPPh_2\}]$ prepared as above was added $[Au(tht)(PPh_3)]ClO_4$ (0.194 g, 0.3 mmol). After 2 h of stirring the solvent was removed from the yellow solution. The product was obtained as a yellow (**3a**, **3c**) or pale yellow (**3b**) solid by adding diethyl ether and separated by filtration.

$[NBu_4][M(CO)_4\{(PPh_2)_2CPPh_2Au(C_6F_5)\}]$ (M = Cr **4a**, Mo **4b** *or* W **4c**). Addition of a slight excess of $[NBu_4][acac]$ (0.123 g, 0.36 mmol) to 0.3 mmol of complex **2a** (0.329 g), **2b** (0.342 g) or **2c** (0.369 g) in dichloromethane (25 cm^3) afforded **4a**, **4b** or **4c** after 1 d of stirring at room temperature. The solvent was then partially removed *in vacuo*, whereupon the products were obtained by addition of hexane as pale yellow (**4a**, **4b**) or yellow (**4c**) solids.

$[M(CO)_4\{(PPh_2)_2CPPh_2Au(PPh_3)\}]$ (M = Cr **5a**, Mo **5b** *or* W **5c**). *Method* 1. Reaction of $[Au(acac)(PPh_3)]$ (0.200 g, 0.36 mmol) with 0.3 mmol of $[M(CO)_4\{(PPh_2)_2CHPPh_2\}]$ (M = Cr, 0.220; Mo, 0.233; or W, 0.259 g) in dichloromethane (25 cm^3) produced after 1 d a yellow (**5a**, **5b**) or colourless (**5c**) solution, which was filtered through Celite to remove a small quantity of solid. The solution was concentrated under reduced pressure and addition of hexane gave a yellow precipitate, which was filtered off and washed with hexane.

Method 2. To a dichloromethane solution (25 cm^3) of 0.3 mmol of complex **3a** (0.387), **3b** (0.400), or **3c** (0.427 g) was added a slight excess of $[NBu_4][acac]$ (0.123 g, 0.36 mmol). After stirring for 1 d at room temperature the solution was concentrated *in vacuo* and $[NBu_4][ClO_4]$ precipitated by addition of diethyl ether (10 cm^3) and filtered off; the solvent was evaporated and the products precipitated with hexane. This method leads to lower yields because of the partial solubility of the complexes in diethyl ether.

$[NBu_4][\{M(CO)_4[(PPh_2)_2CPPh_2]\}_2Au]$ (M = Cr **6a**, Mo **6b** *or* W **6c**). To a solution of 0.3 mmol of $[M(CO)_4\{(PPh_2)_2CHPPh_2\}]$ (M = Cr, 0.220; Mo, 0.233; or W, 0.259 g) in dichloromethane (25 cm^3) was added $[NBu_4][Au(acac)_2]$

Table 8 Analytical data and some properties of complexes **1a**–**6c**

Compound	Yield (%)	Analysis (%)[a] C	H	N	M.p. (°C)[b]	Λ_M[c]/ S cm^2 mol^{-1}
1a	65	50.75	3.40		227 (decomp.)	2
		(51.05)	(3.25)			
1b	87	48.55	3.35		210 (decomp)	1
		(48.80)	(3.10)			
1c	70	45.30	3.20		205	1
		(44.90)	(2.85)			
2a	62	51.60	2.90		240 (decomp.)	3
		(51.50)	(2.85)			
2b	82	49.35	2.65		224 (decomp.)	1
		(49.50)	(2.75)			
2c	76	46.10	2.55		196 (decomp.)	5
		(45.95)	(2.55)			
3a	82	54.65	3.95		164	121
		(54.90)	(3.60)			
3b	86	52.75	3.55		150 (decomp.)	153
		(53.05)	(3.45)			
3c	58	49.75	3.45		157	149
		(49.80)	(3.25)			
4a	81	56.50	5.05	0.80	136	95
		(56.55)	(4.95)	(1.05)		
4b	88	55.25	5.05	1.20	108	130
		(54.80)	(4.80)	(1.0)		
4c	90	51.25	4.55	1.15	172	124
		(51.50)	(4.55)	(0.95)		
5a	76	59.15	4.05		146 (decomp.)	2
		(59.50)	(3.80)			
5b	67	57.0	3.90		213 (decomp.)	1
		(57.40)	(3.65)			
5c	72	53.70	3.45		212 (decomp.)	2
		(53.60)	(3.45)			
6a	77	61.55	5.20	0.90	99	88
		(61.85)	(5.10)	(0.75)		
6b	76	58.90	5.10	0.95	125	104
		(59.15)	(4.85)	(0.70)		
6c	79	54.05	4.60	0.85	110	116
		(54.35)	(4.45)	(0.65)		

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

Table 9 Details of data collection and structure refinement for complexes **1b**, **2b** and **4b**

	1b·CH_2Cl_2	**2b**	**4b**·$2CH_2Cl_2$
Chemical formula	$C_{42}H_{33}AuCl_3MoO_4P_3$	$C_{47}H_{31}AuF_5MoO_4P_3$	$C_{65}H_{70}AuCl_4F_5MoNO_4P_3$
M	1093.85	1140.53	1551.84
T/°C	−130	−100	−95
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	Pc	$P2_1/n$
a/Å	9.789(3)	10.752(3)	19.000(4)
b/Å	19.121(4)	11.627(4)	18.915(5)
c/Å	22.551(5)	17.584(4)	19.592(4)
β/°	100.10(3)	96.40(2)	107.93(2)
U/Å^3	4156(2)	2184.5(11)	6699(3)
Z	4	2	4
D_c/Mg m^{-3}	1.748	1.734	1.539
$F(000)$	2136	1112	3112
μ(Mo-Kα)/mm^{-1}	4.18	3.82	2.66
Crystal size/mm	0.80 × 0.35 × 0.15	0.50 × 0.40 × 0.10	0.55 × 0.25 × 0.15
Transmission	0.62–0.80	0.58–1.0	0.73–0.9
$2\theta_{max}$/°	50	55	50
Reflections measured	9011	10 212	12 255
Unique reflections	7354	9285	11 794
R_{int}	0.027	0.076	0.028
$R[F, F > 4\sigma(F)]$	0.032	0.051	0.041
$wR(F^2$, all reflections)*	0.073	0.146	0.109
No. of parameters	491	551	747
No. of restraints	382	479	619
S	1.068	1.031	1.03
Maximum Δ/σ	0.001	< 0.001	0.001
Maximum $\Delta\rho$/e Å^{-3}	1.2	2.14	1.68

* $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $3P = F_o^2 + 2F_c^2$ and a and b are constants.

(0.096 g, 0.15 mmol). After 1 d of stirring the solution was filtered through Celite to remove a small quantity of solid and the resulting solution was concentrated *in vacuo*. The products were obtained as yellow (**6a**, **6c**) or pale yellow (**6b**) solids by addition of hexane and then filtered off and washed with hexane.

Crystal Structure Determinations.—Crystals were mounted in inert oil (type RS3000, donated by Riedel de Haën) on glass fibres. Data were collected using monochromated Mo-Kα radiation (λ = 0.710 73 Å). Diffractometer type: Siemens R3 (**2b**, **4b**), Stoe STADI-4 (**1b**), both with Siemens LT-2 low-temperature attachment. Scan type: ω (**2b**, **4b**), ω–θ (**1b**). Cell constants were refined from setting angles (**2b**, **4b**) or $\pm\omega$ angles (**1b**) of *ca.* 50 reflections in the range 2θ 20–23°. Absorption corrections were applied on the basis of ψ scans.

Structures were solved by the heavy-atom method and refined anisotropically on F^2 using the program SHELXL 93.[19] Hydrogen atoms were included using a riding model. Special features of refinement: **1b** crystallizes with one molecule of dichloromethane, disordered over two positions; **2b** was refined as an enantiomeric twin, the origin being fixed by the method of Flack and Schwarzenbach;[20] **4b** crystallizes with two molecules of dichloromethane. Other data are collected in Table 9.

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

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