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The Heteronuclear Cluster Chemistry of the Group 1B Metals. Part 11.[1] Effect of the Nature of the Bidentate Diphosphine Ligand on the Metal Framework Structures of the Gold Heteronuclear Cluster Compounds $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (*n* = 1—6). *X*-Ray Crystal Structures of $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$(*n* = 1 or 2)†

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Treatment of acetone solutions of the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$ with a dichloromethane solution of the appropriate complex $[Au_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}Cl_2]$ (*n* = 1—6), in the presence of $TlPF_6$, affords the mixed-metal cluster compounds $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ [*n* = 1, (**2**); 2, (**3**); 3, (**4**); 4, (**5**); 5, (**6**); or 6, (**7**)] in *ca.* 60—70% yield. *X*-Ray diffraction studies on (**2**) and (**3**) reveal that the formal replacement of the two PPh_3 ligands attached to the Au atoms in $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2]$ (**1**) by $Ph_2P(CH_2)_nPPh_2$ (*n* = 1 or 2) alters the capped trigonal-bipyramidal skeletal geometry adopted by (**1**). The cluster (**2**) crystallizes in two forms, monoclinic and orthorhombic, but *X*-ray diffraction studies on both forms show that the molecular structures adopted by (**2**) are closely similar in each case. The metal core of (**2**) consists of a square-based pyramid, defined by two Au atoms and two Ru atoms in the basal plane and a Ru atom at the apex, with the Ru_3 face of this Au_2Ru_3 unit capped by a Ru atom [Au–Au 2.823(1), Au–Ru 2.682(1)—2.947(2), Ru–Ru 2.791(2)—3.006(2) Å for the monoclinic form and Au–Au 2.833(2), Au–Ru 2.691(3)—2.862(3), Ru–Ru 2.805(4)—3.037(3) Å for the orthorhombic form]. The $Ph_2PCH_2PPh_2$ ligand bridges the two Au atoms, one hydrido ligand caps a Ru_3 face and one bridges a Ru–Ru edge of the metal framework, and each Ru atom is ligated by three terminal CO groups. The skeletal geometry of (**3**) is reasonably similar to that exhibited by (**1**), but one of the Au–Ru distances [3.446(4) Å] is too long for any significant bonding interaction between the two atoms. Thus, the metal framework of (**3**) is somewhat distorted towards a capped square-based pyramid [Au–Au 2.828(4), Au–Ru 2.777(4)—2.965(4), Ru–Ru 2.782(4)—3.008(4) Å]. Variable-temperature ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. studies show that, at ambient temperature in solution, the metal cores of (**3**)—(**7**) all undergo dynamic behaviour involving gold atom site exchange.

The metal frameworks of heteronuclear cluster compounds containing $M(PR_3)$ (M = Cu, Ag, or Au; R = alkyl or aryl) units can often exhibit great flexibility because of the bonding characteristics of the Group 1B metal moieties. Thus, the skeletal geometries adopted can be altered considerably by relatively small changes in the nature of the attached ligands[2] and when two or more $M(PR_3)$ fragments adopt inequivalent positions in the ground-state structures of these species, dynamic behaviour involving coinage metal site exchange is often observed in solution.[2,3] For example, the capped trigonal-bipyramidal metal skeleton of the cluster $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(CO)_{12}(PPh_3)_2]$ (**1**) is stereochemically non-rigid at ambient temperature in solution.[4] We wished to synthesize a series of analogous clusters of formula $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (*n* = 1—6) to investigate the effect of the formal replacement of the two PPh_3 groups attached to the Au atoms in compound (**1**) by the bidentate diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ on the metal-core structure and dynamic behaviour of the cluster. Preliminary accounts describing some of our results[5] and the synthesis and spectroscopic data of $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$[6] (**3**) have already been published.

Results and Discussion

A solution of the complex $[Au_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}Cl_2]$ (*n* = 1—6) was prepared by treating a dichloromethane solution containing 2 equivalents of $[AuCl(SC_4H_8)]$ with 1 equivalent of the appropriate bidentate diphosphine ligand. The addition of an acetone solution of the salt $[N(PPh_3)_2]_2[Ru_4(\mu\text{-}H)_2(CO)_{12}]$,[7] together with solid $TlPF_6$, to the resultant solution, afforded, after working up, 60—70% yields of the dark red mixed-metal cluster compounds $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ [*n* = 1, (**2**); 2, (**3**); 3, (**4**); 4, (**5**); 5, (**6**); or 6, (**7**)]. The new clusters (**2**) and (**4**)—(**7**) were characterized by microanalysis and by spectroscopic measurements (Tables 1 and 2). The high-field ^1H n.m.r. hydrido ligand signal for compound (**2**) is a singlet at ambient temperature, in contrast to the triplets [*J*(PH) 5—9 Hz] observed for clusters (**1**),[4] and (**3**),[6] and (**4**)—(**7**). In addition, at −90 °C, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**2**) consists of a sharp single resonance, whereas a broad or very broad singlet is visible for

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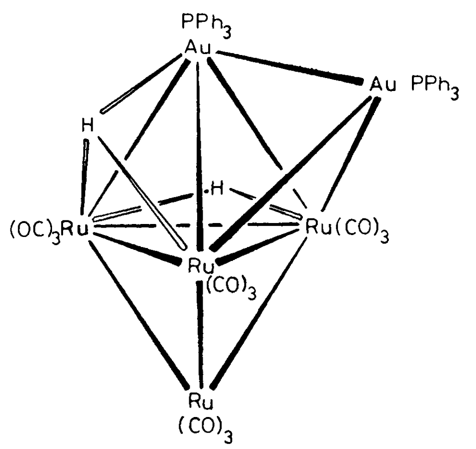
† 1,2-μ-[Bis(diphenylphosphino)methane-*P,P′*]-3,3,3,4,4,4,5,5,5,6,6,6-dodecacarbonyl-3,5-μ-hydrido-3,4,6-μ_3-hydrido-digoldtetraruthenium (*Au–Au*)(4*Au–Ru*)(6*Ru–Ru*) and 1,2-μ-[1′,2′-bis(diphenylphosphino)ethane-*P,P′*]-3,3,3,4,4,4,5,5,5,6,6,6-dodecacarbonyl-3,4-μ-hydrido-1,4,5-μ_3-hydrido-digoldtetraruthenium (*Au–Au*)(4*Au–Ru*)(6*Ru–Ru*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.



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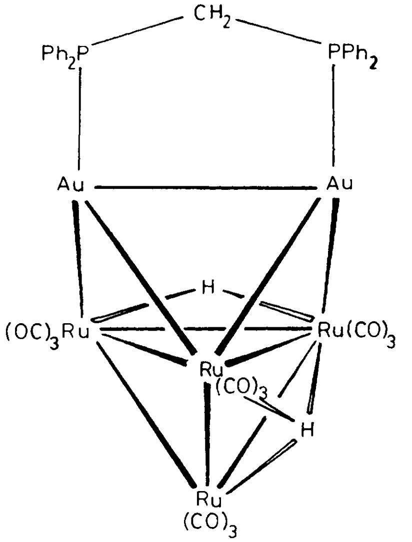

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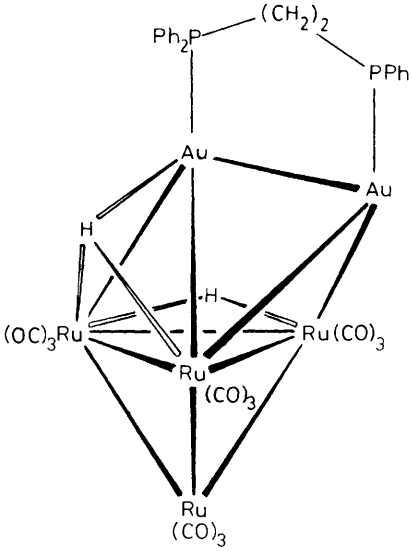

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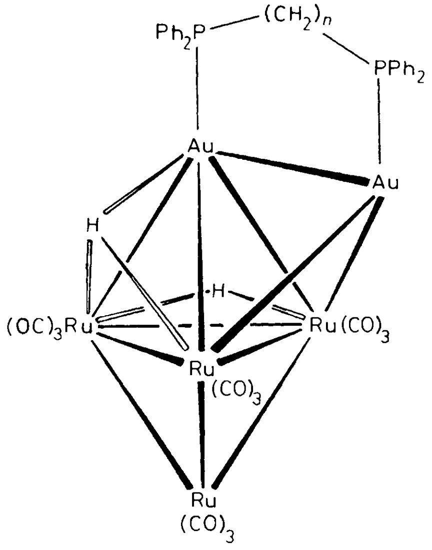

	n
(**4**)	3
(**5**)	4
(**6**)	5
(**7**)	6

Table 1. Analytical[a] and physical data for the new gold heteronuclear cluster compounds

Compound[b]	M.p. (θ_c/°C) (decomp.)	$\nu_{max.}$(CO)[c]/cm^{-1}	Yield[d] (%)	Analysis (%) C	H
(**2**) $[Au_2Ru_4H_2(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$	160—164	2 073s, 2 043s, 2 021vs (br), 1 996 (sh), 1 976m (br), 1 933w (br)	63	29.6 (29.2)	1.8 (1.6)
(**4**) $[Au_2Ru_4H_2\{\mu\text{-}Ph_2P(CH_2)_3PPh_2\}(CO)_{12}]$	133—136	2 067s, 2 031s, 2 018vs, 2 006 (sh), 1 974m (br), 1 949w (br)	65	30.5 (30.2)	2.1 (1.8)
(**5**) $[Au_2Ru_4H_2\{\mu\text{-}Ph_2P(CH_2)_4PPh_2\}(CO)_{12}]$	138—140	2 071s, 2 034s, 2 022vs, 2 008s, 1 979m (br), 1 957w (br)	68	30.7 (30.7)	1.9 (1.9)
(**6**) $[Au_2Ru_4H_2\{\mu\text{-}Ph_2P(CH_2)_5PPh_2\}(CO)_{12}]$	111—113	2 070s, 2 041 (sh), 2 033vs, 2 021vs, 2 006s, 1 977m (br), 1 956w (br)	64	31.2 (31.2)	2.0 (2.0)
(**7**) $[Au_2Ru_4H_2\{\mu\text{-}Ph_2P(CH_2)_6PPh_2\}(CO)_{12}]$	142—145	2 070s, 2 040 (sh), 2 033s, 2 022vs, 2 006s, 1 976m (br), 1 957w (br)	60	31.7 (31.7)	2.2 (2.1)

[a] Calculated values in parentheses. [b] The data for $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$ (**3**) have been reported previously. See ref. 6 for details. [c] Measured in dichloromethane solution. [d] Based on ruthenium reactant.

Table 2. Hydrogen-1 and phosphorus-31 n.m.r. data[a] for the new gold heteronuclear cluster compounds

Compound[b]	Ambient-temperature ^{1}H n.m.r. data[c]	Low-temperature ^{1}H hydrido ligand signal[c,d]	Ambient-temperature ^{31}P-{^{1}H} data[e]	Low-temperature ^{31}P-{^{1}H} data[d,e]
(**2**)	−16.94 (s, 2 H, hydrido H), 3.79 [t, 2 H, $\mathrm{PCH_2P}$, *J*(PH) 11], 7.18—7.58 (m, 20 H, Ph)	Signal not visible	52.3 (s)	50.5 (s)
(**4**)	−15.32 [t, 2 H, hydrido H, *J*(PH) 8], 2.00—2.40 (m, 2 H, $\mathrm{PCH_2C}H_2\mathrm{CH_2P}$), 2.70—2.75 (m, 4 H, $\mathrm{PC}H_2\mathrm{CH_2C}H_2\mathrm{P}$), 7.47—7.63 (m, 20 H, Ph)	*ca.* −15 (s, vbr)	56.0 (s)	*ca.* 47 (s, vbr) *ca.* 57 (s, vbr)
(**5**)	−14.51 [t, 2 H, hydrido H, *J*(PH) 9], 1.95—2.02 [m, 4 H, $\mathrm{PCH_2(C}H_2\mathrm{)_2CH_2P}$], 2.68—2.74 [m, 4 H, $\mathrm{PC}H_2\mathrm{(CH_2)_2C}H_2\mathrm{P}$], 7.47—7.65 (m, 20 H, Ph)	*ca.* −14 (s, vbr)[f]	51.9 (s)	47.6 (s, br)
(**6**)	−14.55 [t, 2 H, hydrido H, *J*(PH) 6], 1.50—1.63 (m, 4 H, $\mathrm{PCH_2C}H_2\mathrm{CH_2C}H_2\mathrm{CH_2P}$), 2.05—2.08 (m, 2 H, $\mathrm{PCH_2CH_2C}H_2\mathrm{CH_2CH_2P}$), 2.60—2.68 [m, 4 H, $\mathrm{PC}H_2\mathrm{(CH_2)_3C}H_2\mathrm{P}$], 7.43—7.63 (m, 20 H, Ph)	*ca.* −14 (s, vbr)	52.2 (s)	*ca.* 49 (s, vbr)
(**7**)	−14.18 [t, 2 H, hydrido H, *J*(PH) 7], 1.47—1.52 [m, 4 H, $\mathrm{PCH_2C}H_2\mathrm{(CH_2)_2C}H_2\mathrm{CH_2P}$], 1.79—1.81 [m, 4 H, $\mathrm{PCH_2CH_2(C}H_2\mathrm{)_2CH_2CH_2P}$], 2.46—2.48 [m, 4 H, $\mathrm{PC}H_2\mathrm{(CH_2)_4C}H_2\mathrm{P}$], 7.44—7.65 (m, 20 H, Ph)	*ca.* −13.5 (s, vbr)	56.5 (s)	48.0 (s, br) 59.0 (s, br)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. [b] The data for $[\mathrm{Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}}]$ (**3**) have been reported previously. See ref. 6 for details. [c] Measured in $[^2\mathrm{H_2}]$dichloromethane solution. [d] Measured at −90 °C, unless otherwise stated. [e] Hydrogen-1 decoupled, measured in $\mathrm{CD_2Cl_2–CH_2Cl_2}$ solution, chemical shifts positive to high frequency of 85% $\mathrm{H_3PO_4}$ (external). [f] Measured at −100 °C.

each of (**1**),[4] (**3**),[6] (**5**), and (**6**), and two broad or very broad singlets are observed for (**4**) and (**7**). Thus, the n.m.r. data suggest that the structure of the $\mathrm{Ph_2PCH_2PPh_2}$-containing cluster (**2**) might be significantly different to those of compounds (**1**) and (**3**)—(**7**). To investigate the skeletal geometry of (**2**) in detail, a single-crystal *X*-ray diffraction study was performed and further discussion of the variable-temperature n.m.r. data is deferred until the *X*-ray diffraction results have been presented.

The cluster (**2**) crystallizes in two forms, monoclinic and orthorhombic, but the molecular structures of (**2**) are closely similar in each case (Figure 1). Selected interatomic distances and angles for both crystalline forms are summarized in Table 3.

The metal skeleton of (**2**) adopts a capped square-based pyramidal geometry, with the basal atoms Au(1), Au(2), Ru(1), and Ru(4) and the apical atom Ru(3) defining the square-based pyramid and Ru(2) capping its Ru(1)Ru(3)Ru(4) face. The bidentate diphosphine ligand bridges the Au–Au vector and each Ru atom carries three terminal CO groups. The hydrido ligands, which were located by HYDEX,[8] adopt two different bonding modes. One occupies a site edge-bridging the Ru(1)–Ru(4) vector, whereas the other caps the Ru(2)Ru(3)Ru(4) face.

Although the gross molecular structure of (**2**) is the same in the two crystal forms, there are some noticeable changes induced by the differing crystal fields. The conformation of the $\mathrm{Ph_2PCH_2PPh_2}$ ligand varies substantially. The bidentate diphosphine has near mirror symmetry in the monoclinic form, but it adopts a less symmetrical geometry in the orthorhombic

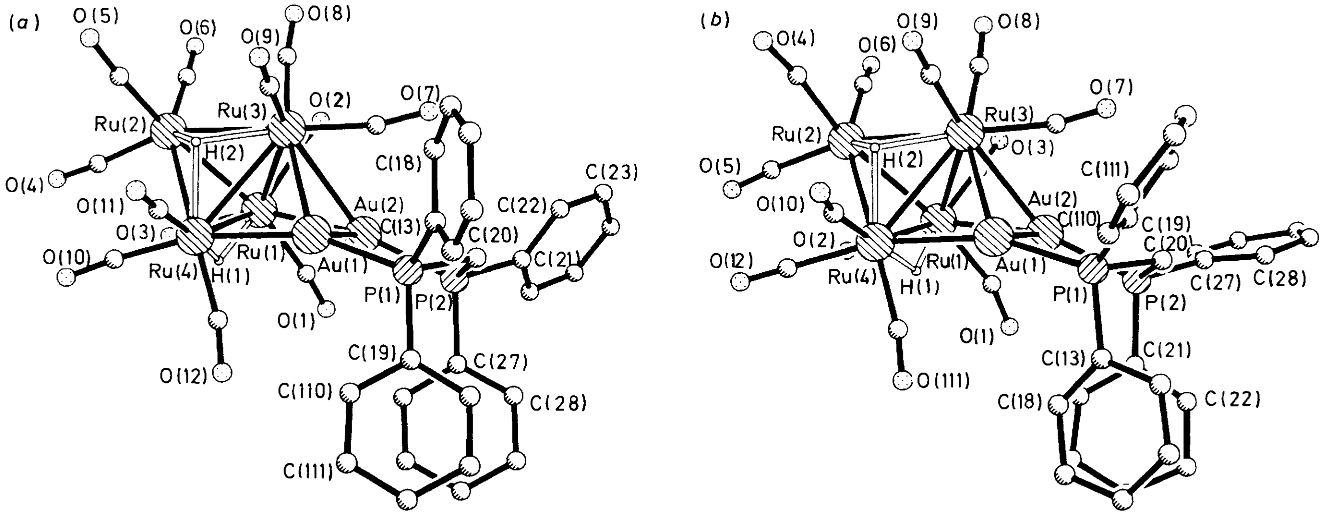

Figure 1. Molecular structures of the monoclinic (*a*) and orthorhombic (*b*) forms of $[\mathrm{Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}}]$ (**2**), showing the crystallographic numbering. The carbon atom of each carbonyl group has the same number as the oxygen atom

structure. Among the bond lengths, the metal–metal separations show the most significant distortions (Figure 2). The r.m.s. deviations of these distances between the two forms of (**2**) is 0.037 Å, compared with 0.002—0.004 Å for the standard deviations of the individual distances. This reflects the relative 'softness' of the metal–metal bonds, which allows the modest forces of crystal packing to cause differences of up to 0.091 Å [Au(2)–Ru(3)] in the lengths of the equivalent metal–metal separations in the two crystalline forms.

Thus, the formal replacement of two PPh_3 groups bonded to the Au atoms in complex (**1**) by a $Ph_2PCH_2PPh_2$ ligand in complex (**2**) causes a change in skeletal geometry from capped trigonal bipyramidal to capped square-based pyramidal. The trigonal-bipyramidal Au_2Ru_3 unit in the metal core of $[Au_3Ru_4(\mu_3\text{-H})(CO)_{12}(PPh_3)_3]$ undergoes a somewhat similar distortion, although to a lesser extent, when two PPh_3 ligands are formally replaced by $Ph_2PCH_2PPh_2$ in $[Au_3Ru_4(\mu\text{-H})(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}(PPh_3)]$.[9] Interestingly, metal framework structures based on square-based pyramidal rather than trigonal bipyramidal $M_2M'_3$ (M = Cu, Ag, or Au; M′ = transition metal other than Cu, Ag, or Au) units are rare for Group 1B metal heteronuclear clusters.[2] However, square-based pyramidal Au_2M_3 (M = Ru or Os) units have been observed in the metal cores of $[Au_2Ru_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-}Ph_2AsCH_2EPh_2)(CO)_{12}]$ (E = As or P),[6] $[Au_2Os_4L_2(CO)_{13}]$ (L = PPh_3, $PMePh_2$, or PEt_3),[10] and $[Au_2Ru_3(\mu\text{-H})(\mu_3\text{-COMe})(CO)_9(PPh_3)_2]$.[11]

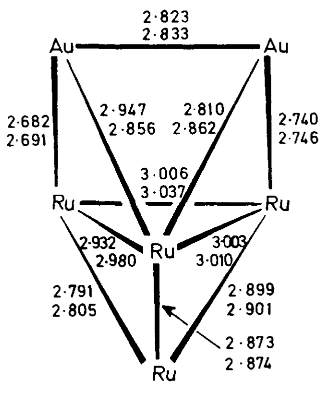

Figure 2. A comparison of the metal–metal separations in the capped square-based pyramidal metal cores of the two crystalline forms of $[Au_2Ru_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$ (**2**). Distances are given first for the monoclinic form, then for the orthorhombic form

The $Ph_2P(CH_2)_2PPh_2$-containing cluster (**3**) was previously thought to adopt a similar capped trigonal-bipyramidal metal framework structure to that of the analogous PPh_3-ligated species (**1**) because of the close similarity between the ^{197}Au Mössbauer spectra of the two compounds.[6] However, in view of the change in skeletal geometry observed for compound (**2**),

Table 3. Selected bond lengths (Å) and bond angles (°), with estimated standard deviations (e.s.d.s) in parentheses, for $[Au_2Ru_4(\mu_3\text{-H})(\mu\text{-H})(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$ (**2**)

Monoclinic form				Orthorhombic form			
Au(2)–Au(1)	2.823(1)	Au(2)–Ru(3)	2.947(2)	Au(1)–Au(2)	2.833(2)	Au(1)–Ru(3)	2.862(3)
Au(2)–Ru(1)	2.682(1)	Au(2)–P(2)	2.304(3)	Au(1)–Ru(4)	2.746(3)	Au(1)–P(1)	2.316(6)
Au(2)–C(7)	2.666(21)	Au(2)–C(1)	2.554(16)	Au(2)–Ru(1)	2.691(3)	Au(2)–Ru(3)	2.856(3)
Au(1)–Ru(3)	2.810(2)	Au(1)–Ru(4)	2.740(1)	Au(2)–P(2)	2.300(6)	Au(2)–C(1)	2.557(27)
Au(1)–P(1)	2.309(3)	Ru(3)–Ru(4)	3.003(2)	Ru(1)–Ru(3)	2.980(3)	Ru(1)–Ru(4)	3.037(3)
Ru(3)–Ru(1)	2.932(2)	Ru(3)–Ru(2)	2.873(2)	Ru(1)–Ru(2)	2.805(4)	Ru(1)–C(1)	1.945(32)
Ru(3)–C(7)	1.900(13)	Ru(3)–C(8)	1.891(17)	Ru(1)–C(2)	1.892(26)	Ru(1)–C(3)	1.872(34)
Ru(3)–C(9)	1.889(18)	Ru(3)–H(2)	1.97(9)	Ru(3)–Ru(4)	3.010(3)	Ru(3)–Ru(2)	2.874(3)
Ru(4)–Ru(1)	3.006(2)	Ru(4)–Ru(2)	2.899(2)	Ru(3)–C(7)	1.991(27)	Ru(3)–C(8)	1.920(31)
Ru(4)–C(10)	1.913(13)	Ru(4)–C(11)	1.931(17)	Ru(3)–C(9)	2.001(37)	Ru(4)–Ru(2)	2.901(3)
Ru(4)–C(12)	1.904(16)	Ru(4)–H(1)	1.75(14)	Ru(4)–C(10)	1.929(35)	Ru(4)–C(11)	1.966(25)
Ru(4)–H(2)	2.00(12)	Ru(1)–Ru(2)	2.791(2)	Ru(4)–C(12)	2.019(31)	Ru(2)–C(4)	1.979(37)
Ru(1)–C(1)	1.935(19)	Ru(1)–C(2)	1.860(15)	Ru(2)–C(5)	2.031(39)	Ru(2)–C(6)	2.000(37)
Ru(1)–C(3)	1.916(15)	Ru(1)–H(1)	1.76(7)	P(1)–C(20)	1.863(21)	P(1)–C(13)	1.804(25)
Ru(2)–C(4)	1.921(15)	Ru(2)–C(5)	1.885(23)	P(1)–C(19)	1.810(25)	P(2)–C(20)	1.831(23)
Ru(2)–C(6)	1.918(18)	Ru(2)–H(2)	1.97(9)	P(2)–C(21)	1.813(22)	P(2)–C(27)	1.812(23)
P(1)–C(20)	1.844(12)	P(2)–C(20)	1.839(13)	C(1)–O(1)	1.177(37)	C(2)–O(2)	1.144(32)
C(7)–O(7)	1.147(17)	C(8)–O(8)	1.093(22)	C(3)–O(3)	1.163(43)	C(7)–O(7)	1.096(35)
C(9)–O(9)	1.120(24)	C(10)–O(10)	1.129(17)	C(8)–O(8)	1.139(39)	C(9)–O(9)	1.016(44)
C(11)–O(11)	1.108(23)	C(12)–O(12)	1.125(21)	C(10)–O(10)	1.120(40)	C(11)–O(11)	1.088(33)
C(1)–O(1)	1.146(26)	C(2)–O(2)	1.142(18)	C(12)–O(12)	1.082(39)	C(4)–O(4)	1.124(53)
C(3)–O(3)	1.124(20)	C(4)–O(4)	1.119(18)	C(5)–O(5)	1.044(43)	C(6)–O(6)	1.023(47)
C(5)–O(5)	1.150(30)	C(6)–O(6)	1.105(22)				
Au(1)–Au(2)–Ru(3)	58.2(1)	Au(1)–Au(2)–Ru(1)	96.9(1)	Au(2)–Au(1)–Ru(3)	60.2(1)	Au(1)–Au(2)–Ru(3)	60.4(1)
Ru(3)–Au(2)–Ru(1)	62.6(1)	Au(1)–Au(2)–P(2)	89.6(1)	Ru(3)–Au(1)–Ru(4)	64.9(1)	Au(1)–Au(2)–P(2)	89.3(2)
Ru(3)–Au(2)–P(2)	131.0(1)	Ru(1)–Au(2)–P(2)	165.9(1)	Ru(3)–Au(1)–P(1)	131.8(2)	Ru(3)–Au(2)–P(2)	134.7(2)
Au(1)–Au(2)–C(7)	65.6(3)	Ru(3)–Au(2)–C(7)	39.2(3)	Au(1)–Au(2)–Ru(1)	98.1(1)	Ru(1)–Au(2)–C(1)	43.4(7)
Ru(1)–Au(2)–C(7)	97.9(3)	P(2)–Au(2)–C(7)	96.2(3)	Ru(1)–Au(2)–Ru(3)	64.9(1)	P(2)–Au(2)–C(1)	116.4(7)
Au(1)–Au(2)–C(1)	123.5(3)	Ru(3)–Au(2)–C(1)	105.8(4)	Ru(1)–Au(2)–P(2)	158.9(2)	Au(2)–Ru(1)–Ru(4)	82.9(1)
Ru(1)–Au(2)–C(1)	43.3(4)	P(2)–Au(2)–C(1)	123.1(4)	Au(1)–Au(2)–C(1)	122.0(7)	Au(2)–Ru(1)–Ru(2)	118.9(1)
C(7)–Au(2)–C(1)	137.8(5)	Au(2)–Au(1)–Ru(3)	63.1(1)	Ru(3)–Au(2)–C(1)	108.3(7)	Ru(4)–Ru(1)–Ru(2)	59.4(1)
Au(2)–Au(1)–Ru(4)	85.7(1)	Ru(3)–Au(1)–Ru(4)	65.5(1)	Au(2)–Ru(1)–Ru(3)	60.2(1)	Ru(3)–Ru(1)–C(1)	124.9(8)
Au(2)–Au(1)–P(1)	96.9(1)	Ru(3)–Au(1)–P(1)	132.5(1)	Ru(3)–Ru(1)–Ru(4)	60.0(1)	Ru(2)–Ru(1)–C(1)	170.9(8)
Ru(4)–Au(1)–P(1)	160.7(1)	Au(2)–Ru(3)–Au(1)	58.7(1)	Ru(3)–Ru(1)–Ru(2)	59.5(1)	Ru(3)–Ru(1)–C(2)	139.3(9)
Au(2)–Ru(3)–Ru(4)	79.0(1)	Au(1)–Ru(3)–Ru(4)	56.1(1)	Au(2)–Ru(1)–C(1)	64.6(8)	Ru(2)–Ru(1)–C(2)	79.9(9)
Au(2)–Ru(3)–Ru(1)	54.3(1)	Au(1)–Ru(3)–Ru(1)	91.7(1)	Ru(4)–Ru(1)–C(1)	114.5(8)	Au(2)–Ru(1)–C(3)	89.7(10)
Ru(4)–Ru(3)–Ru(1)	60.9(1)	Au(2)–Ru(3)–Ru(2)	110.8(1)	Au(2)–Ru(1)–C(2)	159.8(9)	Ru(4)–Ru(1)–C(3)	147.6(10)
Au(1)–Ru(3)–Ru(2)	115.2(1)	Ru(4)–Ru(3)–Ru(2)	59.1(1)	Ru(4)–Ru(1)–C(2)	102.8(9)	C(1)–Ru(1)–C(3)	90.0(13)

Table 3 (*continued*)

Monoclinic form				Orthorhombic form			
Ru(1)–Ru(3)–Ru(2)	57.5(1)	Au(2)–Ru(3)–C(7)	62.4(6)	C(1)–Ru(1)–C(2)	95.7(12)	Au(1)–Ru(3)–Au(2)	59.4(1)
Au(1)–Ru(3)–C(7)	75.7(5)	Ru(4)–Ru(3)–C(7)	129.5(6)	Ru(3)–Ru(1)–C(3)	89.0(10)	Au(2)–Ru(3)–Ru(1)	54.9(1)
Ru(1)–Ru(3)–C(7)	111.3(6)	Ru(2)–Ru(3)–C(7)	163.0(5)	Ru(2)–Ru(1)–C(3)	98.3(11)	Au(2)–Ru(3)–Ru(4)	80.7(1)
Au(2)–Ru(3)–C(8)	119.9(5)	Au(1)–Ru(3)–C(8)	167.9(4)	C(2)–Ru(1)–C(3)	95.0(13)	Au(1)–Ru(3)–Ru(2)	114.7(1)
Ru(4)–Ru(3)–C(8)	136.0(4)	Ru(1)–Ru(3)–C(8)	96.4(5)	Au(1)–Ru(3)–Ru(1)	91.1(1)	Ru(1)–Ru(3)–Ru(2)	57.2(1)
Ru(2)–Ru(3)–C(8)	76.9(4)	C(7)–Ru(3)–C(8)	92.9(6)	Au(1)–Ru(3)–Ru(4)	55.7(1)	Au(1)–Ru(3)–C(7)	70.5(8)
Au(2)–Ru(3)–C(9)	135.3(5)	Au(1)–Ru(3)–C(9)	81.6(5)	Ru(1)–Ru(3)–Ru(4)	60.9(1)	Ru(1)–Ru(3)–C(7)	119.4(8)
Ru(4)–Ru(3)–C(9)	96.1(5)	Ru(1)–Ru(3)–C(9)	155.0(4)	Au(2)–Ru(3)–Ru(2)	111.4(1)	Ru(2)–Ru(3)–C(7)	173.0(8)
Ru(2)–Ru(3)–C(9)	103.7(4)	C(7)–Ru(3)–C(9)	90.4(7)	Ru(4)–Ru(3)–Ru(2)	59.0(1)	Au(2)–Ru(3)–C(8)	108.4(10)
C(8)–Ru(3)–C(9)	94.6(8)	Au(2)–Ru(3)–H(2)	120.1(34)	Au(2)–Ru(3)–C(7)	66.7(8)	Ru(4)–Ru(3)–C(8)	142.4(9)
Au(1)–Ru(3)–H(2)	84.2(31)	Ru(4)–Ru(3)–H(2)	41.3(34)	Ru(4)–Ru(3)–C(7)	125.9(8)	C(7)–Ru(3)–C(8)	90.0(12)
Ru(1)–Ru(3)–H(2)	85.6(31)	Ru(2)–Ru(3)–H(2)	43.1(27)	Au(1)–Ru(3)–C(8)	159.7(9)	Au(2)–Ru(3)–C(9)	147.7(10)
C(7)–Ru(3)–H(2)	153.7(27)	C(8)–Ru(3)–H(2)	105.4(32)	Ru(1)–Ru(3)–C(8)	93.8(9)	Ru(4)–Ru(3)–C(9)	95.4(8)
C(9)–Ru(3)–H(2)	69.8(31)	Au(1)–Ru(4)–Ru(3)	58.4(1)	Ru(2)–Ru(3)–C(8)	84.3(9)	C(7)–Ru(3)–C(9)	91.3(12)
Au(1)–Ru(4)–Ru(1)	91.6(1)	Ru(3)–Ru(4)–Ru(1)	58.5(1)	Au(1)–Ru(3)–C(9)	91.8(9)	Au(1)–Ru(4)–Ru(1)	92.2(1)
Au(1)–Ru(4)–Ru(2)	116.6(1)	Ru(3)–Ru(4)–Ru(2)	58.2(1)	Ru(1)–Ru(3)–C(9)	148.2(9)	Ru(1)–Ru(4)–Ru(3)	59.1(1)
Ru(1)–Ru(4)–Ru(2)	56.4(1)	Au(1)–Ru(4)–C(10)	163.9(5)	Ru(2)–Ru(3)–C(9)	93.1(10)	Ru(1)–Ru(4)–Ru(2)	56.3(1)
Ru(3)–Ru(4)–C(10)	137.7(5)	Ru(1)–Ru(4)–C(10)	99.1(5)	C(8)–Ru(3)–C(9)	94.2(13)	Au(1)–Ru(4)–C(10)	85.5(9)
Ru(2)–Ru(4)–C(10)	79.5(5)	Au(1)–Ru(4)–C(11)	82.5(4)	Au(1)–Ru(4)–Ru(3)	59.4(1)	Ru(3)–Ru(4)–C(10)	97.4(8)
Ru(3)–Ru(4)–C(11)	95.3(5)	Ru(1)–Ru(4)–C(11)	151.3(5)	Au(1)–Ru(4)–Ru(2)	117.6(1)	Au(1)–Ru(4)–C(11)	70.5(7)
Ru(2)–Ru(4)–C(11)	101.4(5)	C(10)–Ru(4)–C(11)	93.5(7)	Ru(3)–Ru(4)–Ru(2)	58.1(1)	Ru(3)–Ru(4)–C(11)	126.7(7)
Au(1)–Ru(4)–C(12)	68.8(4)	Ru(3)–Ru(4)–C(12)	124.3(4)	Ru(1)–Ru(4)–C(10)	153.0(8)	C(10)–Ru(4)–C(11)	95.5(11)
Ru(1)–Ru(4)–C(12)	110.1(5)	Ru(2)–Ru(4)–C(12)	164.2(5)	Ru(2)–Ru(4)–C(10)	101.2(8)	Ru(1)–Ru(4)–C(12)	100.4(8)
C(10)–Ru(4)–C(12)	96.1(7)	C(11)–Ru(4)–C(12)	94.0(7)	Ru(1)–Ru(4)–C(11)	109.1(7)	Ru(2)–Ru(4)–C(12)	79.3(9)
Au(1)–Ru(4)–H(1)	102.5(38)	Ru(3)–Ru(4)–H(1)	88.4(38)	Ru(2)–Ru(4)–C(11)	161.8(7)	C(11)–Ru(4)–C(12)	94.3(12)
Ru(1)–Ru(4)–H(1)	31.1(39)	Ru(2)–Ru(4)–H(1)	77.5(46)	Au(1)–Ru(4)–C(12)	162.9(9)	Ru(1)–Ru(2)–Ru(4)	64.3(1)
C(10)–Ru(4)–H(1)	81.4(37)	C(11)–Ru(4)–H(1)	174.9(45)	Ru(3)–Ru(4)–C(12)	137.4(9)	Ru(1)–Ru(2)–C(4)	161.6(9)
C(12)–Ru(4)–H(1)	86.8(46)	Au(1)–Ru(4)–H(2)	85.5(22)	C(10)–Ru(4)–C(12)	88.4(12)	Ru(4)–Ru(2)–C(4)	106.6(9)
Ru(3)–Ru(4)–H(2)	40.6(26)	Ru(1)–Ru(4)–H(2)	83.1(31)	Ru(1)–Ru(2)–Ru(3)	63.3(1)	Ru(3)–Ru(2)–C(5)	164.2(9)
Ru(2)–Ru(4)–H(2)	42.6(26)	C(10)–Ru(4)–H(2)	107.6(23)	Ru(3)–Ru(2)–Ru(4)	62.8(1)	C(4)–Ru(2)–C(5)	93.5(13)
C(11)–Ru(4)–H(2)	68.4(31)	C(12)–Ru(4)–H(2)	150.9(24)	Ru(3)–Ru(2)–C(4)	98.4(9)	Ru(3)–Ru(2)–C(6)	99.9(10)
H(1)–Ru(4)–H(2)	112.8(53)	Au(2)–Ru(1)–Ru(3)	63.1(1)	Ru(1)–Ru(2)–C(5)	104.1(8)	C(4)–Ru(2)–C(6)	91.7(15)
Au(2)–Ru(1)–Ru(4)	83.2(1)	Ru(3)–Ru(1)–Ru(4)	60.7(1)	Ru(4)–Ru(2)–C(5)	103.8(10)	Au(1)–P(1)–C(20)	109.6(7)
Au(2)–Ru(1)–Ru(2)	122.1(1)	Ru(3)–Ru(1)–Ru(2)	60.2(1)	Ru(1)–Ru(2)–C(6)	93.6(11)	C(20)–P(1)–C(13)	100.0(11)
Ru(4)–Ru(1)–Ru(2)	59.9(1)	Au(2)–Ru(1)–C(1)	64.8(4)	Ru(4)–Ru(2)–C(6)	156.0(11)	C(20)–P(1)–C(19)	101.1(11)
Ru(3)–Ru(1)–C(1)	128.0(4)	Ru(4)–Ru(1)–C(1)	114.5(4)	C(5)–Ru(2)–C(6)	90.1(15)	Au(2)–P(2)–C(20)	113.6(7)
Ru(2)–Ru(1)–C(1)	168.1(4)	Au(2)–Ru(1)–C(2)	92.4(4)	Au(2)–C(1)–O(1)	123.6(21)	C(20)–P(2)–C(21)	105.3(11)
Ru(3)–Ru(1)–C(2)	85.0(6)	Ru(4)–Ru(1)–C(2)	143.6(6)	Ru(1)–C(2)–O(2)	172.8(26)	C(20)–P(2)–C(27)	103.7(10)
Ru(2)–Ru(1)–C(2)	93.7(6)	C(1)–Ru(1)–C(2)	95.7(7)	Ru(3)–C(7)–O(7)	167.8(25)	Au(2)–C(1)–Ru(1)	71.9(9)
Au(2)–Ru(1)–C(3)	155.8(6)	Ru(3)–Ru(1)–C(3)	139.8(6)	Ru(3)–C(9)–O(9)	177.0(23)	Ru(1)–C(1)–O(1)	163.2(23)
Ru(4)–Ru(1)–C(3)	101.9(5)	Ru(2)–Ru(1)–C(3)	79.6(6)	Ru(4)–C(11)–O(11)	171.3(24)	Ru(1)–C(3)–O(3)	176.0(26)
C(1)–Ru(1)–C(3)	91.9(7)	C(2)–Ru(1)–C(3)	96.7(7)	Ru(2)–C(4)–O(4)	172.4(31)	Ru(3)–C(8)–O(8)	174.2(30)
Au(2)–Ru(1)–H(1)	89.1(38)	Ru(3)–Ru(1)–H(1)	90.6(54)	Ru(2)–C(6)–O(6)	168.5(38)	Ru(4)–C(10)–O(10)	167.4(27)
Ru(4)–Ru(1)–H(1)	31.0(56)	Ru(2)–Ru(1)–H(1)	80.6(56)	Ru(1)–H(1)–Ru(4)	119.8	Ru(4)–C(12)–O(12)	176.5(27)
C(1)–Ru(1)–H(1)	90.1(57)	C(2)–Ru(1)–H(1)	174.1(52)	Ru(3)–H(2)–Ru(2)	93.5	Ru(2)–C(5)–O(5)	171.6(35)
C(3)–Ru(1)–H(1)	84.1(40)	Ru(3)–Ru(2)–Ru(4)	62.7(1)	Au(2)–Au(1)–Ru(4)	85.8(1)	P(1)–C(20)–P(2)	114.0(12)
Ru(3)–Ru(2)–Ru(1)	62.3(1)	Ru(4)–Ru(2)–Ru(1)	63.7(1)	Au(2)–Au(1)–P(1)	96.7(2)	Ru(3)–H(2)–Ru(4)	99.3
Ru(3)–Ru(2)–C(4)	158.3(6)	Ru(4)–Ru(2)–C(4)	97.5(5)	Ru(4)–Au(1)–P(1)	161.6(2)	Ru(4)–H(2)–Ru(2)	94.6
Ru(1)–Ru(2)–C(4)	102.2(6)	Ru(3)–Ru(2)–C(5)	100.1(5)				
Ru(4)–Ru(2)–C(5)	103.2(6)	Ru(1)–Ru(2)–C(5)	161.1(5)				
C(4)–Ru(2)–C(5)	92.6(8)	Ru(3)–Ru(2)–C(6)	100.1(4)				
Ru(4)–Ru(2)–C(6)	154.7(5)	Ru(1)–Ru(2)–C(6)	92.3(5)				
C(4)–Ru(2)–C(6)	95.4(6)	C(5)–Ru(2)–C(6)	97.8(8)				
Ru(3)–Ru(2)–H(2)	43.3(29)	Ru(4)–Ru(2)–H(2)	43.5(35)				
Ru(1)–Ru(2)–H(2)	89.6(34)	C(4)–Ru(2)–H(2)	127.8(29)				
C(5)–Ru(2)–H(2)	71.9(35)	C(6)–Ru(2)–H(2)	135.2(31)				
P(1)–C(20)–P(2)	114.2(5)	Au(2)–C(7)–Ru(3)	78.4(6)				
Au(2)–C(7)–O(7)	113.4(14)	Ru(3)–C(7)–O(7)	167.6(17)				
Ru(3)–C(8)–O(8)	170.8(13)	Ru(3)–C(9)–O(9)	177.9(15)				
Ru(4)–C(10)–O(10)	170.5(15)	Ru(4)–C(11)–O(11)	178.0(15)				
Ru(4)–C(12)–O(12)	169.2(10)	Au(2)–C(1)–Ru(1)	71.9(6)				
Au(2)–C(1)–O(1)	120.7(10)	Ru(1)–C(1)–O(1)	167.3(12)				
Ru(1)–C(2)–O(2)	176.0(16)	Ru(1)–C(3)–O(3)	170.7(17)				
Ru(2)–C(4)–O(4)	175.4(17)	Ru(2)–C(5)–O(5)	175.1(18)				
Ru(2)–C(6)–O(6)	177.7(14)	Ru(4)–H(1)–Ru(1)	117.8(93)				
Ru(3)–H(2)–Ru(4)	98.1(48)	Ru(3)–H(2)–Ru(2)	93.6(47)				
Ru(4)–H(2)–Ru(2)	93.8(45)						

Table 4. Selected bond lengths (Å) and bond angles (°), with estimated standard deviations (e.s.d.s) in parentheses, for $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$ (**3**)

Au(2)–Au(1)	2.828(4)	C(7)–Ru(3)	1.837(15)	Ru(3)–Au(1)	2.777(4)	C(8)–Ru(3)	1.930(12)
Ru(4)–Au(1)	2.784(4)	C(9)–Ru(3)	1.886(14)	P(1)–Au(1)	2.286(4)	C(10)–Ru(4)	1.882(13)
Ru(1)–Au(2)	2.851(4)	C(11)–Ru(4)	1.906(12)	Ru(3)–Au(2)	2.965(4)	C(12)–Ru(4)	1.870(16)
Ru(4) ··· Au(2)	3.446(4)	C(37)–P(1)	1.840(12)	P(2)–Au(2)	2.276(4)	C(38)–P(2)	1.855(12)
Ru(2)–Ru(1)	2.782(4)	C(1)–O(1)	1.140(20)	Ru(3)–Ru(1)	3.008(4)	C(2)–O(2)	1.134(14)
Ru(4)–Ru(1)	2.984(4)	C(3)–O(3)	1.158(15)	C(1)–Ru(1)	1.948(17)	C(4)–O(4)	1.171(18)
C(2)–Ru(1)	1.886(12)	C(5)–O(5)	1.158(20)	C(3)–Ru(1)	1.887(14)	C(6)–O(6)	1.135(17)
Ru(3)–Ru(2)	2.844(4)	C(7)–O(7)	1.174(18)	Ru(4)–Ru(2)	2.783(4)	C(8)–O(8)	1.128(15)
C(4)–Ru(2)	1.873(16)	C(9)–O(9)	1.153(16)	C(5)–Ru(2)	1.847(17)	C(10)–O(10)	1.137(15)
C(6)–Ru(2)	1.865(15)	C(11)–O(11)	1.149(14)	Ru(4)–Ru(3)	2.947(4)	C(12)–O(12)	1.176(19)

Ru(3)–Au(1)–Au(2)	63.9(1)	Ru(2)–Ru(4)–Au(2)	98.7(1)	P(1)–Au(1)–Au(2)	110.4(2)	Ru(3)–Ru(4)–Au(2)	54.6(1)
Ru(4)–Au(1)–Ru(3)	64.0(1)	Ru(3)–Ru(4)–Au(1)	57.9(1)	P(1)–Au(1)–Ru(4)	150.0(1)	Ru(3)–Ru(4)–Ru(2)	59.4(1)
P(1)–Au(1)–Ru(3)	145.7(1)	Ru(3)–Ru(4)–Ru(1)	60.9(1)	Ru(3)–Au(2)–Au(1)	57.2(1)	C(10)–Ru(4)–Au(2)	140.6(4)
Ru(1)–Au(2)–Au(1)	102.7(1)	C(10)–Ru(4)–Au(1)	161.6(4)	Ru(4)–Au(2)–Au(1)	51.5(1)	C(10)–Ru(4)–Ru(2)	78.1(4)
Ru(3)–Au(2)–Ru(1)	62.3(1)	C(10)–Ru(4)–Ru(1)	97.2(5)	Ru(4)–Au(2)–Ru(3)	54.1(1)	C(11)–Ru(4)–Au(1)	71.4(4)
Ru(4)–Au(2)–Ru(1)	55.6(1)	C(10)–Ru(4)–Ru(3)	137.5(3)	P(2)–Au(2)–Ru(1)	146.8(1)	C(11)–Ru(4)–Ru(1)	110.6(4)
P(2)–Au(2)–Au(1)	97.8(2)	C(11)–Ru(4)–Au(2)	76.1(4)	P(2)–Au(2)–Ru(4)	126.0(2)	C(11)–Ru(4)–Ru(3)	123.5(4)
P(2)–Au(2)–Ru(3)	149.8(1)	C(11)–Ru(4)–Ru(2)	166.1(4)	Ru(3)–Ru(1)–Au(2)	60.7(1)	C(12)–Ru(4)–Au(1)	76.2(5)
Ru(2)–Ru(1)–Au(2)	114.8(1)	C(11)–Ru(4)–C(10)	97.6(6)	Ru(4)–Ru(1)–Au(2)	72.4(1)	C(12)–Ru(4)–Ru(1)	150.8(4)
Ru(3)–Ru(1)–Ru(2)	58.7(1)	C(12)–Ru(4)–Au(2)	128.4(5)	Ru(4)–Ru(1)–Ru(3)	58.9(1)	C(12)–Ru(4)–Ru(3)	94.7(5)
Ru(4)–Ru(1)–Ru(2)	57.6(1)	C(12)–Ru(4)–Ru(2)	97.2(5)	C(1)–Ru(1)–Ru(2)	171.4(4)	C(12)–Ru(4)–C(11)	96.0(6)
C(1)–Ru(1)–Au(2)	69.3(4)	C(12)–Ru(4)–C(10)	90.7(6)	C(1)–Ru(1)–Ru(4)	119.2(5)	C(37)–P(1)–Au(1)	109.4(4)
C(1)–Ru(1)–Ru(3)	127.9(4)	C(37)–P(1)–C(13)	106.4(6)	C(2)–Ru(1)–Ru(2)	80.6(4)	C(37)–P(1)–C(19)	103.5(6)
C(2)–Ru(1)–Au(2)	146.0(3)	C(38)–P(2)–C(25)	103.7(5)	C(2)–Ru(1)–Ru(4)	94.6(4)	C(38)–P(2)–Au(2)	113.7(4)
C(2)–Ru(1)–Ru(3)	138.6(3)	Ru(1)–H(1)–Au(2)	104.7(2)	C(3)–Ru(1)–Au(2)	116.7(4)	C(38)–P(2)–C(31)	103.2(5)
C(2)–Ru(1)–C(1)	92.0(6)	Ru(3)–H(1)–Ru(1)	113.3(2)	C(3)–Ru(1)–Ru(3)	94.8(5)	Ru(3)–H(1)–Au(2)	110.9(2)
C(3)–Ru(1)–Ru(2)	90.2(5)	O(1)–C(1)–Ru(1)	168.2(11)	C(3)–Ru(1)–C(1)	94.5(7)	Ru(4)–H(2)–Ru(1)	112.0(12)
C(3)–Ru(1)–Ru(4)	145.3(4)	O(3)–C(3)–Ru(1)	178.1(11)	Ru(3)–Ru(2)–Ru(1)	64.6(1)	O(2)–C(2)–Ru(1)	174.2(10)
C(3)–Ru(1)–C(2)	92.1(5)	O(5)–C(5)–Ru(2)	178.9(14)	Ru(4)–Ru(2)–Ru(3)	63.2(1)	O(4)–C(4)–Ru(2)	175.6(11)
Ru(4)–Ru(2)–Ru(1)	64.9(1)	O(7)–C(7)–Ru(3)	176.8(12)	C(4)–Ru(2)–Ru(3)	98.1(5)	O(6)–C(6)–Ru(2)	175.9(11)
C(4)–Ru(2)–Ru(1)	98.9(5)	O(9)–C(9)–Ru(3)	172.9(11)	C(5)–Ru(2)–Ru(1)	157.1(4)	O(8)–C(8)–Ru(3)	169.4(11)
C(4)–Ru(2)–Ru(4)	158.7(4)	O(11)–C(11)–Ru(4)	171.8(10)	C(5)–Ru(2)–Ru(4)	93.9(5)	O(10)–C(10)–Ru(4)	172.5(11)
C(5)–Ru(2)–Ru(3)	98.9(5)	C(38)–C(37)–P(1)	113.6(7)	C(6)–Ru(2)–Ru(1)	101.5(5)	O(12)–C(12)–Ru(4)	175.5(12)
C(5)–Ru(2)–C(4)	99.2(7)	H(1)–Au(2)–Au(1)	90.9(1)	C(6)–Ru(2)–Ru(4)	104.6(5)	C(37)–C(38)–P(2)	112.6(8)
C(6)–Ru(2)–Ru(3)	164.0(4)	H(1)–Au(2)–Ru(3)	34.6(1)	C(6)–Ru(2)–C(5)	91.8(7)	H(1)–Au(2)–Ru(1)	37.6(1)
C(6)–Ru(2)–C(4)	91.7(6)	H(1)–Au(1)–P(2)	167.0(1)	Ru(1)–Ru(3)–Au(1)	100.1(1)	H(1)–Au(2)–Ru(4)	67.0(1)
Au(2)–Ru(3)–Au(1)	58.9(1)	H(1)–Ru(1)–Ru(2)	91.5(1)	Ru(2)–Ru(3)–Au(1)	114.2(1)	H(1)–Ru(1)–Au(2)	37.6(1)
Ru(1)–Ru(3)–Au(2)	57.0(1)	C(1)–Ru(1)–Ru(4)	79.7(1)	Ru(2)–Ru(3)–Ru(1)	56.7(1)	H(1)–Ru(1)–Ru(3)	33.3(1)
Ru(2)–Ru(3)–Au(2)	109.5(1)	C(2)–Ru(1)–Ru(2)	90.1(7)	Ru(4)–Ru(3)–Au(2)	71.3(1)	H(2)–Ru(1)–Au(2)	60.4(32)
Ru(4)–Ru(3)–Au(1)	58.1(1)	C(3)–Ru(1)–Ru(4)	34.0(7)	Ru(4)–Ru(3)–Ru(2)	57.4(1)	H(2)–Ru(1)–Ru(3)	82.7(27)
Ru(4)–Ru(3)–Ru(1)	60.1(1)	C(1)–Ru(1)–H(1)	95.8(5)	C(7)–Ru(3)–Au(2)	138.5(4)	H(2)–Ru(1)–H(1)	87.6(34)
C(7)–Ru(3)–Au(1)	79.8(5)	C(2)–Ru(1)–H(1)	171.9(3)	C(7)–Ru(3)–Ru(2)	89.1(4)	C(1)–Ru(1)–H(2)	85.6(7)
C(7)–Ru(3)–Ru(1)	142.8(4)	C(3)–Ru(1)–H(1)	89.2(5)	C(8)–Ru(3)–Au(1)	73.6(5)	C(2)–Ru(1)–H(2)	91.0(34)
C(7)–Ru(3)–Ru(4)	90.6(5)	H(1)–Ru(3)–Au(1)	92.5(1)	C(8)–Ru(3)–Ru(1)	121.3(5)	C(3)–Ru(1)–H(2)	176.8(33)
C(8)–Ru(3)–Au(2)	72.1(5)	H(1)–Ru(3)–Ru(1)	33.3(1)	C(8)–Ru(3)–Ru(4)	129.6(5)	H(1)–Ru(3)–Au(2)	34.6(1)
C(8)–Ru(3)–Ru(2)	171.9(4)	H(1)–Ru(3)–Ru(4)	81.0(1)	C(9)–Ru(3)–Au(1)	161.7(4)	H(1)–Ru(3)–Ru(2)	89.5(1)
C(8)–Ru(3)–C(7)	94.6(6)	C(8)–Ru(3)–H(1)	87.9(5)	C(9)–Ru(3)–Ru(1)	96.5(5)	C(7)–Ru(3)–H(1)	170.8(4)
C(9)–Ru(3)–Au(2)	126.8(5)	H(2)–Ru(4)–Au(1)	95.9(35)	C(9)–Ru(3)–Ru(4)	138.7(3)	C(9)–Ru(3)–H(1)	97.2(5)
C(9)–Ru(3)–Ru(2)	81.4(4)	H(2)–Ru(4)–Ru(1)	34.0(14)	C(9)–Ru(3)–C(8)	91.3(6)	H(2)–Ru(4)–Au(2)	44.7(32)
C(9)–Ru(3)–C(7)	91.6(7)	H(2)–Ru(4)–Ru(3)	84.5(20)	Ru(1)–Ru(4)–Au(1)	100.5(1)	H(2)–Ru(4)–Ru(2)	90.1(21)
Au(2)–Ru(4)–Au(1)	52.7(1)	C(11)–Ru(4)–H(2)	77.2(19)	Ru(2)–Ru(4)–Au(1)	115.9(1)	C(10)–Ru(4)–H(2)	96.0(33)
Ru(1)–Ru(4)–Au(2)	52.0(1)	Ru(4)–Au(1)–Au(2)	75.8(1)	Ru(2)–Ru(4)–Ru(1)	57.5(1)	C(12)–Ru(4)–H(2)	171.0(31)

a single-crystal *X*-ray diffraction study was performed on cluster (**3**) to investigate its structure in detail.

The molecular structure of compound (**3**) is illustrated in Figure 3, which also shows the crystallographic numbering. Selected interatomic distances and angles are summarized in Table 4.

The metal core of (**3**) consists of a Ru_4 tetrahedron, with the Ru(1)–Ru(3) and Ru(3)–Ru(4) edges bridged by Au(2) and Au(1), respectively, so that the Au atoms are in close contact [Au(1)–Au(2) 2.828(4) Å]. The $Ph_2P(CH_2)_2PPh_2$ ligand bridges the Au–Au vector and each Ru atom carries three terminal CO groups. One hydrido ligand caps the Au(2)Ru(1)-Ru(3) face, whereas the other bridges the Ru(1)–Ru(4) edge of the metal framework.

The skeletal geometry of (**3**) is reasonably similar to that adopted by (**1**),[4] but one of the Au–Ru distances [Au(2) ··· Ru(4) 3.446(4) Å] in (**3**) is considerably larger than the equivalent separation in (**1**) [2.859(1) or 2.949(1) Å] and it is too long for any significant bonding interaction to occur between the atoms. Elongations of one of the equatorial Au–Ru vectors in a trigonal-bipyramidal Au_2Ru_3 unit are also caused by the stereochemical demands of the $Ph_2PCH_2PPh_2$ ligand in the clusters $[Au_2Ru_3(\mu_3\text{-}S)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_9]$ [Au ··· Ru 3.335(1) Å][12] and $[Au_3Ru_4(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}(PPh_3)]$ [Au ··· Ru 3.549(3) Å].[9] Thus, the formal replacement of the two PPh_3 groups attached to the Au atoms in cluster (**1**) by a $Ph_2P(CH_2)_2PPh_2$ ligand in compound (**3**) distorts the metal framework structure from a capped trigonal

Table 5. Crystal structure analyses of $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ [n = 1 (**2**) or 2 (**3**)]

Cluster	(**2**)	(**2**)	(**3**)
Formula	$C_{37}H_{24}Au_2O_{12}P_2Ru_4$	$C_{37}H_{24}Au_2O_{12}P_2Ru_4$	$C_{38}H_{26}Au_2O_{12}P_2Ru_4$
M	1 520.7	1 520.7	1 534.8
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$C2/c$ (no. 15)	$P2_12_12_1$ (no. 19)	$P2_1/n$ (no. 14)
a/Å	24.773(12)	15.096(9)	14.347(1)
b/Å	17.892(7)	16.543(8)	12.727(2)
c/Å	21.473(9)	17.374(10)	24.480(4)
β/°	115.79(3)		104.29(1)
U/Å^3	8 569(7)	4 340(4)	4 332(1)
Z	8	4	4
D_c/g cm^{-3}	2.358	2.327	2.353
F(000)	5 646	2 823	2 856
Diffractometer	Nicolet P3m	Nicolet P3m	Nonius CAD-4
Crystal size/mm	0.4 × 0.3 × 0.25	0.45 × 0.35 × 0.25	0.82 × 0.68 × 0.13
μ/cm^{-1} (Mo-K_α)	83.3	81.9	82.02
Absorption correction (min., max. transmission coefficients)	0.011, 0.031	0.017, 0.037	0.45, 1.00
2θ range/°	4.0—50.0	4.0—50.0	3.0—50.0
h, k, l range	−30 to 30, 0 to 22, 0 to 27	0 to 18, 0 to 20, 0 to 21	0 to 17, 0 to 15, −29 to 29
Intensity variation/%	<3	<3	<3
Total no. of reflections	7 887	3 877	8 314
No. of unique reflections	5 709	3 674	7 591
Significance test	$F_o \geqslant 2\sigma(F_o)$	$F_o \geqslant 2\sigma(F_o)$	$F_o \geqslant 6.0\sigma(F_o)$
No. of reflections used in the refinement	5 019	3 168	5 374
No. of refined parameters; total	524	508	539
Block (1)			295
Block (2)			235
Max. least-squares shift-to-error ratio	0.02	0.03	0.02
Min. and max. height in final Fourier difference map, Δρ/e Å^{-3}	−0.75, +0.95	−1.4, +1.8	−0.51, +0.38
Function minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Weighting scheme parameter g, in $w = 1/[\sigma^2(F_o) + gF_o^2]$	0.000 75	0.000 8	0.000 8
Final R	0.046	0.056	0.037
Final R'	0.044	0.052	0.040

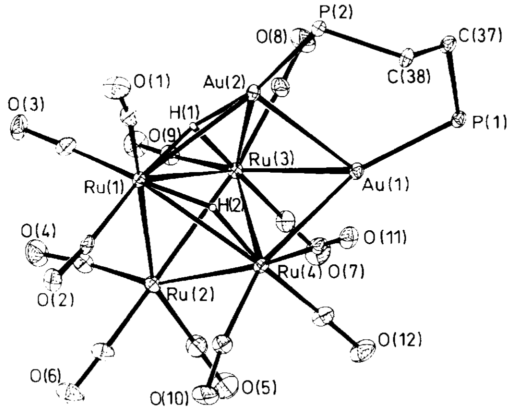

Figure 3. Molecular structure of $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_2\text{-}PPh_2\}(CO)_{12}]$ (**3**), showing the crystallographic numbering. The phenyl groups have been omitted for clarity and the carbon atom of each carbonyl group has the same number as the oxygen atom

bipyramid towards a capped square-based pyramid, but the extent of the structural change is very much smaller than that caused by the $Ph_2PCH_2PPh_2$ ligand in (**2**). Interestingly, a similar change in the nature of ligands attached to the Group 1B metals in the analogous copper- and silver-containing clusters $[M_2Ru_4(\mu_3\text{-}H)_2(CO)_{12}L_2]$ [M = Cu or Ag; L = PPh_3 or L_2 = $\mu\text{-}Ph_2P(CH_2)_nPPh_2$ (n = 1 or 2)] does not result in any significant alteration of the capped trigonal-bipyramidal skeletal geometries adopted by the PPh_3-ligated species.[4,13,14]

From the above results, it seems likely that the steric constraints of the bidentate diphosphine ligands $Ph_2P(CH_2)_nPPh_2$ (n = 3—6) will be insufficient to alter the metal framework structures of compounds (**4**)—(**7**) significantly and that these species probably exhibit very similar capped trigonal-bipyramidal skeletal geometries to that established for the PPh_3-ligated cluster (**1**).[4]

Although the X-ray crystal structure of the $Ph_2P(CH_2)_2PPh_2$-containing species (**3**) clearly shows that there are two phosphorus and two gold sites in the ground-state structure, the ambient-temperature ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of the cluster show a single, averaged phosphorus environment.[6] Thus, it seems that compound (**3**) undergoes similar dynamic behaviour involving gold-atom site exchange to that previously established for (**1**).[4] At −90 °C, the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of (**3**) is a very broad singlet, but no spectrum consistent with the ground-state structure could be obtained.[6] The spectroscopic data for compounds (**4**)—(**7**) suggest that the metal cores of these clusters are also stereochemically non-rigid at ambient temperature in solution. In each case, the room-temperature ^1H and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra show a single, averaged phosphorus environment. At −90 °C, however, two broad or very broad singlets, consistent with the proposed ground-state structures, are visible for (**4**) and (**7**) and a broad or very broad singlet is observed for each of (**5**) and (**6**). Thus, as previously observed for the analogous copper- and silver-containing clusters $[M_2Ru_4(\mu_3\text{-}H)_2\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (M = Cu or Ag, n = 1—6)[13,14] the metal frameworks of complexes (**3**)—(**7**) still undergo intramolecular rearrangements in solution, even when the two Group 1B metals are linked together by bidentate diphosphine ligands.

Table 6. Atomic positional parameters (fractional co-ordinates) (× 10^4) for the monoclinic form of $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$ (**2**), with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Au(2)	1 191(1)	2 134(1)	1 727(1)	C(112)	1 746(10)	5 545(10)	3 625(12)
Au(1)	1 542(1)	3 504(1)	1 362(1)	C(113)	2 210(11)	5 071(10)	3 985(9)
Ru(3)	1 375(1)	2 290(1)	466(1)	C(114)	2 381(7)	4 553(8)	3 636(7)
Ru(4)	448(1)	3 476(1)	232(1)	C(20)	2 477(5)	2 929(6)	2 968(6)
Ru(1)	246(1)	1 879(1)	511(1)	C(7)	2 047(7)	2 013(9)	1 296(8)
Ru(2)	247(1)	2 270(1)	−747(1)	O(7)	2 495(5)	1 805(7)	1 716(5)
P(1)	2 285(1)	3 791(2)	2 444(2)	C(8)	1 433(7)	1 428(9)	−9(8)
P(2)	1 826(2)	2 362(2)	2 870(2)	O(8)	1 542(5)	926(7)	−223(6)
C(21)	2 134(6)	1 533(6)	3 396(6)	C(9)	1 872(6)	2 880(8)	201(8)
C(22)	2 669(6)	1 201(7)	3 473(6)	O(9)	2 173(5)	3 212(7)	38(7)
C(23)	2 850(7)	533(8)	3 809(7)	C(10)	−343(6)	3 713(9)	−446(8)
C(24)	2 526(8)	189(8)	4 098(7)	O(10)	−791(5)	3 951(7)	−815(6)
C(25)	1 998(8)	495(8)	4 016(8)	C(11)	821(7)	4 218(8)	−107(7)
C(26)	1 784(8)	1 177(8)	3 667(8)	O(11)	1 041(5)	4 627(6)	−309(7)
C(27)	1 513(6)	2 874(7)	3 376(6)	C(12)	433(6)	4 107(8)	938(7)
C(28)	1 825(8)	2 938(9)	4 074(8)	O(12)	339(4)	4 513(6)	1 279(6)
C(29)	1 597(8)	3 337(9)	4 460(8)	C(1)	99(7)	1 738(8)	1 317(8)
C(210)	1 053(8)	3 654(9)	4 125(9)	O(1)	−87(6)	1 600(9)	1 708(7)
C(211)	740(8)	3 607(1)	3 434(10)	C(2)	484(8)	899(8)	476(8)
C(212)	957(7)	3 202(9)	3 049(8)	O(2)	630(6)	291(6)	492(6)
C(13)	2 998(5)	4 084(7)	2 463(6)	C(3)	−585(7)	1 742(9)	−102(8)
C(14)	3 294(7)	4 720(8)	2 767(7)	O(3)	−1 074(5)	1 601(9)	−394(7)
C(15)	3 802(7)	4 939(10)	2 744(7)	C(4)	−587(7)	2 462(9)	−1 321(8)
C(16)	4 026(8)	4 517(11)	2 368(9)	O(4)	−1 068(5)	2 549(8)	−1 690(6)
C(17)	3 730(8)	3 883(11)	2 050(9)	C(5)	482(8)	2 692(11)	−1 396(9)
C(18)	3 227(7)	3 653(8)	2 086(8)	O(5)	638(7)	2 897(9)	−1 799(7)
C(19)	2 093(6)	4 477(7)	2 940(7)	C(6)	225(6)	1 245(10)	−1 018(7)
C(110)	1 637(6)	4 958(7)	2 585(7)	O(6)	206(5)	662(7)	−1 195(6)
C(111)	1 453(8)	5 487(9)	2 919(10)				

Table 7. Atomic positional parameters (fractional co-ordinates) (× 10^4) for the orthorhombic form of $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)(\mu\text{-}Ph_2PCH_2PPh_2)(CO)_{12}]$ (**2**), with e.s.d.s in parentheses

Atom	x	y	z	Atom	x	y	z
Au(1)	1 176(1)	71(1)	1 195(1)	C(5)	−2 784(30)	−228(18)	2 486(17)
Au(2)	56(1)	424(1)	−70(1)	O(5)	−3 218(17)	−654(14)	2 719(15)
Ru(1)	−1 500(1)	47(1)	594(1)	C(6)	−2 699(20)	1 352(26)	1 834(22)
Ru(3)	−262(1)	1 181(1)	1 381(1)	O(6)	−3 214(15)	1 687(17)	1 623(30)
Ru(4)	−310(1)	−560(1)	1 880(1)	C(20)	2 303(15)	629(15)	−430(11)
Ru(2)	−1 801(1)	517(1)	2 123(1)	C(13)	3 019(18)	−767(14)	249(13)
P(1)	2 503(4)	171(4)	533(3)	C(14)	3 918(17)	−771(15)	−38(13)
P(2)	1 259(4)	320(4)	−877(3)	C(15)	4 337(20)	−1 461(15)	−241(14)
C(1)	−1 285(18)	−454(16)	−401(19)	C(16)	3 906(19)	−2 168(16)	−212(14)
O(1)	−1 312(15)	−890(13)	−935(12)	C(17)	3 063(19)	−2 196(15)	99(15)
C(2)	−2 579(16)	−497(17)	787(17)	C(18)	2 660(18)	−1 479(15)	313(14)
O(2)	−3 250(13)	−818(12)	824(13)	C(19)	3 351(17)	835(15)	910(14)
C(3)	−2 028(20)	933(21)	106(20)	C(110)	3 975(19)	540(15)	1 439(16)
O(3)	−2 394(18)	1 452(15)	−213(18)	C(111)	4 631(18)	967(16)	1 802(15)
C(7)	701(19)	1 706(17)	778(14)	C(112)	4 692(22)	1 755(18)	1 614(17)
O(7)	1 149(15)	2 112(13)	468(12)	C(113)	4 075(21)	2 075(18)	1 196(19)
C(8)	−1 006(19)	2 107(19)	1 215(19)	C(114)	3 477(25)	1 625(19)	807(20)
O(8)	−1 446(17)	2 665(14)	1 182(15)	C(21)	1 458(15)	−689(12)	−1 244(15)
C(9)	240(23)	1 601(14)	2 369(22)	C(22)	2 125(17)	−857(14)	−1 741(13)
O(9)	476(19)	1 841(13)	2 866(14)	C(23)	2 328(23)	−1 619(17)	−2 001(19)
C(10)	329(16)	−432(16)	2 834(22)	C(24)	1 759(21)	−2 246(18)	−1 724(16)
O(10)	806(15)	−283(17)	3 307(13)	C(25)	1 114(18)	−2 133(13)	−1 165(16)
C(11)	433(16)	−1 444(16)	1 486(14)	C(26)	1 018(16)	−1 341(15)	−951(15)
O(11)	785(17)	−1 992(12)	1 324(16)	C(27)	1 197(15)	936(13)	−1 738(13)
C(12)	−1 156(19)	−1 304(20)	2 436(17)	C(28)	1 900(17)	1 284(17)	−2 100(13)
O(12)	−1 576(17)	−1 711(15)	2 759(14)	C(29)	1 736(22)	1 767(16)	−2 754(16)
C(4)	−1 636(21)	1 008(19)	3 151(22)	C(210)	961(20)	1 859(19)	−3 096(19)
O(4)	−1 572(23)	1 208(23)	3 767(21)	C(211)	282(18)	1 445(18)	−2 738(14)
				C(212)	435(19)	1 019(17)	−2 095(17)

The hydrido ligands in compounds (**2**)—(**7**) also undergo site exchange. The *X*-ray crystal structures of (**2**) and (**3**) show two distinct hydrido-ligand sites for each cluster, but only a single high-field hydrido ligand resonance is observed in the ambient-temperature ^{1}H n.m.r. spectrum in each case.[6] At −90 °C, the hydrido ligand signal is very broad for (**3**)[6] and so broad that

Table 8. Atomic positional parameters (fractional co-ordinates) (× 10^4) for $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_2PPh_2\}(CO)_{12}]$ (**3**), with e.s.d.s in parentheses

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au(1)	155.3(3)	1 823.1(3)	2 087.3(1)	C(10)	517(9)	2 913(9)	3 923(4)
Au(2)	−1 183.7(3)	444.5(1)	2 385.8(1)	C(11)	−667(9)	3 067(8)	2 804(4)
Ru(1)	−440(1)	211(1)	3 571.8(3)	C(12)	1 349(9)	2 979(10)	3 061(5)
Ru(2)	1 478(1)	791(1)	3 971.0(3)	C(13)	−430(8)	3 729(8)	1 039(4)
Ru(3)	925(1)	198(1)	2 816.1(3)	C(14)	−52(18)	4 421(12)	1 415(6)
Ru(4)	344(1)	2 209(1)	3 228.7(3)	C(15)	−64(25)	5 472(14)	1 337(10)
P(1)	−374(2)	2 331(2)	1 167(1)	C(16)	−536(18)	5 859(15)	844(12)
P(2)	−2 477(2)	857(2)	1 671(1)	C(17)	−854(18)	5 183(18)	416(13)
O(1)	−2 626(8)	−106(11)	3 333(5)	C(18)	−831(19)	4 167(14)	523(9)
O(2)	−570(7)	953(6)	4 721(3)	C(19)	305(8)	1 787(8)	701(4)
O(3)	38(9)	−2 006(7)	4 022(3)	C(20)	1 229(9)	1 473(13)	894(6)
O(4)	2 309(9)	−1 282(9)	4 492(4)	C(21)	1 775(12)	1 048(15)	562(7)
O(5)	3 319(8)	1 917(11)	3 972(5)	C(22)	1 325(14)	937(15)	−4(7)
O(6)	1 539(7)	1 585(9)	5 132(4)	C(23)	424(14)	1 213(15)	−221(6)
O(7)	2 750(7)	1 144(10)	2 638(4)	C(24)	−81(10)	1 652(13)	121(4)
O(8)	479(8)	−840(8)	1 660(3)	C(25)	−2 863(7)	−141(7)	1 137(4)
O(9)	2 031(8)	−1 793(7)	3 241(4)	C(26)	−3 461(8)	107(9)	603(4)
O(10)	634(7)	3 435(7)	4 311(3)	C(27)	−3 742(8)	−691(10)	208(4)
O(11)	−1 309(7)	3 600(6)	2 608(3)	C(28)	−3 492(10)	−1 687(11)	335(5)
O(12)	1 953(8)	3 524(9)	2 967(4)	C(29)	−2 913(10)	−1 958(9)	857(5)
C(1)	−1 824(11)	−23(11)	3 363(4)	C(30)	−2 607(8)	−1 183(8)	1 258(4)
C(2)	−476(8)	703(7)	4 293(4)	C(31)	−3 531(7)	1 195(7)	1 916(3)
C(3)	−140(9)	−1 168(10)	3 842(4)	C(32)	−4 414(8)	734(9)	1 707(5)
C(4)	−1 978(10)	−504(12)	4 271(5)	C(33)	−5 187(8)	1 018(11)	1 916(6)
C(5)	2 614(10)	1 473(13)	3 972(5)	C(34)	−5 092(8)	1 770(10)	2 328(6)
C(6)	1 486(8)	1 307(11)	4 685(5)	C(35)	−4 234(9)	2 215(11)	2 530(6)
C(7)	2 034(9)	802(11)	2 715(4)	C(36)	−3 448(8)	1 946(9)	2 339(5)
C(8)	562(9)	−406(10)	2 070(4)	C(37)	−1 596(8)	1 822(8)	878(4)
C(9)	1 589(9)	−1 038(10)	3 111(4)	C(38)	−2 292(7)	2 034(7)	1 263(4)

it is not visible for (**2**). The variable-temperature ^1H n.m.r. data of clusters (**4**)—(**7**) closely resemble those reported for (**3**),[6] suggesting that the hydrido ligands in the former species adopt similar positions and undergo similar dynamic behaviour to those in (**3**). Site exchange between edge-bridging and face-capping hydrido ligands has also been previously observed at ambient temperature in solution for the analogous PPh_3-containing cluster (**1**).[4]

Experimental

The clusters $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (n = 1[15] or 2[6]) were prepared as previously described and adaptations of published routes[6,15] were utilized to synthesize $[Au_2Ru_4(\mu_3\text{-}H)(\mu\text{-}H)\{\mu\text{-}Ph_2P(CH_2)_nPPh_2\}(CO)_{12}]$ (n = 3—6). The ligands $Ph_2P(CH_2)_nPPh_2$ (n = 3—6) were purchased from Strem Chemicals Inc. and used without further purification. The instrumentation employed has been described elsewhere.[6] Analytical and other physical data for the new cluster compounds are presented in Table 1, together with their i.r. spectra. Table 2 summarizes the results of n.m.r. spectroscopic measurements.

Crystal Structure Analyses.—Crystals of (**2**) in the monoclinic and orthorhombic forms were grown from dichloromethane–light petroleum mixtures by slow layer diffusion at −20 °C. Crystals of (**3**) were grown by the same technique from a tetrahydrofuran–diethyl ether–light petroleum mixture. The unit cell dimensions and intensity data were obtained using previously described procedures.[16] Intensity data were collected for unique portions of reciprocal space by ω—2θ scans using graphite-monochromated Mo-K_α radiation (λ = 0.710 69 Å) and corrected for Lorentz, polarization and absorption effects, the latter on the basis of azimuthal scan data.[17,18] The details of experimental parameters, data reductions, and the results of structure refinement for all three structure determinations are listed in Table 5.

The structures were solved by heavy-atom methods[18,19] and refined by least squares [block-cascade full matrix for (**2**)[18] and blocked full matrix for (**3**)[20]] to the final residuals quoted in Table 5. All non-hydrogen atoms were refined anisotropically, except oxygen atoms O(7), O(8), and O(12) for the orthorhombic form of (**2**). Phenyl and methylene group hydrogens were incorporated at idealized positions with fixed isotropic displacement parameters. Hydrido hydrogens were placed at calculated positions and held fixed, except for the monoclinic form of (**2**), where they were refined with Ru–H constrained to be near 1.80 Å. Final atomic co-ordinates for the non-hydrogen atoms are listed in Tables 6, 7, and 8 for the monoclinic and orthorhombic forms of (**2**), and for (**3**), respectively. The chirality of the orthorhombic crystal of (**2**) used was confirmed by eta refinement [η = 0.96(3)]. Crystallographic calculations were performed using software written by Sheldrick.[18–20] Complex neutral-atom scattering factors were taken from refs. 21 and 22.

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