Replacement of Hydrido-ligands in Triruthenium Complexes by Triphenylphosphinegold Groups. Crystal Structures of [$AuRu_3$(μ-COMe)$(CO)_{10}(PPh_3)$], [$AuRu_3(\mu$-$H)_2(\mu_3$-COMe)$(CO)_9(PPh_3)$], and [$Au_3Ru_3(\mu_3$-COMe)$(CO)_9(PPh_3)_3$]†

Lawrence W. Bateman, Michael Green, Kevin A. Mead, Rona M. Mills, Ian D. Salter, F. Gordon A. Stone, and Peter Woodward
Department of Inorganic Chemistry, The University, Bristol BS8 1TS

The compound [$AuMe(PPh_3)$] reacts under mild conditions (diethyl ether, ambient temperatures) with the compounds [$M_3(\mu$-H)(μ-COMe)$(CO)_{10}$] and [$Ru_3(\mu$-$H)_3(\mu_3$-COMe)$(CO)_9$] to give the complexes [$AuM_3(\mu$-COMe)$(CO)_{10}(PPh_3)$] [M = Fe (1) or Ru (2)], [$AuRu_3(\mu$-$H)_2(\mu_3$-COMe)$(CO)_9(PPh_3)$] (3), [$Au_2Ru_3(\mu$-H)$(\mu_3$-COMe)$(CO)_9(PPh_3)_2$] (4), and [$Au_3Ru_3(\mu_3$-COMe)$(CO)_9(PPh_3)_3$] (5). Spectroscopic properties of the new species are reported and discussed, and the structures of (2), (3), and (5) have been established by *X*-ray diffraction studies. The structure of [$AuRu_3(\mu$-COMe)$(CO)_{10}(PPh_3)$] (2) can be regarded as a molecule of [$Ru_3(\mu$-H)(μ-COMe)$(CO)_{10}$] in which the bridging hydrido-ligand is replaced by a bridging $AuPPh_3$ group, thus producing a ' butterfly ' metal atom core (interplanar angle 117°) with the gold atom occupying a ' wing-tip ' site. The COMe ligand bridges the body of the butterfly on the convex side. The Au–Ru bonds [2.760(2) and 2.762(2) Å] are *ca.* 0.1 Å shorter than the non-bridged Ru–Ru bonds [2.845(2) and 2.839(3) Å] but the bridged Ru–Ru bond is significantly longer at 2.879(2) Å. Crystals of (2) are triclinic, space group $P\bar{1}$, and the asymmetric unit comprises two molecules of complex. The structure has been refined to *R* 0.075 for 4 868 intensities measured to $2\theta = 40°$ at 220 K. In [$AuRu_3(\mu$-$H)_2(\mu_3$-COMe)$(CO)_9(PPh_3)$] (3) the carbyne ligand triply bridges an equilateral triangle [Ru–Ru 2.865(2)—2.879(2) Å] of ruthenium atoms, while on the opposite side of the triangle there are two edge-bridging hydrido-ligands and one edge-bridging $AuPPh_3$ group. Each ruthenium atom carries three terminal carbonyl ligands, giving octahedral co-ordination if the Ru–Ru bonds are ignored. The molecule has approximate C_s symmetry, not required crystallographically. The structure is triclinic, space group $P\bar{1}$, and has been refined to *R* 0.042 for 3 247 intensities measured to $2\theta = 45°$ at 293 K. The complex [$Au_3Ru_3(\mu_3$-COMe)$(CO)_9(PPh_3)_3$] (5) crystallises with half a molecule of CH_2Cl_2 per molecule of (5) incorporated into the crystals. Again the carbyne ligand triply bridges a near-equilateral triangle of Ru atoms [Ru–Ru 2.895(3)—2.929(2) Å], but on the opposite side of this triangle one gold atom is co-ordinated to form a tetrahedron [Au–Ru 2.818(2), 2.825(2), and 2.987(2) Å]. The two faces of this tetrahedron adjacent to the long Au–Ru bond are each further triply bridged by $AuPPh_3$ ligands. The two Au–Au distances in this bicapped tetrahedral structure are 2.930(1) and 3.010(1) Å; the difference between these probably arises from the packing of the bulky triphenylphosphine ligands. Crystals of (5) are monoclinic, space group $P2_1/n$, and the structure has been refined to *R* 0.050 for 4 279 intensities measured to $2\theta = 45°$ at 293 K.

Compounds in which $AuPR_3$ groups are bonded to transition elements were first obtained twenty years ago,[1] but until recently interest in such species lapsed. However, during the last five years, several metal-cluster carbonyl compounds have been described with structures having $AuPR_3$ groups edge- or face-bridging metal–metal bonds. It is useful to relate the observed molecular geometries of the species obtained with the isolobal mapping [2,3] shown below. Thus the compounds

$$H \xleftrightarrow{o} AuPR_3 \xleftrightarrow{o} CH_3$$

[$Co_3Fe(\mu_3$-$AuPPh_3)(CO)_{12}$][4] and [$Os_4(\mu$-$H)_3(\mu$-$AuPEt_3)(CO)_{12}$][5] have structures closely resembling those of their hydrido-counterparts [$Co_3Fe(\mu_3$-$H)(CO)_{12}$] and [$Os_4(\mu$-$H)_4(CO)_{12}$], respectively. The $AuPR_3$ groups in these two gold-containing complexes bridge a Co_3 face and an Os–Os edge, sites occupied by hydrido-ligands in the latter pair of compounds.

The majority of heteronuclear metal cluster complexes containing gold have been prepared by treating polynuclear metal–carbonyl anions with [$AuX(PR_3)$] (X = Cl [5–10] or NO_3 [4]), [$Au(PR_3)_2]PF_6$,[11] or [$\{Au(PPh_3)\}_3O]BF_4$.[12] When [$AuCl(PR_3)$] is employed the method is much enhanced if a source of Tl^+ is added to remove Cl^- and generate [$AuPR_3]^+$ *in situ*.[5–7,13] Prior to these syntheses, we prepared the gold-triosmium cluster [$AuOs_3(\mu$-$H)(CO)_{10}(PPh_3)$] by treating [$Os_3(\mu$-$H)_2(CO)_{10}$] with [$AuMe(PPh_3)$].[14] The synthesis of [$AuOs_3(\mu$-$H)(CO)_{10}(PPh_3)$] in this manner suggested an attractive alternative route to heteronuclear metal clusters containing gold, namely by treating hydrido-carbonyl polynuclear metal compounds with [$AuMe(PPh_3)$]. The reaction of metal alkyls with metal hydrides to generate metal–metal bonds *via* release of an alkane has long been known. It was with the idea of establishing the generality of this approach for gold that the work described herein was carried out. A preliminary account has been given.[15,16] For studies with [$AuMe(PPh_3)$] the species [$M_3(\mu$-H)(μ-COMe)$(CO)_{10}$] (M = Fe or Ru) and [$Ru_3(\mu$-$H)_3(\mu_3$-COMe)$(CO)_9$] were chosen since

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† 1,1,1,2,2,2,3,3,3-Decacarbonyl-2,3-μ-methoxymethylidyne-2,3-μ-triphenylphosphineaurio-*triangulo*-triruthenium, 1,1,1,2,2,2,3,3,3-nonacarbonyl-1,2;1,3-di-μ-hydrido-μ_3-methoxymethylidyne-2,3-μ-triphenylphosphineaurio-*triangulo*-triruthenium, and 2,2,2,3,3,3,4,4,4-nonacarbonyl-2,3,4-μ_3-methoxymethylidyne-1-triphenylphosphine-1,2,3;1,2,4-bis(μ_3-triphenylphosphineaurio)-*tetrahedro*-goldtriruthenium.

Supplementary data available (No. SUP 23722, 107 pp.): observed and calculated structure factors, hydrogen atom co-ordinates, thermal parameters, and complete bond lengths and angles for complexes (2), (3), and (5). See Instructions for Authors, Section 4.0, *J. Chem. Soc., Dalton Trans.*, 1983, Issue 3, p. xvii.

Table 1. Analytical [a] and physical data for the cluster complexes

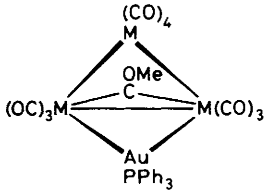
Compound [b]	M.p. (θ_c/°C) (decomp.)	$\nu_{max.}$(CO) [c]/cm^{-1}	Yield [d] (%)	Analysis (%) C	H
(1) $[AuFe_3(\mu\text{-}COMe)(CO)_{10}(PPh_3)]$	181—184	2 068m, 2 014s, 2 009 (sh), 1 996m, 1 978m, 1 967 (sh), 1 959w, 1 946w	62	38.2 (37.9)	1.8 (1.9)
(2) $[AuRu_3(\mu\text{-}COMe)(CO)_{10}(PPh_3)]$	134—138	2 080m, 2 033vs, 2 027s, 2 001vs, 1 990m, 1 971m, 1 960w	61	33.3 (33.2)	1.7 (1.7)
(3) $[AuRu_3(\mu\text{-}H)_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)]$	143—147	2 091m, 2 085 (sh), 2 054s, 2 039vs, 2 023m, 2 001 (sh), 1 995m, 1 982 (sh), 1 974m, 1 967 (sh)	27	33.2 (32.9)	1.8 (1.9)
(4) $[Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_9(PPh_3)_2]$	155—158	2 064s, 2 038vs, 2 022vs, 1 992w, 1 985m, 1 972m, 1 961 (sh), 1 920w br	21	37.3 (37.2)	2.3 (2.2)
(5) $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3]$ [e]	188—192 [f]	2 038s, 2 007vs, 1 959m, 1 940m br	12	39.3 (39.0)	2.6 (2.4)

[a] Calculated values are given in parentheses. [b] All compounds are orange, except (1) which is purple in colour. [c] Measured in cyclohexane, unless otherwise stated. [d] Based on ruthenium reactant. [e] Crystallises with $0.5CH_2Cl_2$. [f] Measured in CH_2Cl_2.

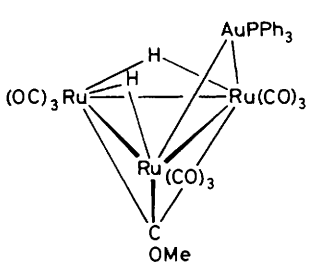
Table 2. Hydrogen-1, ^{31}P-{^{1}H}, and ^{13}C-{^{1}H} n.m.r. data [a] for the gold–ruthenium complexes

Compound	^{1}H [b] (δ)	^{31}P [b,c] (δ)	^{13}C [d,e] (δ)
(2) $[AuRu_3(\mu\text{-}COMe)(CO)_{10}(PPh_3)]$	4.62 (s, 3 H, OMe), 7.44—7.50 (m, 15 H, Ph)	66.4	381.8 (μ-*C*OMe), 210.4, 199.0, 193.6 (CO), 134.3—129.5 (Ph), 75.2 (CO*Me*)
(3) $[AuRu_3(\mu\text{-}H)_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)]$	−18.62 [d, 2 H, μ-H, *J*(PH) 2], 3.93 (s, 3 H, OMe), 7.42—7.55 (m, 15 H, Ph)	61.5	274.6 (μ-*C*OMe), 211 (br, CO), 194 (br, CO), 192.7 (CO), 189.4 (CO), 134.3 [d, C^2 (Ph), *J*(PC) 12], 132.4 [d, C^1 (Ph), *J*(PC) 46], 131.4 [C^4 (Ph)], 129.3 [d, C^3 (Ph), *J*(PC) 12], 68.8 (CO*Me*)
(4) $[Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_9(PPh_3)_2]$	−19.00 [t, 1 H, μ-H, *J*(PH) 2], 4.03 (s, 3 H, OMe), 7.16—7.33 (m, 30 H, Ph)	62.2	300.0 (μ-*C*OMe), 200 (vbr, CO), 134.3 [d, C^2 (Ph), *J*(PC) 15], 132.9 [d, C^1 (Ph), *J*(PC) 43], 131.0 [C^4 (Ph)], 129.1 [d, C^3 (Ph), *J*(PC) 9], 68.6 (CO*Me*)
(5) $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3]$	3.93 (s, 3 H, OMe), 7.04—7.49 (m, 45 H, Ph)	[f] 62.4	320.7 (μ-*C*OMe), 206.9 (CO), 134.4 [d, C^2 (Ph), *J*(PC) 12], 133.3 [d, C^1 (Ph), *J*(PC) 43], 130.7 [C^4 (Ph)], 129.0 [d, C^3 (Ph), *J*(PC) 9], 68.1 (CO*Me*)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] Measured in [^{2}H$_1$]chloroform unless otherwise stated. [c] Hydrogen-1 decoupled, chemical shifts positive to high frequency of 85% H_3PO_4 (external). [d] Hydrogen-1 decoupled, chemical shifts to high frequency of $SiMe_4$. [e] Measured in [^{2}H$_2$]dichloromethane-CH_2Cl_2. [f] Measured in [^{2}H$_2$]dichloromethane at −90 °C.



M
(1) Fe
(2) Ru



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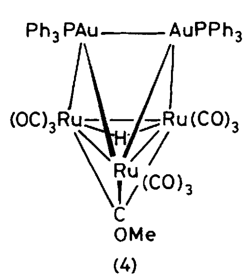

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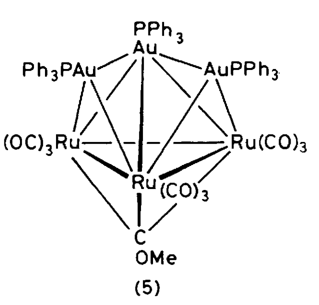

(5)

they are readily accessible and their structures have been well established.[17-19]

Results and Discussion

The compounds $[M_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ (M = Fe or Ru) react with $[AuMe(PPh_3)]$ in diethyl ether at room temperature to give a purple cluster complex (1) and an orange cluster complex (2), in good yield (*ca.* 60%). These species were characterised by microanalyses and by spectroscopic measurements (Tables 1 and 2). Proton and ^{13}C-{^{1}H} n.m.r. data for the two compounds showed the presence of the μ-COMe ligand, and the absence of any hydride–metal linkage. Moreover, the ^{13}C chemical shifts of the ligated carbon atoms of the former groups, δ 361.3 p.p.m. in (1) and δ 381.8 p.p.m. in (2), are little shifted from those reported[17,19] for the μ-*C*OMe resonances in their precursors $[M_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$, suggesting that the methoxymethylidyne group retains its edge-bridging environment in these products. Compounds (1) and (2) were, therefore, formulated as having the structures shown, with the $AuPPh_3$ groups bridging the same metal–metal bond as the carbyne ligand, as do the hydrido-groups in the precursors. This was confirmed by an *X*-ray diffraction study on (2). Discussion of the results of this work is deferred, however, until other gold–ruthenium species are described.

Treatment of a diethyl ether solution of $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}COMe)(CO)_9]$ with $[AuMe(PPh_3)]$ at room temperature

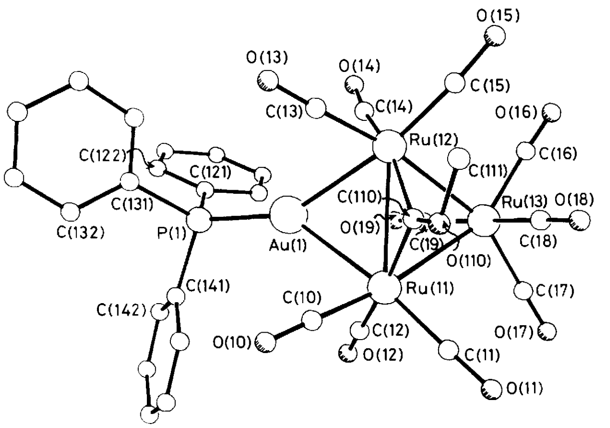

Figure 1. Molecular structure of $[AuRu_3(\mu\text{-}COMe)(CO)_{10}(PPh_3)]$ (2), molecule 1, showing the crystallographic numbering. For molecule 2 the first digit of each atom number is changed from 1 to 2

afforded a mixture of three cluster complexes (3)—(5), separated by chromatography on an alumina column. Data for these new compounds are given in Tables 1 and 2. The ^{1}H and $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectra establish that the μ_3-COMe ligand is retained in the three complexes, while the signals at δ −18.62 and −19.00 in the ^{1}H n.m.r. spectra of (3) and (4), respectively, establish that these two species contain $\mu\text{-}HRu_2$ groups, with the protons coupled to phosphorus. The $^{13}C\text{-}\{^{1}H\}$ n.m.r. data for (3)—(5) measured at room temperature (Table 2) show that these molecules are undergoing dynamic behaviour involving CO site-exchange. The spectra of (4) and of (5) have only one RuCO resonance, that for (4) being very broad. In the spectrum of (3) four CO peaks are seen, but two are broad. Low-temperature $^{13}C\text{-}\{^{1}H\}$ n.m.r. spectra were measured but discussion of the results is deferred until after the *X*-ray diffraction data, described below. The chemical shifts observed in the $^{31}P\text{-}\{^{1}H\}$ spectra of (3)—(5) are as expected for $AuPPh_3$ groups bound to ruthenium.

The compound $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}COMe)(CO)_9]$, the precursor to (3)—(5), is prepared by reaction of $[Ru_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ with hydrogen.[18] We therefore hydrogenated (2) in an attempt to obtain (3). The latter species was produced in this way, but compound (4) was also formed, indicating that migration of $AuPPh_3$ groups occurred between the clusters during reaction with hydrogen.

The spectroscopic data for (3)—(5) did not uniquely define the structures of these complexes and hence single-crystal *X*-ray diffraction studies were undertaken. The results for (3) and (5) are described below; those for (4) are reported elsewhere [20] and confirm that the molecule is as depicted, with a distorted square-pyramidal Au_2Ru_3 core having a ruthenium atom at the apex. Although the spectroscopic data for (2) fairly well defined the molecular structure, nevertheless an *X*-ray diffraction study was performed in order to compare the data with those for the other compounds.

The molecular configuration of (2), shown in Figure 1 with the crystallographic numbering, confirms that the structure deduced by spectroscopic methods is correct. It can be envisaged as a molecule of $[Ru_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$ in which the bridging hydrido-ligand has been replaced by $AuPPh_3$. The result of this replacement is to modify significantly the dimensions of the metal framework: the bridged Ru–Ru bond is now 2.879(2) Å as compared with 2.803(2) Å in the hydrido-compound,[19] and the other two Ru–Ru bonds are 2.839(3) and 2.845(2) Å as compared with 2.810(2) and 2.821(2) Å. The two Au–Ru distances are not significantly different [2.760(2) and 2.762(2) Å],* and the Au–P separation is 2.301(6) Å. The structure could be regarded as a ' butterfly ' with the methoxycarbyne ligand bridging the body of the butterfly on the convex side, and the gold atom occupying a ' wing-tip ' site. The interplanar angle between the two metal triangles is 117°. In the parent hydrido-cluster [19] it was found that the metal–carbonyl bonds *trans* to the carbyne ligand were some 0.07 Å longer than the other metal–carbon bonds and that in the $Ru(CO)_4$ moiety the axial Ru–C bonds were significantly longer than the equatorial bonds; the accuracy of the present determination is not sufficient either to substantiate or contravene this finding. However, the Ru–C(carbyne) bond length of *ca.* 1.98 Å and the widened Ru–C–Ru angle of *ca.* 94° (90.3 in the parent hydrido-cluster) are suggestive of increased electron density in the Ru–C(carbyne) bond, while the C–OMe distance of 1.31(3) Å is intermediate between double- and single-bond values and is considerably shorter than the O–Me distance of 1.46(3) Å. In crystals of (2) the asymmetric unit comprises two molecules of the complex, and these are closely similar (Table 3 gives selected bond distances and angles for both molecules) except for the orientation of the phenyl groups of the phosphine ligands.

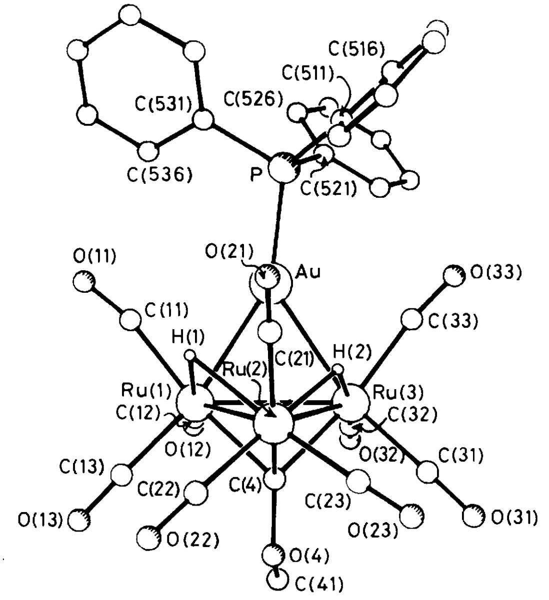

Figure 2. Molecular structure of $[AuRu_3(\mu\text{-}H)_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)]$ (3), showing the crystallographic numbering

The internuclear distances and angles for (3) are summarised in Table 4 and the molecular geometry is illustrated in Figure 2, which also shows the crystallographic numbering. In view of the considerable differences found (see above) between the bond distances in (2) and those in the parent hydrido-cluster, a similar relationship might have been expected for (3). Unfortunately in this case the parent hydrido-compound has not been the subject of an accurate *X*-ray diffraction study, al-

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* The interatomic distances quoted here are all for molecule 1 of the crystallographic asymmetric unit. Inspection of Table 3 shows that the differences between molecule 1 and molecule 2 are marginal except in the case of the Ru(21)–Au(2) bond, for which an apparently significant difference exists. For the reasons given in the Experimental section, it was not possible to apply a satisfactory correction for *X*-ray absorption, and the final *R* value is rather high (0.075). We suggest that no chemical significance should be inferred in this case.

Table 3. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses, for [AuRu$_3$(μ-COMe)(CO)$_{10}$(PPh$_3$)] (2)

Molecule 1		Molecule 2	
(*i*) Distances			
Ru(11)–Ru(12)	2.879(2)	Ru(21)–Ru(22)	2.874(3)
Ru(11)–Ru(13)	2.845(2)	Ru(21)–Ru(23)	2.847(2)
Ru(12)–Ru(13)	2.839(3)	Ru(22)–Ru(23)	2.830(3)
Ru(12)–Au(1)	2.762(2)	Ru(22)–Au(2)	2.762(2)
Ru(11)–Au(1)	2.760(2)	Ru(21)–Au(2)	2.782(2)
Au(1)–P(1)	2.301(6)	Au(2)–P(2)	2.324(6)
P(1)–C(121)	1.804(12)	P(2)–C(221)	1.822(14)
P(1)–C(131)	1.829(15)	P(2)–C(231)	1.813(15)
P(1)–C(141)	1.800(13)	P(2)–C(241)	1.808(11)
C–C (phenyl)	1.395 [a]	C–C (phenyl)	1.395 [a]
Ru(12)–C(110)	1.99(2)	Ru(22)–C(210)	1.98(3)
Ru(11)–C(110)	1.94(3)	Ru(21)–C(210)	1.98(3)
C(110)–O(110)	1.31(3)	C(210)–O(210)	1.31(3)
O(110)–C(111)	1.46(3)	O(210)–C(211)	1.47(4)
Ru–C (carbonyl)	1.90(3) [b]	Ru–C (carbonyl)	1.91(3) [b]
C–O (carbonyl)	1.16(4) [b]	C–O (carbonyl)	1.15(4) [b]
C–H	0.960 [a]	C–H	0.960 [a]
(*ii*) Angles			
Ru(11)–Ru(12)–Ru(13)	59.7(1)	Ru(21)–Ru(22)–Ru(23)	59.9(1)
Ru(11)–Ru(13)–Ru(12)	60.9(1)	Ru(21)–Ru(23)–Ru(22)	60.8(1)
Ru(12)–Ru(11)–Ru(13)	59.5(1)	Ru(22)–Ru(21)–Ru(23)	59.3(1)
Ru(12)–Au(1)–Ru(11)	62.8(1)	Ru(22)–Au(2)–Ru(21)	62.4(1)
Ru(12)–Au(1)–P(1)	152.5(1)	Ru(22)–Au(2)–P(2)	150.1(2)
Ru(11)–Au(1)–P(1)	144.7(1)	Ru(21)–Au(2)–P(2)	147.5(2)
Au(1)–P(1)–C(121)	117.1(5)	Au(2)–P(2)–C(221)	111.6(5)
Au(1)–P(1)–C(131)	113.1(6)	Au(2)–P(2)–C(231)	113.2(6)
Au(1)–P(1)–C(141)	111.9(5)	Au(2)–P(2)–C(241)	113.2(6)
Ru(12)–C(110)–Ru(11)	94.0(9)	Ru(22)–C(210)–Ru(21)	92.9(11)
Ru(12)–C(110)–O(110)	136.6(15)	Ru(22)–C(210)–O(210)	129(2)
Ru(11)–C(110)–O(110)	129.4(13)	Ru(21)–C(210)–O(210)	138(2)
C(110)–O(110)–C(111)	121.8(15)	C(210)–O(210)–C(211)	118(2)

Fixed value. [b] Mean value.

Table 4. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses, for [AuRu$_3$(μ-H)$_2$(μ$_3$-COMe)(CO)$_9$(PPh$_3$)] (3)

(*i*) Distances							
Ru(1)–Ru(2)	2.875(2)	Ru(2)–Ru(3)	2.865(2)	Ru(2)–C(21)	1.993(13)	C(21)–O(21)	1.10(2)
Ru(1)–Ru(3)	2.879(2)	Au–P	2.308(3)	C(11)–O(11)	1.13(2)	C(33)–O(33)	1.143(14)
Au–Ru(1)	2.727(1)	Au–Ru(3)	2.763(1)	C(12)–O(12)	1.16(2)	C(32)–O(32)	1.17(2)
Ru(1)–H(1)	1.99(11)	Ru(3)–H(2)	1.62(11)	C(13)–O(13)	1.122(15)	C(31)–O(31)	1.14(3)
Ru(2)–H(1)	2.01(13)	Ru(2)–H(2)	1.78(10)	C(22)–O(22)	1.13(2)	C(23)–O(23)	1.13(3)
Ru(1)–C(11)	1.978(14)	Ru(3)–C(33)	1.952(11)	Ru(1)–C(4)	2.115(13)	Ru(3)–C(4)	2.063(10)
Ru(1)–C(12)	1.90(2)	Ru(3)–C(32)	1.865(15)	Ru(2)–C(4)	2.065(11)	C(4)–O(4)	1.376(10)
Ru(1)–C(13)	1.904(12)	Ru(3)–C(31)	1.91(2)	O(4)–C(41)	1.41(2)	P–C(511)	1.829(15)
Ru(2)–C(22)	1.917(13)	Ru(2)–C(23)	1.91(2)	P–C(521)	1.818(14)	P–C(531)	1.81(2)
(*ii*) Angles							
Au–Ru(1)–Ru(3)	59.0(1)	Au–Ru(3)–Ru(1)	57.8(1)	Ru(1)–Ru(3)–Ru(2)	60.1(1)	Ru(3)–Ru(1)–Ru(2)	59.7(1)
Ru(1)–Au–Ru(3)	63.2(1)	Au–P–C(511)	110.5(4)	Ru(1)–Ru(2)–Ru(3)	60.2(1)	Ru(1)–Au–P	154.7(1)
Au–P–C(521)	115.5(4)	Au–P–C(531)	115.0(4)	Ru(3)–Au–P	141.3(1)	C(4)–O(4)–C(41)	115.6(9)
Ru(1)–C(11)–O(11)	168.0(10)	Ru(3)–C(33)–O(33)	171.2(14)				

though a detailed study has been carried out [21] on [Ru$_3$(μ-H)$_3$(μ$_3$-CMe)(CO)$_9$] which differs only in the ligand on the triply-bridging carbyne species. Surprisingly, in the light of the results for (2), comparison of (3) with [Ru$_3$(μ-H)$_3$(μ-CMe)(CO)$_9$] reveals differences which are only marginally significant except, of course, for the reduction of symmetry consequent upon replacement of one bridging hydrido-ligand by AuPPh$_3$. In [Ru$_3$(μ-H)$_3$(μ-CMe)(CO)$_9$] the molecule has nearly exact C_{3v} symmetry, though the crystal symmetry imposes only C_s; the two distinct Ru–Ru bond lengths are 2.841(6) and 2.844(6) Å. In (3) there is no imposed crystallographic symmetry, and the near-mirror symmetry of the Ru$_3$(μ-H)$_2$(μ$_3$-COMe)(CO)$_9$ moiety is seriously distorted by the AuPPh$_3$ bridge. Nevertheless, the H-bridged Ru–Ru bonds are 2.865(2) and 2.875(2) Å with the Au-bridged Ru–Ru bond remarkably similar at 2.879(2) Å. Furthermore, this is exactly the same as the distance found for the Au-bridged bond in (2). However, the two Au–Ru distances are considerably different [Au–Ru(1) 2.727(1), Au–Ru(3) 2.763(1) Å] and the two Ru–Au–P angles are different [Ru(1)–Au–P 154.7(1), Ru(3)–Au–P 141.3(1)°]. That the bulky phosphine ligands in the packing of the crystal may be the cause of this distortion is

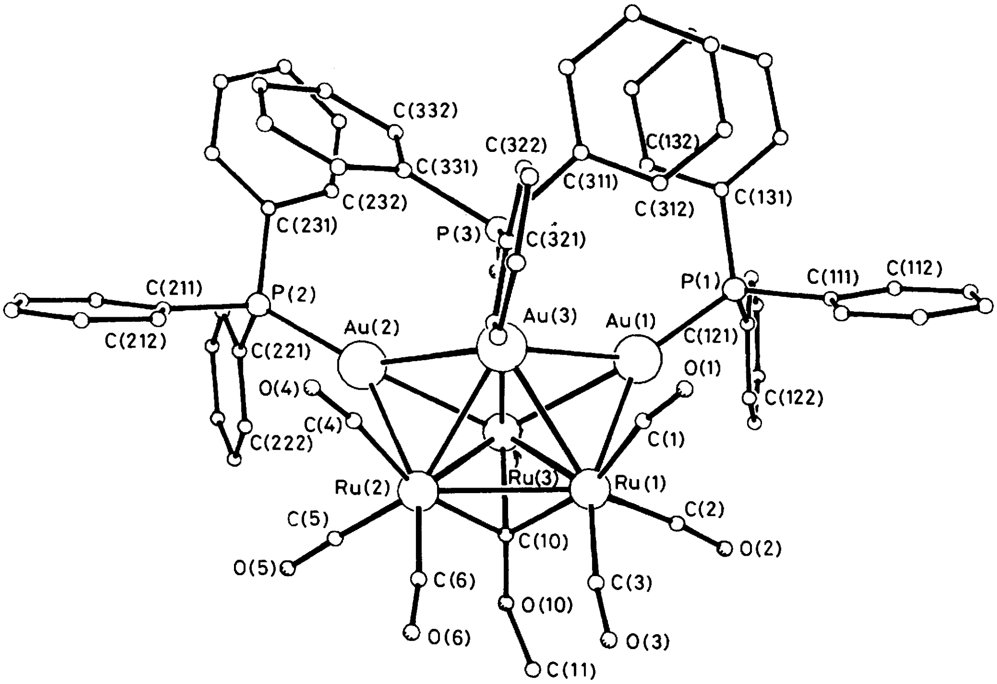


Figure 3. Molecular structure of $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3]$ (5), showing the crystallographic numbering. Three carbonyl ligands on Ru(3), labelled (7), (8), and (9), have been omitted because they are obscured by the bonds Ru(3)–Au(3), Ru(3)–Ru(1), and Ru(3)–Ru(2), respectively

supported by the fact that the shortest intermolecular contacts in the crystal involve the phenyl hydrogen atoms [the only contacts <2.5 Å are H(525) $\cdots$ O(4) 2.33 and H(523) $\cdots$ O(32) 2.45 Å]. The triply-bridging carbyne ligand has bond distances to Ru(1), Ru(2), and Ru(3) of 2.115(13), 2.065(11), and 2.063(10) Å, respectively [*i.e.* the difference between Ru(1)–C and the other two Ru–C bonds is only marginally significant within the accuracy of this determination]. If the overall structure is viewed without regard to the Ru–Ru bonds, each Ru atom is approximately octahedrally co-ordinated, with one carbonyl group *trans* to the carbyne ligand and two carbonyl groups *trans* to the edge-bridging moieties. There are significant differences between the metal–carbonyl bond lengths, as was observed for $[Ru_3(\mu\text{-}H)(\mu\text{-}COMe)(CO)_{10}]$, the precursor of (2): those *trans* to the μ_3-carbyne ligand have Ru–C separations in the range 1.952(11)—1.993(13) Å, whereas those *trans* to the μ_2-ligands are in the range 1.865(15)—1.917(13) Å, reflecting the stronger *trans* influence of the methoxymethylidyne ligand. The carbonyl ligands, which are all terminal, are also all essentially linear except for the two which are adjacent to, and approximately coplanar with, the bridging $AuPPh_3$ group, *viz.* Ru(1)–C(11)–O(11) and Ru(3)–C(33)–O(33). For these, angles of 168(1) and 171(1)° were found, but there is also a comparatively short distance between each C atom and the Au atom [Au $\cdots$ C(11) 2.76, Au $\cdots$ C(33) 2.74 Å], suggesting an incipiently semi-bridging relationship. The interplanar angles between the Ru_3 triangle and the planes of the edge-bridging moieties Ru(1)Ru(2)H(1), Ru(2)Ru(3)H(2), and Ru(1)Ru(3)Au are 128.2, 118.8, and 111.8°, respectively. The Ru–H separations lie in the range 1.6—2.0(1) Å, in agreement with those found by other workers.[21–23] A closely analogous compound, $[AuRu_3(\mu\text{-}H)(\mu_3\text{-}PPh)(CO)_9(PMe_2Ph)]$, has recently been described.[11]

The third structural investigation concerns complex (5), $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3]$. Its molecular configuration is shown, with the crystallographic numbering, in Figure 3. The three ruthenium atoms form a nearly equilateral triangle (Table 5), triply bridged on one side by the methoxymethylidyne ligand, and on the other side by one of the gold atoms, Au(3). Of the three Au–Ru bonds so formed, those to Ru(1) and Ru(2) [2.825(2) and 2.818(2) Å] are notably shorter than that to Ru(3) [2.987(2) Å]. This is perhaps because the $AuRu_3$ tetrahedron is further capped by the other two gold atoms, and these triply bridge the two faces which have Au(3)–Ru(3) as a common edge. Each gold atom carries a triphenylphosphine ligand, and each ruthenium atom three terminal carbonyl groups. A stereo-pair space-filling representation of (5) is shown in Figure 4, from which it can be seen that the introduction of three triphenylphosphine ligands into the molecule on adjacent gold atoms produces severe steric crowding. This may explain the extraordinary difference found between the two Au–Au bond distances [Au(1)–Au(3) 2.930(1), Au(2)–Au(3) 3.010(1) Å], in spite of near-mirror symmetry for the molecule as a whole (excluding phenyl groups). These Au–Au bonds are indeed longer than those in gold metal itself (2.884 Å)[24] and are towards the upper end of the range previously observed [2.784(1)—3.176(1) Å].[20] The Au–P bonds are approximately symmetrically disposed with respect to the tetrahedra of the metal cluster and have a mean bond length of 2.309(6) Å. Around the phosphorus atoms there is significant distortion of the tetrahedral angles to the phenyl groups; the largest angles for P(1) and P(2) are to the rings C(131)—C(136) and C(231)—C(236), respectively, which point towards the centre of the molecule, thus indicating the steric strain. The three Ru–C(carbyne) bond lengths are not very accurately determined, but appear to show no significant differences. Likewise, it is not possible to detect small differences among the Ru–C(carbonyl) bond lengths. The configuration of the metal cluster is closely similar to that found[25,26] for $[Os_6(CO)_{18}]$ which is, like (5), an 84-valence-electron cluster.

Having established the molecular structures of compounds (3) and (4) in the solid state, it is possible to interpret the variable-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. spectra of these species.

Table 5. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses, for $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3]$ (5)

(*i*) Distances

Ru(1)-Ru(2)	2.895(3)	Ru(1)-Ru(3)	2.929(2)	Au(3)-P(3)	2.304(6)	P(1)-C(111)	1.827(14)
Ru(2)-Ru(3)	2.913(2)	Ru(1)-Au(3)	2.825(2)	P(1)-C(121)	1.859(15)	P(1)-C(131)	1.802(13)
Ru(2)-Au(3)	2.818(2)	Ru(3)-Au(3)	2.987(2)	P(2)-C(211)	1.837(15)	P(2)-C(221)	1.837(14)
Ru(2)-Au(2)	2.807(2)	Ru(1)-Au(1)	2.796(2)	P(2)-C(231)	1.828(14)	P(3)-C(311)	1.847(14)
Ru(3)-Au(2)	2.844(2)	Ru(3)-Au(1)	2.833(2)	P(3)-C(321)	1.832(12)	P(3)-C(331)	1.833(15)
Au(3)-Au(2)	3.010(1)	Au(1)-Au(3)	2.930(1)	C-C (phenyl)	1.395 [a]	Ru-C (carbonyl)	1.92(3) [b]
Au(2)-P(2)	2.313(6)	Au(1)-P(1)	2.310(6)	C-O (carbonyl)	1.14(4) [b]		

(*ii*) Angles

Ru(1)-Ru(2)-Ru(3)	60.6(1)	Ru(2)-Ru(1)-Ru(3)	60.0(1)	Ru(2)-Au(3)-P(3)	139.2(2)	Ru(1)-Au(3)-P(3)	140.1(2)
Ru(2)-Ru(3)-Ru(1)	59.4(1)			Au(2)-Au(3)-P(3)	112.3(2)	Au(1)-Au(3)-P(3)	112.9(2)
Ru(2)-Ru(3)-Au(3)	57.0(1)	Ru(1)-Ru(3)-Au(3)	57.0(1)	Ru(3)-Au(3)-P(3)	152.6(1)	Ru(3)-C(10)-O(10)	117.4(14)
Ru(3)-Ru(2)-Au(3)	62.8(1)	Ru(3)-Ru(1)-Au(3)	62.5(1)	Ru(2)-C(10)-O(10)	128.8(14)	Ru(1)-C(10)-O(10)	130.6(14)
Ru(2)-Au(3)-Ru(3)	60.2(1)	Ru(1)-Au(3)-Ru(3)	60.4(1)	Au(2)-P(2)-C(211)	117.9(5)	Au(1)-P(1)-C(111)	116.4(5)
Ru(2)-Au(2)-Ru(3)	62.1(1)	Ru(1)-Au(1)-Ru(3)	62.7(1)	Au(2)-P(2)-C(221)	108.4(5)	Au(1)-P(1)-C(121)	108.7(5)
Au(2)-Ru(3)-Au(1)	115.7(1)	Au(2)-Au(3)-Au(1)	108.0(1)	Au(2)-P(2)-C(231)	118.2(5)	Au(1)-P(1)-C(131)	117.3(6)
Au(3)-Au(2)-P(2)	144.6(1)	Au(3)-Au(1)-P(1)	142.1(2)	Au(3)-P(2)-C(311)	119.7(5)	Au(3)-P(3)-C(321)	113.6(5)
Ru(2)-Au(2)-P(2)	146.9(2)	Ru(1)-Au(1)-P(1)	148.5(2)	Au(3)-P(3)-C(331)	113.6(5)	C(10)-O(10)-C(11)	120(2)
Ru(3)-Au(2)-P(2)	142.0(2)	Ru(3)-Au(1)-P(1)	140.8(2)				

[a] Fixed value. [b] Mean value.

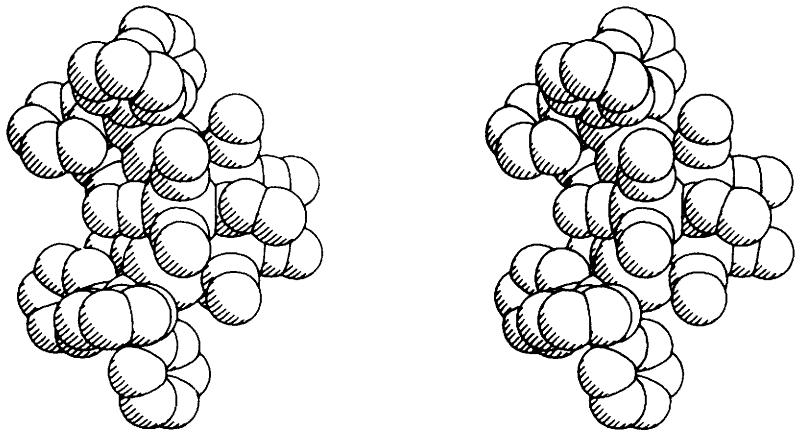
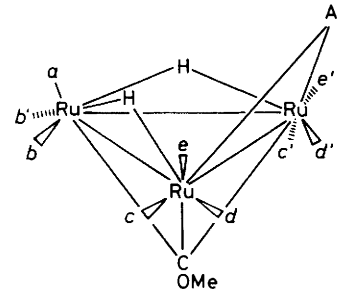


Figure 4. Stereo-pair drawing of a space-filling representation of complex (5), showing steric crowding arising from three adjacent $AuPPh_3$ ligands

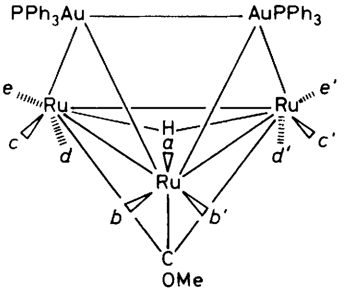
In the spectrum of (3), measured at −50 °C, there are five resonances [relative intensity (r.i.) 2 : 2 : 2 : 1 : 2] for the CO ligands (Figure 5). This pattern is consistent with the structure established by *X*-ray diffraction and contrasts with the room-temperature spectrum which shows two broad and two sharp signals (Table 2). The assignment of the peaks measured at −50 °C (Figure 5) is based on the fact that the CO ligands on the unique Ru atom of (3) are likely to be static at room temperature [see Table 2, signals for (3) at δ 192.7 and 189.4 p.p.m.], as is observed for the corresponding CO groups in the spectrum of $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}COMe)(CO)_9]$ (δ 191.3 and 190.5 p.p.m., r.i. 1 : 2). The doublet resonance in the low-temperature spectrum of (3) (Figure 5) is assigned to the CO ligands *transoid* to the PPh_3 group (*c* and *c′*). The remaining two resonances are due to the two pairs of CO groups, *d* and *d′* and *e* and *e′*, but these signals cannot be distinguished on the basis of the information available.

The $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (4) at −60 °C shows five CO resonances (Figure 5) and again the pattern is consistent with the structure established in the solid state.[20] By comparison with the chemical shift data for (3), the doublet resonance in the spectrum of (4) at δ 194.6 can be assigned to CO ligands *d* and *d′*; the other doublet at 201.5 p.p.m. is due to *b* and *b′*, these CO groups being *transoid* to the $AuPPh_3$ fragments. The signal due to the unique CO ligand (*a*) appears at δ 222.5, while the resonances for the two pairs of CO groups *c* and *c′*, and *e* and *e′* are seen at 212.3 and 193.3 p.p.m., but cannot be distinguished.

It was not possible to obtain a satisfactory low-temperature $^{13}C\text{-}\{^1H\}$ n.m.r. spectrum of (5) because of its relative insolubility. An interesting feature of these n.m.r. studies was the observation that the dynamic behaviour of the $Ru(CO)_3$ groups appears to depend on whether hydrido-ligands or $AuPPh_3$ groups are attached to ruthenium. The activation energy for CO site-exchange decreases as hydrido-ligands are replaced by $AuPPh_3$. Thus at ambient temperatures all nine



(3)



(4)

Figure 5. Assignment of ^{13}C-{^{1}H} n.m.r. signals for CO ligands *a*—*e* in compounds (3) and (4). For (3) at −50 °C: δ (p.p.m.) 212.0 (s, 2 × CO, *d* and *d'* or *e* and *e'*), 195.7 [d, 2 × CO, *c* and *c'*, *J*(PC) 15 Hz], 193.9 (s, 2 × CO, *e* and *e'* or *d* and *d'*), 193.0 (s, 1 × CO, *a*), and 189.3 (s, 2 × CO, *b* and *b'*). For (4) at −60 °C: δ (p.p.m.) 222.5 (s, 1 × CO, *a*), 212.3 (s, 2 × CO, *c* and *c'* or *e* and *e'*), 201.5 [d, 2 × CO, *b* and *b'*, *N*(PC) 15 Hz], 194.6 [d, 2 × CO, *d* and *d'*, *N*(PC) 12 Hz], and 193.3 (s, 2 × CO, *e* and *e'* or *c* and *c'*) *N*(PC) = |*J*(PC) + *J*(P'C)|

carbonyl groups of [$Ru_3(\mu$-$H)_3(\mu_3$-COMe)$(CO)_9$] are static, whereas for compound (3) only three of these ligands (see above) are not undergoing a polytopal rearrangement. When one of the remaining hydrido-ligands in (3) is replaced by a $AuPPh_3$ group to give (4) all the CO groups show dynamic behaviour, only one resonance being observed at room temperature (Table 2). However, whereas this signal is very broad, the spectrum of (5) shows a single very sharp resonance for the nine carbonyl groups, indicating an even lower energy barrier to site-exchange when no hydrido-ligands are present.

In addition to the exchange of the carbonyl groups, there is another dynamic process occurring in (5). Although the solid-state structure shows two separate phosphorus environments, the ^{31}P-{^{1}H} n.m.r. spectrum of (5) is a singlet, even at −90 °C (Table 2). The mechanism for the low-energy dynamic behaviour almost certainly involves the ready rupture and reformation of gold–ruthenium and gold–gold bonds, previously reported in pentanuclear gold–ruthenium compounds,[20] and in homonuclear gold clusters.[27] Dissociation of PPh_3 groups can be ruled out as a possible explanation for the observed spectra, as addition of triphenylphosphine to a ^{31}P-{^{1}H} n.m.r. sample of (5) caused no change in the spectrum, apart from the appearance of the signal due to free PPh_3. A similar dynamic process has also been observed for [$Au_3Ru_4(\mu$-H)$(CO)_{12}(PPh_3)_3$],[16] although the ^{31}P-{^{1}H} n.m.r. spectrum of this complex at −60 °C is consistent with the solid-state structure. Evidently, the dynamic process for [$Au_3Ru_4(\mu$-H)$(CO)_{12}(PPh_3)_3$] is of higher energy than that for (5).

It is interesting to relate the metal atom core geometries found for compounds (3)—(5) with those predicted on the basis of electron-pair counting schemes.[2,28,29] For compound (3), with 60 c.v.e. (cluster valence electrons), a *closo* tetrahedral structure might have been expected instead of the butterfly core observed. It is noteworthy that in (3) the $AuPPh_3$ moiety is behaving stereochemically like the isolobal H group. In contrast, the capped trigonal-bipyramidal metal atom core of (5) (84 c.v.e.) is as predicted by the Wade [2] and the Lauher [29] skeletal electron pair schemes. Wade's [2] scheme also accounts for the observed bicapped trigonal-bipyramidal metal atom core geometries of [$Au_3Ru_4(\mu$-H)$(CO)_{12}(PPh_3)_3$] [16] and [$Au_3CoRu_3(CO)_{12}(PPh_3)_3$],[12] both species having 96 c.v.e. In these compounds and in (5) gold–gold bonds are present, and the $AuPPh_3$ groups no longer behave as *pseudo*-hydrido-ligands. Interestingly, the electron-pair counting schemes do not account for the distorted square-pyramidal metal atom core of (4) (72 c.v.e.), although they do predict the trigonal-bipyramidal Au_2Ru_3 core of [$Au_2Ru_3(\mu_3$-S)$(CO)_8(PPh_3)_3$],[20] also having 72 c.v.e. The reader is referred elsewhere,[3] however, for a discussion on the nature of the bonding in clusters containing gold; it is too simplistic to ignore the contributions made by the $6p_x$ and $6p_y$ orbitals of the Au atoms. Nevertheless, the $AuPPh_3$ groups in (4) are behaving somewhat like the hydrido-ligands in the precursor, [$Ru_3(\mu$-$H)_3(\mu_3$-COMe)$(CO)_9$]. Although an Au–Au bond is present in (4), it is relatively long [3.176(1) Å]. As mentioned earlier, the Au–Au distance in gold metal is 2.884 Å, and evidently in (4) the metal–metal bond is weak.

The synthesis of compounds (1)—(5) demonstrates that the reagent [AuMe(PPh_3)] readily replaces up to three hydrido-ligands by $AuPPh_3$ groups, in reactions which proceed under mild conditions.

Experimental

The techniques used and the instrumentation employed have been described elsewhere.[20] Light petroleum refers to that fraction of b.p. 40—60 °C. Established methods were used to prepare [AuMe(PPh_3)],[30] [$M_3(\mu$-H)$(\mu$-COMe)$(CO)_{10}$] (M = Fe [17] or Ru [19]), and [$Ru_3(\mu$-$H)_3(\mu_3$-COMe)$(CO)_9$].[18] Analytical and other data for the new compounds are given in Table 1. Alumina for chromatography was BDH Brockman Activity II.

Synthesis of the Compounds [$AuM_3(\mu$-COMe)$(CO)_{10}(PPh_3)$].—A diethyl ether (150 cm^3) solution of [$Fe_3(\mu$-H)$(\mu$-COMe)$(CO)_{10}$] (0.30 g, 0.61 mmol) was treated with [AuMe(PPh_3)] (0.29 g, 0.61 mmol), and the mixture stirred at room temperature overnight. After removal of solvent *in vacuo*, the residue was dissolved in dichloromethane–light petroleum (1 : 4) and chromatographed on a silica gel column (30 × 3 cm). Elution with dichloromethane–light petroleum (1 : 4) afforded a red band, yielding unreacted [$Fe_3(\mu$-H)$(\mu$-COMe)$(CO)_{10}$], followed by a purple band containing the product. Evaporation of solvent, and crystallisation from light petroleum gave purple *microcrystals* of [$AuFe_3(\mu$-COMe)$(CO)_{10}(PPh_3)$] (1) (0.36 g). N.m.r.: ^{1}H ([^{2}H$_1$]chloroform), δ 4.63 (s, 3 H, OMe) and 7.47—7.53 p.p.m. (m, 15 H, Ph); ^{31}P-{^{1}H}, δ 55.6 p.p.m.; ^{13}C-{^{1}H} ([^{2}H$_2$]dichloromethane–CH_2Cl_2), δ 361.3 (μ-*C*OMe), 214.6 (CO), 134.3—129.5 (Ph), and 72.1 p.p.m. (CO*Me*).

Orange *microcrystals* of [$AuRu_3(\mu$-COMe)$(CO)_{10}(PPh_3)$] (2) (0.21 g) were similarly prepared from [$Ru_3(\mu$-H)$(\mu$-COMe)$(CO)_{10}$] (0.20 g, 0.32 mmol) and [AuMe(PPh_3)] (0.15 g, 0.32 mmol) in diethyl ether (100 cm^3), the product being isolated from unreacted starting materials after chromatography on alumina (15 × 3 cm column).

Reaction of [$Ru_3(\mu$-$H)_3(\mu_3$-COMe)$(CO)_9$] *with* [AuMe-

Table 6. Atomic positional (fractional co-ordinates) parameters with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[\mathrm{AuRu_3}(\mu\text{-COMe})(\mathrm{CO})_{10}(\mathrm{PPh_3})]$ (2)							
Au(1)	0.333 00(7)	0.112 87(5)	0.229 13(5)	Au(2)	0.847 06(7)	0.618 90(5)	0.291 93(5)
Ru(11)	0.474 65(14)	0.067 95(11)	0.338 20(9)	Ru(21)	0.631 63(14)	0.599 74(11)	0.273 04(10)
Ru(12)	0.497 79(14)	0.012 23(11)	0.167 09(10)	Ru(22)	0.760 38(14)	0.453 93(11)	0.284 86(10)
Ru(13)	0.467 23(15)	−0.118 24(11)	0.247 19(10)	Ru(23)	0.611 47(14)	0.430 04 (11)	0.149 20(10)
P(1)	0.183 3(5)	0.188 0(4)	0.215 6(4)	P(2)	0.992 5(5)	0.712 1(4)	0.304 6(4)
C(110)	0.589(2)	0.055 7(13)	0.271 3(11)	C(210)	0.634(2)	0.508 4(15)	0.331 3(13)
O(110)	0.688 0(12)	0.075 0(9)	0.293 3(8)	O(210)	0.579 7(13)	0.487 7(10)	0.383 4(9)
C(111)	0.763(2)	0.065 0(15)	0.233 9(13)	C(211)	0.484(3)	0.535(2)	0.404(2)
C(10)	0.490(2)	0.193 3(15)	0.382 1(13)	C(20)	0.646(2)	0.701 2(15)	0.369 2(13)
O(10)	0.502 4(14)	0.270 9(11)	0.410 3(10)	O(20)	0.653 2(14)	0.762 4(11)	0.425 3(10)
C(11)	0.555(2)	0.041 5(14)	0.421 7(12)	C(21)	0.488(2)	0.605 1(14)	0.246 4(13)
O(11)	0.611 8(14)	0.025 5(11)	0.473 0(10)	O(21)	0.397 8(14)	0.608 6(11)	0.233 1(10)
C(12)	0.339(2)	0.059 0(15)	0.376 5(14)	C(22)	0.673(2)	0.661 3(14)	0.196 9(12)
O(12)	0.259 9(14)	0.050 8(11)	0.398 4(10)	O(22)	0.692 3(13)	0.699 7(10)	0.152 3(9)
C(13)	0.515(2)	0.111 5(15)	0.131 4(13)	C(23)	0.847(2)	0.477 6(14)	0.380 3(13)
O(13)	0.526 1(14)	0.172 9(12)	0.107 4(10)	O(23)	0.904 9(15)	0.487 4(12)	0.440 2(11)
C(14)	0.373(2)	−0.030 4(15)	0.095 7(14)	C(24)	0.867(2)	0.420 2(15)	0.210 5(14)
O(14)	0.306 2(15)	−0.061 0(12)	0.045 5(11)	O(24)	0.927 5(14)	0.398 9(11)	0.164 1(10)
C(15)	0.589(2)	−0.061 8(15)	0.105 1(14)	C(25)	0.724(2)	0.339 0(2)	0.285 8(13)
O(15)	0.644 4(15)	−0.107 5(12)	0.060 0(11)	O(25)	0.703(2)	0.267 5(13)	0.288 0(11)
C(16)	0.463(2)	−0.221 0(14)	0.151 6(13)	C(26)	0.660(2)	0.319 4(15)	0.090 5(14)
O(16)	0.459 0(14)	−0.284 3(11)	0.097 2(10)	O(26)	0.695(2)	0.254 7(13)	0.051 6(12)
C(17)	0.440(2)	−0.166 1(15)	0.331 5(13)	C(27)	0.501(2)	0.446 1(15)	0.076 4(14)
O(17)	0.423 2(14)	−0.196 0(11)	0.381 6(10)	O(27)	0.430 8(2)	0.453 8(12)	0.033 6(11)
C(18)	0.616(2)	−0.116 7(13)	0.269 8(12)	C(28)	0.514(3)	0.384(2)	0.210 6(15)
O(18)	0.704 2(13)	−0.118 1(10)	0.283 5(9)	O(28)	0.456 8(14)	0.350 3(11)	0.238 3(10)
C(19)	0.322(3)	−0.101 7(15)	0.226 4(13)	C(29)	0.713(2)	0.486 2(13)	0.104 9(12)
O(19)	0.233(2)	−0.101 8(12)	0.211 0(11)	O(29)	0.771 6(13)	0.515 0(10)	0.073 6(9)
C(121)	0.073 2(10)	0.121 9(8)	0.154 1(8)	C(221)	1.043 9(12)	0.695 6(11)	0.207 3(7)
C(122)	−0.002 6(10)	0.159 1(8)	0.112 7(8)	C(222)	1.149 2(12)	0.684 5(10)	0.198 2(7)
C(123)	−0.088 9(10)	0.106 4(8)	0.069 1(8)	C(223)	1.184 8(12)	0.672 3(10)	0.122 4(7)
C(124)	−0.099 5(10)	0.016 6(8)	0.066 9(8)	C(224)	1.115 0(12)	0.671 2(10)	0.055 8(7)
C(125)	−0.023 7(10)	−0.020 6(8)	0.108 3(8)	C(225)	1.009 6(12)	0.682 3(10)	0.065 0(7)
C(126)	0.062 6(10)	0.032 1(8)	0.151 9(8)	C(226)	0.974 1(12)	0.694 5(10)	0.140 7(7)
C(131)	0.201 7(13)	0.280 7(8)	0.173 8(8)	C(231)	1.098 6(11)	0.692 7(9)	0.372 4(8)
C(132)	0.175 7(13)	0.369 0(8)	0.212 7(8)	C(232)	1.161 0(11)	0.762 5(9)	0.426 8(8)
C(133)	0.187 4(13)	0.435 8(8)	0.175 7(8)	C(233)	1.239 4(11)	0.743 3(9)	0.479 2(8)
C(134)	0.225 3(13)	0.414 3(8)	0.099 9(8)	C(234)	1.255 5(11)	0.654 3(9)	0.477 1(8)
C(135)	0.251 3(13)	0.326 0(8)	0.061 0(8)	C(235)	1.193 2(11)	0.584 5(9)	0.422 7(8)
C(136)	0.239 6(13)	0.259 2(8)	0.098 0(8)	C(236)	1.114 7(11)	0.603 7(9)	0.370 3(8)
C(141)	0.133 9(12)	0.239 1(10)	0.311 9(7)	C(241)	0.966 8(12)	0.830 7(7)	0.342 6(8)
C(142)	0.028 2(12)	0.234 6(10)	0.320 5(7)	C(242)	1.014 2(12)	0.894 1(7)	0.314 2(8)
C(143)	−0.007 0(12)	0.269 5(10)	0.396 9(7)	C(243)	0.994 4(12)	0.985 4(7)	0.346 0(8)
C(144)	0.063 5(12)	0.308 9(10)	0.464 7(7)	C(244)	0.927 2(12)	1.013 3(7)	0.406 3(8)
C(145)	0.169 2(12)	0.313 4(10)	0.456 1(7)	C(245)	0.879 8(12)	0.949 9(7)	0.434 8(8)
C(146)	0.204 4(12)	0.278 5(10)	0.379 7(7)	C(246)	0.899 6(12)	0.858 7(7)	0.403 0(8)
(*b*) $[\mathrm{AuRu_3}(\mu\text{-H})_2(\mu_3\text{-COMe})(\mathrm{CO})_9(\mathrm{PPh_3})]$ (3)							
Au	0.270 06(4)	−0.006 22(4)	−0.116 16(5)	C(33)	0.287 8(10)	0.112 5(11)	−0.285 5(14)
Ru(1)	0.323 94(7)	0.146 75(7)	0.188 19(10)	O(31)	0.387 4(9)	0.424 1(8)	−0.089 1(13)
Ru(2)	0.197 56(7)	0.259 68(8)	0.131 86(11)	O(32)	0.545 2(8)	0.200 3(11)	−0.071 3(13)
Ru(3)	0.337 86(7)	0.209 45(8)	−0.063 65(11)	O(33)	0.258 7(9)	0.067 7(8)	−0.417 4(10)
P	0.198 3(3)	−0.179 6(3)	−0.315 3(4)	C(511)	0.095 3(10)	−0.182 8(11)	−0.440 7(2)
C(4)	0.347 8(8)	0.296 4(9)	0.173 7(13)	C(512)	0.036 8(10)	−0.121 5(12)	−0.375(2)
C(41)	0.510 0(10)	0.412 0(11)	0.289(2)	C(513)	−0.045 6(12)	−0.122 9(13)	−0.465(2)
O(4)	0.408 7(6)	0.397 8(6)	0.278 5(8)	C(514)	−0.061 5(14)	−0.186 0(15)	−0.621(3)
C(11)	0.260 3(10)	0.000 8(10)	0.175 8(14)	C(515)	−0.003 2(14)	−0.242 8(15)	−0.691(3)
C(12)	0.448 6(12)	0.125 7(12)	0.184 5(15)	C(516)	0.080 1(12)	−0.241 9(13)	−0.604(2)
C(13)	0.346 6(10)	0.226 1(10)	0.409 8(15)	C(521)	0.276 6(9)	−0.232 4(11)	−0.449 1(15)
O(11)	0.227 3(9)	−0.073 2(8)	0.196 4(12)	C(522)	0.331 9(12)	−0.168 2(14)	−0.507(2)
O(12)	0.524 0(8)	0.110 8(10)	0.182 3(13)	C(523)	0.394 6(15)	−0.201(2)	−0.610(3)
O(13)	0.362 7(9)	0.275 8(9)	0.5401(11)	C(524)	0.399 4(13)	−0.304 3(15)	−0.650(2)
C(21)	0.057 6(11)	0.170 0(12)	0.044(2)	C(525)	0.347 7(11)	−0.369 6(14)	−0.595(2)
C(22)	0.189 5(10)	0.336 3(11)	0.346 8(15)	C(526)	0.285 1(10)	−0.336 3(11)	−0.493 6(15)
C(23)	0.192 3(10)	0.381 2(12)	0.094 7(15)	C(531)	0.149 6(9)	−0.284 0(10)	−0.251 8(14)
O(21)	−0.018 9(8)	0.117 3(10)	−0.008 3(14)	C(532)	0.058 2(9)	−0.360 8(11)	−0.315 7(15)
O(22)	0.189 0(9)	0.383 6(9)	0.474 6(12)	C(533)	0.024 1(12)	−0.439 1(13)	−0.262(2)
O(23)	0.187 4(9)	0.451 6(9)	0.070 5(14)	C(534)	0.0838(12)	−0.437 7(14)	−0.142(2)
C(31)	0.367 9(11)	0.343 3(11)	−0.081(2)	C(535)	0.175 4(13)	−0.366 4(15)	−0.080(3)
C(32)	0.465 4(10)	0.203 7(12)	−0.067 5(15)	C(536)	0.209 9(11)	−0.284 9(12)	−0.129(2)

Table 6 (*continued*)

(*c*) $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3]$ (5)

Atom	*x*	*y*	*z*
Au(1)	0.384 84(6)	0.705 32(5)	0.148 37(4)
Au(2)	0.387 71(6)	0.713 55(5)	0.345 55(4)
Au(3)	0.427 93(6)	0.617 15(5)	0.246 97(4)
Ru(1)	0.267 09(12)	0.596 97(10)	0.188 58(7)
Ru(2)	0.270 96(12)	0.601 07(10)	0.307 38(7)
Ru(3)	0.293 38(12)	0.741 21(9)	0.245 94(7)
P(1)	0.449 2(5)	0.763 2(4)	0.073 7(3)
P(2)	0.448 8(4)	0.774 9(4)	0.420 8(3)
P(3)	0.571 5(4)	0.573 2(4)	0.2480(3)
C(1)	0.362(2)	0.536 7(14)	0.154 7(11)
O(1)	0.406 9(11)	0.500 6(10)	0.129 1(8)
C(2)	0.210(2)	0.635 1(12)	0.125 5(10)
O(2)	0.169 3(13)	0.659 8(10)	0.089 5(8)
C(3)	0.192(2)	0.508 5(15)	0.189 2(10)
O(3)	0.148 2(14)	0.458 0(11)	0.183 3(9)
C(4)	0.371(2)	0.549 8(15)	0.348 7(11)
O(4)	0.419 1(12)	0.517 7(12)	0.374 4(8)
C(5)	0.205(2)	0.644 2(13)	0.367 3(11)
O(5)	0.163 8(14)	0.666 2(11)	0.402 7(9)
C(6)	0.201(2)	0.515 1(14)	0.308 3(9)
O(6)	0.165 8(15)	0.456 2(11)	0.313 5(8)
C(7)	0.403(2)	0.800(2)	0.246 9(9)
O(7)	0.463 9(12)	0.841 8(10)	0.245 4(8)
C(8)	0.228 8(2)	0.797(2)	0.190 9(10)
O(8)	0.180 0(12)	0.829 0(11)	0.162 8(8)
C(9)	0.232(2)	0.797 6(13)	0.298 2(10)
O(9)	0.186 9(12)	0.831 4(10)	0.326 4(8)
C(10)	0.197 0(14)	0.654 2(12)	0.246 4(9)
O(10)	0.107 2(11)	0.676 3(10)	0.247 1(7)
C(11)	0.045(2)	0.629(2)	0.230(2)
C(111)	0.446 2(10)	0.710 4(9)	0.009 2(6)
C(112)	0.446 7(10)	0.748 1(9)	−0.041 2(6)
C(113)	0.449 3(10)	0.706 7(9)	−0.089 9(6)
C(114)	0.451 5(10)	0.627 7(9)	−0.088 3(6)
C(115)	0.451 0(10)	0.590 1(9)	−0.038 0(6)
C(116)	0.448 3(10)	0.631 5(9)	0.010 8(6)
C(121)	0.385 3(10)	0.850 2(8)	0.056 5(7)
C(122)	0.293 1(10)	0.845 1(8)	0.055 6(7)
C(123)	0.242 0(10)	0.909 6(8)	0.045 5(7)
C(124)	0.283 2(10)	0.979 1(8)	0.036 4(7)
C(125)	0.375 3(10)	0.984 2(8)	0.037 4(7)
C(126)	0.426 4(10)	0.919 7(8)	0.047 4(7)
C(131)	0.562 7(8)	0.793 3(9)	0.081 1(7)
C(132)	0.593 3(8)	0.804 5(9)	0.134 7(7)
C(133)	0.680 9(8)	0.826 4(9)	0.144 3(7)
C(134)	0.737 8(8)	0.836 9(9)	0.100 2(7)
C(135)	0.707 3(8)	0.825 7(9)	0.046 6(7)
C(136)	0.619 7(8)	0.803 9(9)	0.037 1(7)
C(211)	0.460 6(10)	0.721 2(9)	0.485 0(6)
C(212)	0.468 1(10)	0.642 5(9)	0.482 5(6)
C(213)	0.480 2(10)	0.600 7(9)	0.530 6(6)
C(214)	0.484 9(10)	0.637 6(9)	0.581 2(6)
C(215)	0.477 4(10)	0.716 4(9)	0.583 7(6)
C(216)	0.465 3(10)	0.758 1(9)	0.5355(6)
C(221)	0.374 2(9)	0.852 2(8)	0.440 6(7)
C(222)	0.283 1(9)	0.839 7(8)	0.438 3(7)
C(223)	0.224 6(9)	0.898 0(8)	0.451 5(7)
C(224)	0.257 4(9)	0.968 7(8)	0.467 1(7)
C(225)	0.348 6(9)	0.981 2(8)	0.469 5(7)
C(226)	0.407 0(9)	0.923 0(8)	0.456 3(7)
C(231)	0.554 5(8)	0.823 7(9)	0.412 2(7)
C(232)	0.563 7(8)	0.871 3(9)	0.367 0(7)
C(233)	0.641 5(8)	0.912 9(9)	0.360 3(7)
C(234)	0.710 0(8)	0.906 7(9)	0.398 9(7)
C(235)	0.700 7(8)	0.859 1(9)	0.444 2(7)
C(236)	0.623 0(8)	0.817 6(9)	0.450 8(7)
C(311)	0.646 6(9)	0.598 2(9)	0.191 4(5)
C(312)	0.610 1(9)	0.597 4(9)	0.138 6(5)
C(313)	0.662 9(9)	0.613 8(9)	0.093 5(5)
C(314)	0.752 3(9)	0.631 1(9)	0.101 2(5)
C(315)	0.788 8(9)	0.631 9(9)	0.154 0(5)
C(316)	0.736 0(9)	0.615 5(9)	0.199 1(5)
C(321)	0.579 9(10)	0.469 8(7)	0.244 5(7)
C(322)	0.660 6(10)	0.434 7(7)	0.233 3(7)
C(323)	0.666 4(10)	0.355 9(7)	0.232 4(7)
C(324)	0.5916(10)	0.312 0(7)	0.242 5(7)
C(325)	0.510 9(10)	0.347 0(7)	0.253 6(7)
C(326)	0.505 1(10)	0.425 8(7)	0.254 6(7)
C(331)	0.633 9(10)	0.599 2(9)	0.310 1(6)
C(332)	0.663 2(10)	0.673 8(9)	0.315 8(6)
C(333)	0.708 4(10)	0.696 0(9)	0.363 3(6)
C(334)	0.724 4(10)	0.643 7(9)	0.405 2(6)
C(335)	0.695 2(10)	0.569 2(9)	0.399 5(6)
C(336)	0.649 9(10)	0.546 9(9)	0.352 0(6)
C(100)	0.574(4)	1.006(4)	0.156(2)
Cl(1)	0.611 4(10)	0.998 7(9)	0.216 8(7)
Cl(2)	0.542 6(11)	1.079 0(10)	0.125 7(8)

$(PPh_3)]$.—The compound $[AuMe(PPh_3)]$ (0.50 g, 1.05 mmol) was added to a diethyl ether (150 cm^3) solution of $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}COMe)(CO)_9]$ (0.50 g, 0.83 mmol), and the mixture was stirred for *ca.* 15 h. After removal of solvent *in vacuo*, the residue was dissolved in dichloromethane–light petroleum (1 : 4), and chromatographed on alumina (25 × 3 cm column). Gradient elution with dichloromethane–light petroleum (initially 1 : 4, increasing to 2 : 3 after recovering the first two bands, and finally 3 : 2 proportions to elute the last band) allowed separation of unreacted yellow $[Ru_3(\mu\text{-}H)_3(\mu_3\text{-}COMe)(CO)_9]$, orange *microcrystals* of $[AuRu_3(\mu\text{-}H)_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)]$ (3) (0.24 g), orange *microcrystals* of $[Au_2Ru_3(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_9(PPh_3)_2]$ (4) (0.26 g), and dark orange *microcrystals* of $[Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3]$ (5) (0.20 g). Compounds (3), (4), and (5) could be recrystallised from light petroleum, diethyl ether–light petroleum, and dichloromethane–light petroleum, respectively.

Reaction of $[AuRu_3(\mu\text{-}COMe)(CO)_{10}(PPh_3)]$ *with Hydrogen.*—A toluene (50 cm^3) solution of (2) (0.30 g, 0.28 mmol) under hydrogen in a Schlenk tube fitted with a high-pressure stopcock was heated at 60 °C for 3 d. The mixture was filtered through a Celite pad, and solvent was removed *in vacuo*. The residue was dissolved in dichloromethane–light petroleum (10 cm^3, 1 : 4), and chromatographed on alumina (15 × 3 cm column). Elution with the same solvent mixture (1 : 4 initially, changing to 2 : 3) allowed isolation of compound (3) (0.11 g, 38%) and compound (4) (0.06 g, 14%).

Crystal Structure Determinations.—(*a*) $[AuRu_3(\mu\text{-}COMe)(CO)_{10}(PPh_3)]$ (2). Crystals of (2) were grown from diethyl ether–light petroleum as orange prisms. Two crystals, both cut from larger crystals, were used for data collection. Both were of linear dimensions *ca.* 0.3 mm; the first disintegrated after collection of over 5 000 reflections without any sign of crystal decay. No absorption correction was applied because of lack of azimuthal scan data. Intensities were collected at 220 K in the range $2.9 \leqslant 2\theta \leqslant 40°$ on a Nicolet *P*3*m* four-circle diffractometer. Of the total 6 253 independent intensities, 4 868 for which $I \geqslant 4\sigma(I)$ were used in the solution and refinement of the structure.

Crystal data. $C_{30}H_{18}AuO_{11}PRu_3$, $M = 1\,085.6$, Triclinic,

$a = 12.952(7)$, $b = 15.588(3)$, $c = 17.386(3)$ Å, $\alpha = 107.80(2)$, $\beta = 95.46(3)$, $\gamma = 90.37(3)^\circ$, $U = 3\,325(2)$ Å^3, $D_m = 2.01$, $Z = 4$, $D_c = 2.17$ g cm^{-3}, $F(000) = 2\,048$, space group $P\bar{1}$ (no. 2), Mo-K_α *X*-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 58.1 cm^{-1}.

The structure was solved by heavy-atom methods and refined by blocked-cascade least squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included in calculated positions, with common isotropic thermal parameters for chemically equivalent atoms. Methyl and phenyl groups were constrained to idealised geometry. Weights of the form $w = [\sigma^2(F_o) + g|F_o|^2]^{-1}$ with $g = 0.002\,5$ gave a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks >4.6 or < -5.6 e Å^{-3}, the largest peaks and troughs being in the vicinity of the metal atoms and arising in part from the lack of an absorption correction; *R* 0.075, *R′* 0.077. Scattering factors were from ref. 31. All computations were carried out on an Eclipse (Data General) minicomputer with the SHELXTL system of programs.[32] Atom co-ordinates for all three structures are listed in Table 6.

(*b*) $[\mathrm{AuRu_3(\mu\text{-}H)_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)}]$ (3). Crystals of (3) were grown as red-orange prisms from light petroleum. The one used for data collection was of dimensions 0.15 × 0.15 × 0.10 mm with well developed (1 0 0), $(\bar{1}\ 0\ 0)$, (0 1 0), $(0\ \bar{1}\ 0)$, $(0\ 1\ \bar{2})$, and $(0\ \bar{1}\ 2)$ faces, and was sealed under nitrogen in a Lindemann capillary.

Crystal data. $\mathrm{C_{29}H_{20}AuO_{10}PRu_3}$, $M = 1\,059.6$, Triclinic, $a = 14.421(4)$, $b = 14.136(5)$, $c = 9.535(4)$ Å, $\alpha = 114.02(3)$, $\beta = 93.47(3)$, $\gamma = 105.19(3)^\circ$, $U = 1\,682(1)$ Å^3, D_m not measured, $Z = 2$, $D_c = 2.09$ g cm^{-3}, $F(000) = 1\,000$, space group $P\bar{1}$ (no. 2), μ(Mo-K_α) = 57.3 cm^{-1}.

Conditions were as for (2), except: 4 654 reflections to $2\theta = 45^\circ$ gave 3 247 independent intensities $[I \geqslant 2.0\sigma(I)]$; $T = 293$ K; all atoms were anisotropic except H and C(phenyl); H atoms were in calculated riding positions[33] with isotropic thermal parameters equal to 1.2 times the equivalent isotropic thermal parameter of the attached carbon atom; hydride bridge atoms were located by potential energy minimisation;[34] the methyl group of COMe was constrained to tetrahedral geometry. Weights with $g = 0.000\,5$ were employed and a numerical absorption correction was applied. The maximum electron density by difference was 1.5 e Å^{-3}; $R = 0.042$, R' 0.040.

(*c*) $[\mathrm{Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3}]$ (5). Crystals of (5) were grown from dichloromethane–light petroleum as red-orange plates. The data crystal, of dimensions 0.22 × 0.18 × 0.10 mm, was cut from a larger crystal to give new ' faces ' (1 1 0), $(1\ \bar{1}\ 0)$, $(\bar{1}\ 1\ 0)$, $(\bar{1}\ \bar{1}\ 0)$, (0 0 1), and $(0\ 0\ \bar{1})$, and was mounted in a Lindemann capillary. The *X*-ray investigation showed that the complex crystallises with half a molecule of $\mathrm{CH_2Cl_2}$ per molecule of complex.

Crystal data. $\mathrm{C_{65}H_{48}Au_3O_{10}P_3Ru_3\cdot 0.5CH_2Cl_2}$, $M = 2\,018.6$, Monoclinic, $a = 15.103(4)$, $b = 17.650(3)$, $c = 24.363(6)$ Å, $\beta = 90.59(2)^\circ$, $U = 6\,494(3)$ Å^3, D_m not measured, $Z = 4$, $D_c = 2.07$ g cm^{-3}, $F(000) = 3\,812$, space group $P2_1/n$ (non-standard setting of $P2_1/c$, no. 14), μ(Mo-K_α) = 75.8 cm^{-1}.

Conditions were as for (3), except: 6 284 reflections to $2\theta = 45^\circ$ gave 4 279 independent intensities $[I \geqslant 2.5\sigma(I)]$; anisotropic thermal parameters were used for Au, Ru, P, CO, COMe, and Cl(solvent); isotropic thermal parameters were used for all other non-H atoms and for the H atoms; refinement of the solvent molecule was subjected to a constraint that the two C–Cl bonds be equal. Weights with $g = 0.000\,8$ were employed. The final electron density by difference showed no peaks >1.6 or less than -1.5 e Å^{-3}; *R* 0.050, *R′* 0.048.

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