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FULL PAPER

Auration of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2H)(CO)_9]$: tetrahedral and butterfly isomers of $[AuRu_3(\mu\text{-}H)(\mu_3\text{-}HC_2H)(CO)_9(PPh_3)]$ and related chemistry

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Treatment of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2H)(CO)_9]$ **1** with $K[BHBu^s_3]$ followed by auration with $[AuCl(PPh_3)]$ gave the crystallographically characterised complexes $[AuRu_3(\mu\text{-}H)(\mu_3\text{-}C_2H_2)(CO)_9(PPh_3)]$ **2**, $[Au_2Ru_3(\mu_3\text{-}C{=}CH_2)(CO)_9(PPh_3)_2]$ **3** and $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}CHCHC(OH)\}(CO)_8(PPh_3)]$ **4**. Complex **2** crystallises in a dark red form, in which the $AuRu_3$ core forms a tetrahedron, and a yellow form, in which the $AuRu_3$ core has a butterfly structure; the C_2H_2 ligand is $2\eta^1:\eta^2$ co-ordinated to the Ru_3 face in both. In **3** the Au_2Ru_3 core has a distorted square pyramidal conformation, with the CCH_2 ligand attached to the Ru_3 face. Complex **4** contains a hydroxyallyl ligand spanning the Ru_3 core.

Introduction

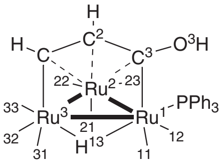
The replacement of cluster-bonded hydrogen atoms by the isolobal $Au(PPh_3)$ group is an extensively investigated sub-section of metal cluster chemistry.[1] From the time of the first enunciation of the concept,[2] innumerable comparisons of aurated clusters with their hydrido counterparts have been made. While in the majority of examples, simple replacement of H by $Au(PR_3)$ occurs, in others the structural equivalence is not found. This is particularly true for complexes containing two or more gold atoms where the aurophilicity principle[3] seems to govern the final structure. In these cases, however, extension of the isolobal resemblance of $Au_2(PR_3)_2$ and $Au_3(PR_3)_3$ to H_2 and H_3, respectively, may be countenanced. In the latter case the low energy difference between open and closed forms of H_3[4] also has a parallel in the structures adopted by the isolobal gold-containing clusters.[5]

Another interesting feature is illustrated by the solid-state structure of $[AuFe_3(\mu_3\text{-}HC{=}NBu^t)(CO)_9(PPh_3)]$, in which the unit cell contains two independent molecules.[6] Not only does the $Au(PPh_3)$ group bridge a different edge of the Fe_3 triangle from that bridged by H in $[Fe_3(\mu\text{-}H)(\mu_3\text{-}HC{=}NBu^t)(CO)_9]$, but the two molecules differ in the dihedral angle of the $AuFe_3$ core, with values of 110.9 and 132.1°. In solution, however, there is no evidence for the presence of different isomers, the different structures being assumed to be the result of "crystal packing forces" or other solid-state effects, and consistent with facile flexing ("flapping") of the butterfly wings.

We have been interested in developing the chemistry of ruthenium cluster complexes derived from ethyne,[7] among which $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2H)(CO)_9]$ **1**[8] has shown unusual reactivity. Previously, we have shown that treatment of hydrido clusters with $K[BHBu^s_3]$ (K-Selectride) readily generates the corresponding anionic cluster, which can be aurated by treatment with $[AuCl(PPh_3)]$ or with $[O\{Au(PPh_3)\}_3]^+$ or related tertiary phosphine or phosphite gold derivatives.[9] This paper describes the results of similar experiments carried out with **1**, including the unusual finding of two *separable* isomeric clusters containing $AuRu_3$ cores which have tetrahedral and butterfly conformations. In one crystal of $[AuRu_5(\mu_5\text{-}C)(CO)_{13}(NO)(PEt_3)]$ two structural isomers containing μ- and $\mu_3\text{-}Au(PEt_3)$ groups are found.[10]

Results and discussion

Treatment of complex **1** with K-Selectride in tetrahydrofuran solution, followed by addition of $[AuCl(PPh_3)]$ and separation of the products by preparative thin-layer chromatography, afforded $[AuRu_3(\mu\text{-}H)(\mu_3\text{-}HC_2H)(CO)_9(PPh_3)]$ **2** (37% yield) and $[Au_2Ru_3(\mu_3\text{-}CCH_2)(CO)_9(PPh_3)_2]$ **3** (8%), together with the gold-free derivative $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}CHCHC(OH)\}(CO)_8(PPh_3)]$ **4** (31%) (Scheme 1). All three complexes were identified by single-crystal structural determinations.



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The orange solution of complex **2** shows two resonances in its ^1H NMR spectrum at δ −20.25 and 8.87 (relative intensities 1:2), which can be assigned to the metal-bonded H and acetylenic H atoms, respectively, together with a multiplet between δ 7.47 and 7.55 for the phenyl protons. The acetylenic carbons resonate at δ 141.6 in the ^{13}C NMR spectrum, but only four CO resonances were found, presumably because of a site-exchange process occurring in solution. Other peaks are detailed in the Experimental section. The IR spectrum contains six $\nu(CO)$ bands in the terminal region. The electrospray (ES) mass spectrum was obtained in negative ion mode after addition of NaOMe: the highest mass ion was found at *m*/*z* 1073, corresponding to $[M + OMe - H]^-$.

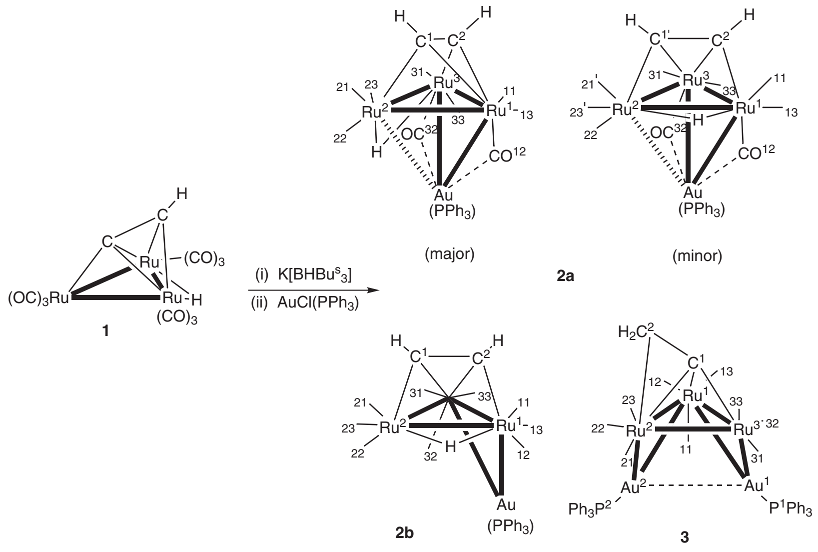
When first isolated from hexane–benzene mixtures, complex **2** was obtained as a bright yellow solid. Subsequent recrystallisation from dichloromethane–ethanol mixtures afforded a mixture of dark red (**2a**) and yellow crystals (**2b**), which were

Table 1 Selected bond distances (Å) and angles (°) for complexes **2a**, **2b** and **3**

	2a	**2a′**	**2b**	**3**
Ru(1)–Ru(2)	2.850(3)		3.0066(6)	2.952(1)
Ru(1)–Ru(3)	2.879(2)		2.8913(7)	2.8923(9)
Ru(2)–Ru(3)	2.836(3)		2.7361(6)	2.7613(9)
Ru(1)–Au(1)	2.749(2)		2.7226(5)	2.7069(7)
Ru(1)–Au(2)				2.7034(8)
Ru(2)–Au(1)	3.114(2)			
Ru(2)–Au(2)				2.8051(8)
Ru(3)–Au(1)	2.742(2)		2.7919(5)	2.7778(8)
Au(1) · · · Au(2)				3.2321(6)
Au(1)–P(1)	2.305(5)		2.296(2)	2.306(2)
Au(2)–P(2)				2.288(2)
Ru(1)–C(1)	2.22(4)			2.045(9)
Ru(1)–C(2)	2.16(2)		2.090(7)	
Ru(2)–C(1)	2.11(4)	2.10(5)	2.066(6)	2.160(7)
Ru(2)–C(2)				2.299(8)
Ru(3)–C(1)		2.28(4)	2.258(7)	2.019(7)
Ru(3)–C(2)	2.15(2)	[2.15(2)]	2.217(6)	
Ru(2)–C(21)	1.57(5)	1.94(5)		1.899(8)
Ru(2)–C(23)	1.96(5)	2.35(7)		1.877(9)
C(1)–C(2)	1.26(4)	1.28(5)	1.366(8)	1.39(1)
Ru(1)–Au(1)–Ru(2)	57.76(5)			
Ru(1)–Au(1)–Ru(3)	63.25(5)		63.23(1)	63.64(2)
Ru(2)–Au(1)–Ru(3)	57.50(6)			
Ru(2)–Ru(3)–Au(1)				87.88(2)
Ru(3)–Ru(2)–Au(2)				100.55(2)
Ru(2)–Au(2)–Au(1)				78.74(2)
Ru(3)–Au(1)–Au(2)				90.53(2)
Ru(1)–C(1)–C(2)				130.1(5)
Ru(1)–C(2)–C(1)		110(2)	112.4(4)	
Ru(2)–C(1)–C(2)	113(2)		113.7(5)	77.5(5)
Ru(3)–C(2)–C(1)	111(2)			
Ru(3)–C(1)–C(2)				133.4(6)

Other distances and angles for **2a**: Ru(1)–C(12) 1.92(2), Ru(3)–C(32) 1.91(2), Au(1)–C(12) 2.59(2) and Au(1)–C(32) 2.66(2); P(1)–Au–Ru(1,2,3) 147.6(1), 139.1(1), 146.3(1), Ru(1)–C(12)–O(12) 168(2) and Ru(3)–C(32)–O(32) 171(2).

Dihedral angles: **2a**, Ru(1,2,3)/AuRu(1,3) 81.10(7); **2b**, Ru(1,2,3)/AuRu(1,3) 70.22(4); **3**, Au(1,2)Ru(2,3)/Ru(1,2,3) 48.26(3), Au(1,2)Ru(2,3)/Au(1)Ru(1,3) 52.71(4), Au(1,2)Ru(2,3)/Au(1,2)Ru(1) 61.88(4), Au(1,2)Ru(2,3)/Au(2)Ru(1,2) 51.29(4).



Scheme 1

easily separated by hand. The two forms each redissolve to give orange solutions which have identical spectroscopic properties. Recrystallisation of each form affords the same mixture of yellow and dark red crystals. Variable temperature measurements of the ^{31}P NMR spectra of these solutions show only one resonance at δ 63.7 (at 27 °C) to 62.2 (at −70 °C).

The molecular and crystal structures of each form were determined by single crystal X-ray methods. Plots of molecules of **2a** and **2b** are shown in Figs. 1 and 2, respectively, and selected structural data are given in Table 1. The structural determination of the former also revealed the presence of a second component [occupancy 0.408(9)], in which the orientation of the ethyne on the Ru_3 face is rotated through 60°.

The three Ru atoms form a closed triangular face with Ru–Ru separations between 2.836 and 2.879(3) Å. The gold atom is close to atoms Ru(1) and Ru(3) [2.742, 2.749(2) Å] but

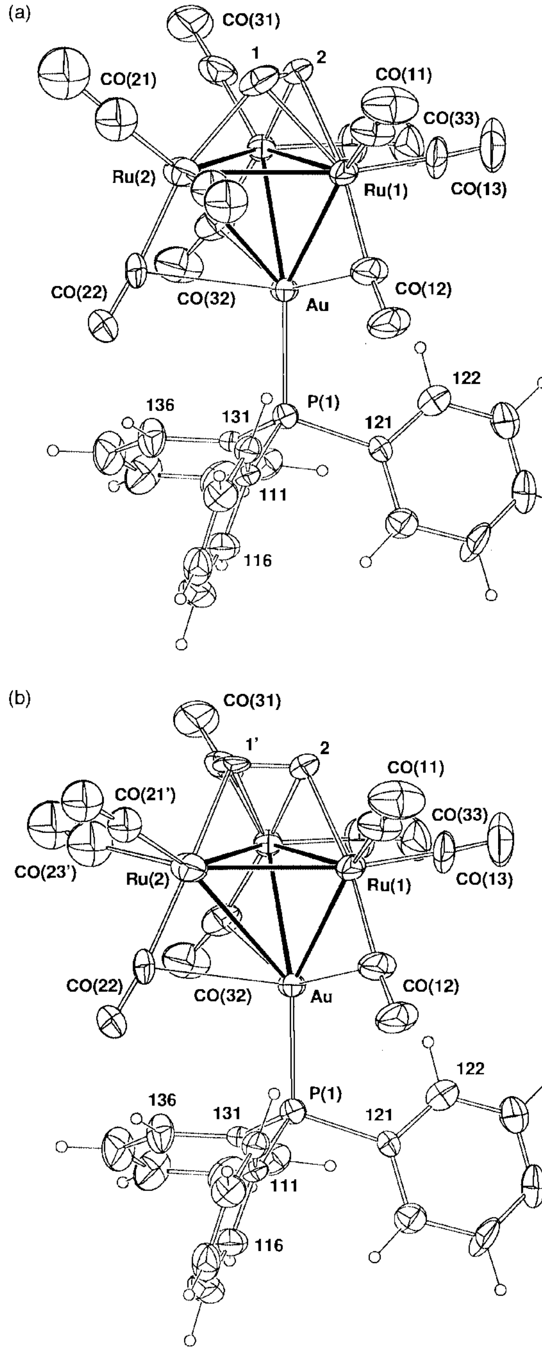


Fig. 1 Projections of (a) major and (b) minor components of tetrahedral $[AuRu_3(\mu\text{-}H)(\mu_3\text{-}HC_2H)(CO)_9(PPh_3)]$ **2a**, showing the atom numbering scheme; 20% thermal ellipsoids are shown for the non-hydrogen atoms.

considerably further away from Ru(2) [3.114(2) Å]. The ethyne ligand is attached in the familiar μ_3-2η^1:η^2 fashion. In the major isomer the C(1)–C(2) vector is approximately parallel to the Ru(2)–Ru(3) bond, whereas in the minor component it is parallel to the Ru(1)–Ru(2) bond. Within the precision available, the Ru–C σ [2.11, 2.15(4) (major); 2.16, 2.10(5) Å (minor)] and π bond lengths [2.22, 2.16(4) (major); 2.28, 2.15(4) Å (minor)] are equal in both components. Co-ordination of the alkyne to the Ru_3 face results in lengthening of the C(1)–C(2) bond to 1.26(4) or 1.28(5) Å in the major and minor isomers, respectively, considerably shorter and thus suggesting a weaker interaction than found in $[Ru_3(\mu_3\text{-}C_2H_2)(\mu\text{-}CO)(CO)_9]$ [1.41(1) Å].[7] The CO ligands at Ru(2) are rotated in association with the different orientations of the ethyne ligand on the Ru(1,2,3) face, with the ascription proposed as shown, CO(22) maintaining a similar disposition throughout.

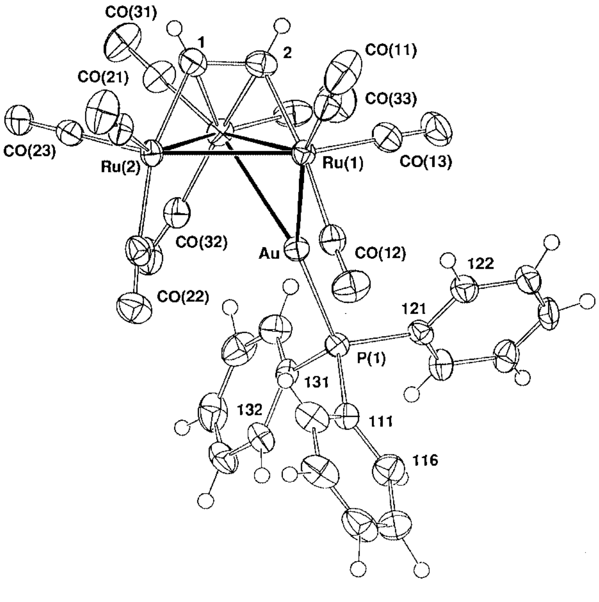


Fig. 2 Projection of butterfly $[AuRu_3(\mu\text{-}H)(\mu_3\text{-}HC_2H)(CO)_9(PPh_3)]$ **2b**, showing the atom numbering scheme; 50% thermal ellipsoids are shown for the non-hydrogen atoms.

Of interest is the close approach of the carbon atoms of the CO(12, 32) ligands to the gold atom, which is distant 2.59 and 2.66(2) Å from C(12) and C(32), respectively; C(22) is much further away, at 2.97(2) Å. These CO ligands are slightly bent [Ru(1)–C(12)–O(12) 168(2), Ru(3)–C(32)–O(32) 171(2)°; *cf.* Ru(2)–C(22)–O(22) 174(2)°]. As noted in other examples, it is not clear whether there are any significant bonding interactions or whether this results from steric interactions in the solid.[1] Nevertheless, it is perhaps significant that all of these are bent more than the remainder of the non-disordered carbonyls. Not located in the structure determination was the H atom, shown to be present by its characteristic ^1H NMR resonance. The usual lengthening of an Ru–Ru bond bridged by H is not found, although the splaying of the CO groups about the Ru(2)–Ru(3) bond suggests that the hydride ligand is bridging this bond.

In the yellow form **2b** the four metal atoms adopt a butterfly conformation, with Ru–Ru distances between 2.7361 and 3.0066(6) Å, and two Au–Ru(1,3) distances of 2.7226 and 2.7919(5) Å; the Au···Ru(2) separation is 3.9554(6) Å. This asymmetry can be related to the attachment of the Au atom to Ru atoms which are σ- and π-bonded to the ethyne ligand, respectively. We ascribe the differences in Ru–Ru separations to the usual lengthening effect of μ-H and μ-Au(PPh$_3$) ligands, which suggests that the (undetected) H atom is bridging the Ru(1)–Ru(2) vector. In this case the long Ru(1)–Ru(3) separation is consistent with the same effect, with the isolobal Au(PPh$_3$) group replacing H.

The ethyne is attached in the μ_3-2η^1:η^2-mode with C(1)–C(2) being parallel to Ru(1)–Ru(2). The Ru–C σ bonds [2.066, 2.090(7) Å] and π bonds [2.217, 2.258(7) Å] are respectively shorter and longer than those found in complex **2a**. In **2b** the C(1)–C(2) bond is lengthened to the more usual 1.366(8) Å. No close approach of any CO ligand to the Au atom is found in **2b**.

The structures of the two forms are determined upon crystallisation. As mentioned above, dissolution of either form in hydrocarbon solvents and subsequent crystallisation gave a mixture of the two solid-state isomers. The change results from a bending of the AuRu(1)Ru(3) face along the Ru–Ru vector, with the Au atom making a closer approach to Ru(2). The long Ru(2)–Au separation in complex **2a** is consistent with only a weak bonding interaction. Variable temperature ^{31}P NMR spectra show no broadening of the single resonance down to

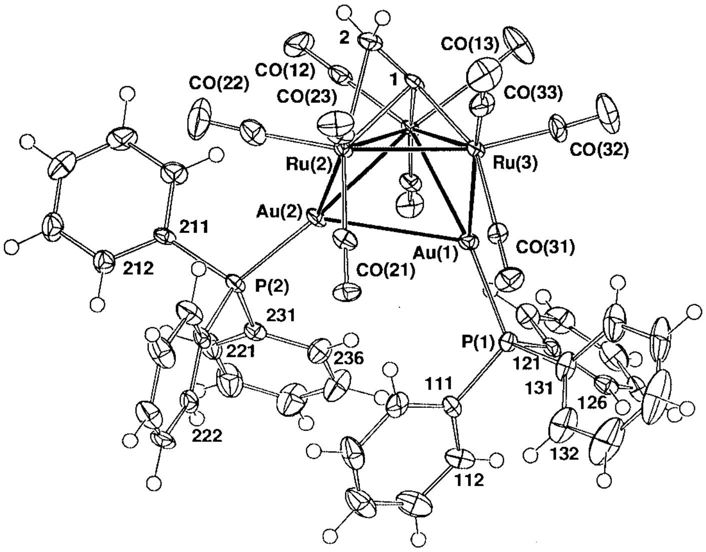


Fig. 3 Projection of $[Au_2Ru_3(\mu_3\text{-}CCH_2)(CO)_9(PPh_3)_2]$ **3** 'through' the Ru_3 plane, showing the atom numbering scheme; 50% thermal ellipsoids are shown for the non-hydrogen atoms.

−70 °C. Either a facile fluxional process is occurring, or only one form is present in solution; we favour the first explanation. Indeed, theoretical calculations[11] suggest that this process is a facile one; exchange of $M(PR_3)$ groups on Ru_4 clusters is thought to proceed *via* this route.[12] In addition, the $Au(PPh_3)$ group in $[AuRu_3\{\mu\text{-}(PMe_2)_2CH\}(CO)_9(PPh_3)]^+$ migrates between the Ru–Ru edges, possibly *via* a $\mu_3\text{-}Au(PPh_3)$ intermediate.[13] The process can be likened to transition from edge-bridging to face-capping, similar to the μ-H/μ_3-H transformation found in metal cluster hydrides, one route whereby hydride ligands may be equilibrated.

Yellow crystals of complex **3** were obtained from dichloromethane–ethanol mixtures. The IR spectrum contained nine terminal ν(CO) bands, while the ^{1}H NMR spectrum contained phenyl proton resonances between δ 7.23 and 7.42 together with a singlet at δ 4.86, assigned to the two protons of the CCH_2 ligand which are presumably rendered equivalent by some fluxional process which may involve migration of the CCH_2 ligand about the metal core, perhaps accompanied by a rearrangement of the metal skeleton akin to that described for other Au_2Ru_3 clusters.[14] No high-field signals were observed. Ions in the ES mass spectrum were formed by initial loss of the $Au(PPh_3)$ group and a hydrogen atom from the parent ion to give $[M - H - Au(PPh_3)]^-$ at *m*/*z* 1041, followed by stepwise loss of up to four CO ligands and a second PPh_3 ligand.

A molecule of complex **3** is shown in Fig. 3; selected bond distances and angles are in Table 1. The structure is based on an asymmetric Au_2Ru_3 square pyramid, the base being decidedly non-square, with edges of 2.7777(8) [Au(1)–Ru(3)], 2.7613(9) [Ru(2)–Ru(3)], 2.8051(8) [Au(2)–Ru(2)] and 3.2321(6) Å [Au(1) ··· Au(2)]. Atom Ru(1) lies at 2.8923(9) and 2.952(1) Å from the ruthenium apices and at 2.7034(8) and 2.7069(7) Å from the gold apices. Indeed, the structure can also be considered to arise from the two $Au(PPh_3)$ units bridging the Ru(1)–Ru(2,3) vectors, with only a weak Au ··· Au interaction resulting from this geometry. This cluster is unusual in that the square-pyramidal Au_2Ru_3 core has been found previously in clusters containing gold atoms bridged by bidentate phosphine ligands, the trigonal bipyramid being favoured when only monodentate phosphines are present.[14]

The CCH_2 (vinylidene) ligand spans the Ru_3 face, thus directing the two $Au(PPh_3)$ groups to the opposite side. Atom C(1) is σ bonded to Ru(1) and Ru(3) [2.045(9), 2.019(7) Å] and asymmetrically π bonded to Ru(2) [Ru(2)–C(1,2) 2.160(7), 2.299(8) Å]. This is similar to other vinylidene ligands, such as that in $[Au_2Ru_3(\mu_3\text{-}C^1{=}C^2HBu^t)(CO)_9(PPh_3)_2]$ [Ru–C^1 2.019, 2.057, 2.157(6); Ru–C^2 2.500(4) Å][15] and $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C^1{=}C^2MePh)(CO)_9]$ [Ru–C^1 2.04, 2.10, 2.19(1); Ru–C^2 2.43(1) Å].[16]

The third product **4** obtained from the reaction formed pale yellow crystals. Its IR spectrum contained seven bands in the terminal ν(CO) region, together with one at 3617 cm^{-1}, assigned to a ν(OH) absorption. In the ^{1}H NMR spectrum the cluster-bound hydride resonated at δ −19.42 as a double doublet, showing coupling both to H(1) and to P. The two protons on the allylic ligand were found at δ 6.71 and 8.39 and are assigned to H(1) and H(2), respectively, from their coupling patterns. The OH resonance was not seen. The negative ion ES mass spectrum contained $[M - 2H]^-$ (*m*/*z* 845) as highest mass ion.

Fig. 4 shows a plot of a molecule of complex **4**, selected bond distances and angles being collected in Table 2. The complex is another example of a well known group of C_3Ru_3 clusters and the bond parameters do not differ significantly from those of previous examples, such as the closely related derivative $[Ru_3(\mu\text{-}H)(\mu_3\text{-}CHCHCMe)(CO)_8(PPh_3)]$.[17] The three metal atoms form an almost equilateral triangle with two shorter Ru–Ru separations [2.783(1), 2.7917(9) Å] and a longer Ru(1)–Ru(3) distance [2.986(1) Å]. These latter are σ bonded to atoms C(3) and C(1) [Ru–C 2.054, 2.050(4) Å], respectively, and are bridged by H(1) [Ru(1,3)–H 1.81, 1.77(5) Å]. The allylic group is asymmetrically η^3 bonded to Ru(2) [Ru(2)–C(1,2,3) 2.224, 2.265, 2.368(5) Å], the longest separation being to C(3) carrying the OH group. The Ru(1,3)C(1–3)O(3) array is essentially planar (χ^2 352), the dihedral angle to the Ru_3 plane being 52.65(7)°. The PPh_3 ligand replaces a CO on Ru(1) [Ru(1)–P 2.334(2) Å].

In contrast to many previous studies in which an anion is formed by loss of a cluster-bound hydride, hydride addition to the cluster-bound ethynyl group in complex **1** has occurred to give an anion which is subsequently staurated to give **2**. Formation of a dianion such as $[Ru_3(C_2H_2)(CO)_9]^{2-}$ or loss of the cluster-bonded hydride from **2** must precede formation of **3**. We cannot say whether addition to form ethyne or vinylidene occurs first, followed by isomerisation of one to the other, or whether two competitive reaction pathways are followed.

An osmium analogue (**5**) of complex **4** has been described as being obtained from reactions of $[Os_3(CO)_{11}(NCMe)]$ with C_2H_2 in the presence of water (70%)[18] or by treatment of

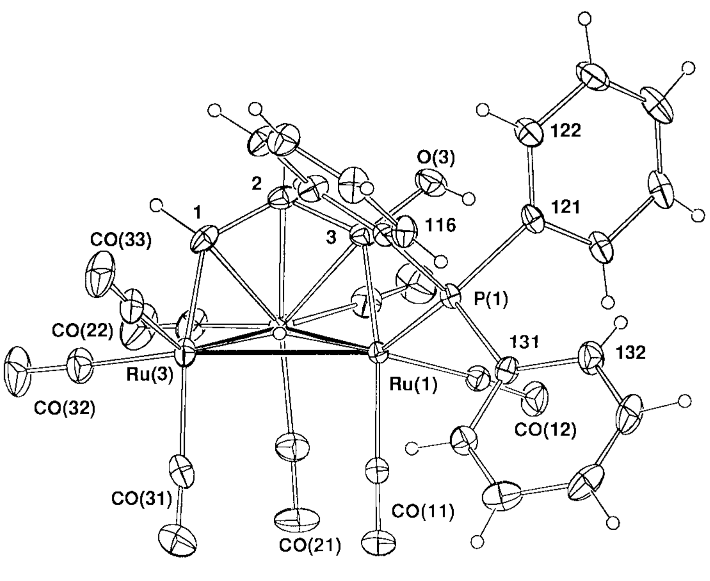


Fig. 4 Projection of $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}CHCHC(OH)\}(CO)_8(PPh_3)]$ **4** 'through' the Ru_3 plane, showing the atom numbering scheme; 50% thermal ellipsoids are shown for the non-hydrogen atoms.

Table 2 Selected bond distances (Å) and angles (°) for complex **4**

Ru(1)–Ru(2)	2.7917(9)	Ru(2)–C(3)	2.368(5)
Ru(1)–Ru(3)	2.986(1)	Ru(3)–C(1)	2.050(4)
Ru(2)–Ru(3)	2.783(1)	Ru(1)–H(13)	1.81(4)
Ru(1)–P	2.334(2)	Ru(3)–H(13)	1.77(5)
Ru(1)–C(3)	2.054(4)	C(3)–O(3)	1.379(6)
Ru(2)–C(1)	2.224(4)	C(1)–C(2)	1.402(7)
Ru(2)–C(2)	2.265(4)	C(2)–C(3)	1.410(6)
Ru(3)–C(1)–C(2)	127.4(3)	C(2)–C(3)–Ru(1)	125.1(3)
C(1)–C(2)–C(3)	122.0(4)		

$[Os_3(\mu_3\text{-}C_2H_2)(\mu\text{-}CO)(CO)_9]$ with $Li[BHEt_3]$, from which reaction a variety of products, including **5**, was obtained.[19] The formation of **4** may proceed by intramolecular reaction between the ethyne and a CO or formyl group. As suggested by Deeming and Manning,[19] two possible routes to the hydroxyallyl complex involve addition of hydride to the alkyne cluster, followed by intramolecuar attack of C_2H_2 (or C_2H_3) ligand on CO to give a CHCHCO [or CHCHC(OH)] ligand; if the former, migration of cluster-bound hydride completes the transformation. Alternatively, addition of hydride to CO to give a formyl group is followed by migration of the latter to the co-ordinated alkyne. Replacement of CO by PPh_3 probably occurs by reaction with $[AuCl(PPh_3)]$ present in the solution.

Conclusion

We have shown that addition of hydride (as $K[BHBu^s{}_3]$) to $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2H)(CO)_9]$ likely proceeds by addition to the alkyne; auration with $[AuCl(PPh_3)]$ gives $[AuRu_3(\mu\text{-}H)(\mu_3\text{-}C_2H_2)(CO)_9(PPh_3)]$, which crystallises in two conformations, and $[Au_2Ru_3(\mu_3\text{-}C{=}CH_2)(CO)_9(PPh_3)_2]$. Also formed is $[Ru_3(\mu\text{-}H)\{\mu_3\text{-}CHCHC(OH)\}(CO)_8(PPh_3)]$.

While formal isolobal replacement of one hydrogen atom in $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C_2H_2)(CO)_9]$ gives the anticipated alkyne complex $[AuRu_3(\mu\text{-}H)(\mu_3\text{-}C_2H_2)(CO)_9(PPh_3)]$ **2**, albeit with interesting structural characteristics, the digold cluster **3** contains the isomeric vinylidene (CCH_2) ligand. To our knowledge, the analogous dihydroruthenium cluster $[Ru_3(\mu\text{-}H)_2(\mu_3\text{-}CCH_2)(CO)_9]$ is presently unknown, although the related osmium complex has been known for many years, having been first obtained from the reaction of ethene with $[Os_3(CO)_{12}]$.[20] In this regard, we also recall the ready isomerisation of the isolobal cluster $[Co_2Ru(\mu_3\text{-}C_2H_2)(CO)_9]$ to $[Co_2Ru(\mu_3\text{-}CCH_2)(CO)_9]$, which occurs on heating in refluxing hexane.[21]

Experimental

General reaction conditions

Reactions were carried out under an atmosphere of nitrogen, but no special precautions were taken to exclude oxygen during work-up. Common solvents were dried and distilled under nitrogen before use. Elemental analyses were performed by Canadian Microanalytical Service, Delta, B.C., Canada. Preparative TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Instrumentation

IR: Perkin-Elmer 1720X FT IR. NMR: Bruker CXP300 or ACP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz) or Varian Gemini 200 (^1H at 199.8 MHz, ^{13}C at 50.29 MHz) spectrometers. Samples were dissolved in $CDCl_3$ (Sigma) or $(CD_3)_2SO$ (Aldrich) and spectra were recorded using 5 mm sample tubes. ES MS: Finnegan LCQ. Solutions in MeOH were injected directly; nitrogen was used as the drying and nebulising gas. Chemical aids to ionisation were used as required.[22]

Reagents

Complex **1**[7,8] and $[AuCl(PPh_3)]$[23] were prepared as previously described; a thf solution of $K[BHBu^s{}_3]$ (Aldrich: K-Selectride) was used as received.

Auration of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2H)(CO)_9]$ 1

Addition of K-Selectride (0.34 ml of a 1 M solution in thf) to a solution of $[Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2H)(CO)_9]$ (100 mg, 0.17 mmol) in thf (5 ml) resulted in the formation of a brown solution. After 5 min, solid $[AuCl(PPh_3)]$ (170 mg, 0.34 mmol) was added and the mixture stirred at r.t. for 30 min until there was no **1** present (TLC). Evaporation of solvent and separation by preparative TLC (silica gel, hexane–benzene 4:1) gave several coloured bands.

The bright orange band (R_f 0.45) contained $[AuRu_3(\mu\text{-}H)(\mu_3\text{-}HC_2H)(CO)_9(PPh_3)]$ **2** (66.3 mg, 37%), isolated as a bright yellow powder, mp 116–117 °C, decomp. 188 °C. Found: C, 33.19; H, 1.60. Calc. for $C_{29}H_{18}AuO_9PRu_3$: C, 33.42; H, 1.73%.

Table 3 Crystal data and refinement details for complexes **2a**, **2b**, **3** and **4**

	2a	**2b**	**3**	**4**
Formula	$C_{29}H_{18}AuO_9PRu_3$	$C_{29}H_{18}AuO_9PRu_3$	$C_{47}H_{32}Au_2O_9P_2Ru_3$	$C_{29}H_{19}O_9PRu_3$
M	1041.6	1041.6	1499.9	845.65
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P\bar{1}$ (no. 2)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	13.821(4)	12.988(1)	18.203(4)	14.567(4)
b/Å	11.566(2)	15.539(2)	12.731(2)	12.553(4)
c/Å	10.433(2)	16.129(2)	21.825(4)	9.122(5)
α/°	74.74(1)			89.16(3)
β/°	87.68(2)	105.509(2)	110.494(3)	81.42(3)
γ/°	89.81(2)			65.88(3)
V/Å^3	1607	3137	4738	1503
Z	2	4	4	2
Crystal size/mm	0.16 × 0.15 × 0.37	0.16 × 0.23 × 0.22	0.65 × 0.35 × 0.25	0.08 × 0.12 × 0.25
μ/cm^{-1}	60	60	70	15.9
$2\theta_{max}$/°	50	58	58	50
N_{total}		34913	50718	
N_r (R_{int})	5646	7920 (0.040)	11919 (0.076)	5274
N_o	3256	6284	8950	
R	0.059	0.035	0.048	0.039
R'	0.057	0.037	0.053	0.063
T/K	293	153	153	293

IR (cyclohexane): ν(CO) 2078w, 2056s, 2033vs, 2006m, 1995m and 1960w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ −20.25 (s, 1 H, RuH), 7.45–7.55 (m, 15 H, Ph) and 8.87 (s, 2 H, C_2H_2). ^{13}C NMR (CDCl$_3$): δ 129.04 [d, J(PC) = 11, *meta*], 131.13 (s, *para*), 131.67 [d, J(PC) = 47.5, *ipso*], 133.90 [d, J(PC) = 14.5 Hz, *ortho*], 141.60 (s, C≡C), 191.18, 192.02, 199.37, 201.53 (4 × s, CO). ES MS (MeOH + NaOMe, negative ion): m/z 1073, [M + OMe − H]$^-$. This complex crystallises from dichloromethane–ethanol as a mixture of yellow and dark red crystals.

The yellow band (R_f 0.31) gave [Au$_2$Ru$_3$(μ$_3$-CCH$_2$)(CO)$_9$(PPh$_3$)$_2$] **3** (20 mg, 7.7%) as yellow crystals from dichloromethane–ethanol. Found: C, 37.91; H, 2.40. Calc. for $C_{47}H_{32}Au_2O_9P_2Ru_3$: C, 37.63; H, 2.14%. IR (cyclohexane): ν(CO) 2053w, 2027s, 2018vs, 2014 (sh), 1992vw, 1982w, 1977w, 1967m and 1943w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 4.86 (s, 2 H, =CH$_2$) and 7.23–7.42 (m, 30 H, Ph). ES MS (acetone, negative ion): m/z 1041, [M − H − Au(PPh$_3$)]$^-$ ≡ M′; 778, [M′ − H − PPh$_3$]$^-$; 751–667, [M′ − H − PPh$_3$ − nCO]$^-$ (n = 1–4).

Extraction of the pale yellow band (R_f 0.1) with MeOH, evaporation and crystallisation (C_6H_6) afforded pale yellow crystals of [Ru$_3$(μ-H){μ$_3$-CHCHC(OH)}(CO)$_8$(PPh$_3$)] **4** (45 mg, 31%). Found: C, 41.52; H, 2.41. Calc. for $C_{29}H_{19}O_9PRu_3$: C, 41.18; H, 2.25%. IR (cyclohexane): ν(OH) 3617; ν(CO) 2080s, 2042vs, 2024vs, 2001s, 1988m, 1967m (br) and 1960 (sh) cm^{-1}. ^{1}H NMR: δ −19.42 [dd, J(H^{1}H^{13}) = 5, J(HP) = 14.5, 1 H, RuH^{13}], 6.71 [dd, J(H^{1}H^{13}) = 5, J(H^{1}H^2) = 7, 1 H, H^1], 7.18–7.36 (m, 15 H, Ph) and 8.39 [d, J(H^{1}H^2) = 7 Hz, 1 H, H^2]. ES MS (MeOH, negative ion): m/z 845, [M − 2H]$^-$; 819–623, [M − H − nCO]$^-$ (n = 1–8); 554, [M − H − CO − PPh$_3$]$^-$.

Several other bands contained a total of 18 mg of unidentified products.

Structure determinations

All determinations were carried out initially at room temperature (T *ca.* 293 K) using a single counter instrument (2θ–θ scan mode; monochromatic Mo-Kα radiation, $\lambda = 0.7107_3$ Å, measuring unique data sets, $2\theta_{max}$ as specified, N independent reflections yielding N_o 'observed' [$I > 3\sigma(I)$] which were used in the full matrix least squares refinements after absorption correction (analytical for complexes **2** and **3**, gaussian for **4**). In all cases, hydrogen atom location was a critical feature of the structure; in **2** and **3** various experimental difficulties precluded achievement of the precision necessary for their refinement.

With the advent of a Bruker AXS CCD facility operating at low temperature (153 K), sample residues were reexamined with a view to achieving resolution of the hydrogen atoms. This was done successfully for **2b** and **3** and for these two compounds those redeterminations are reported. The residue of **2a** was found not to diffract. Full spheres of data were measured, N_{total} reflections merging to N (unique), R_{int} being quoted after 'empirical' absorption correction (proprietary software 'SADABS'), N_o [$F > 4\sigma(F)$] being used in the refinements. Neutral atom complex scattering factors were employed, computation using the XTAL 3.4 program system.[24] Crystal data are given in Table 3.

Individual difficulties/variations/idiosyncrasies are as follows. For complex **2a**, regrettably, improved data were not accessible, the precision of the determination being adversely affected by disorder. This originates in the possibility of alternative dispositions of the C_2 ligand across the Ru$_3$ face, being modelled in terms of two components of C(1) [C(1,1′)], the ligand swivelling about C(2) and the disorder being (presumably) concerted with alternative locations for two of the CO ligands on Ru(2). Refinement of site occupancies of the various particles (after preliminary trials) was in terms of one set of sites (as a 'major' component) with occupancy 0.592(8), the 'minor' component as its complement. Doubtless, the disorder extends beyond the immediate components, but it was not resolvable, nor were hydrogen atom components associated with the C_2 or Ru$_3$ moieties. Values of $(x, y, z, U_{iso})_H$ for the phenyl groups were included constrained at estimated values. For **2b**, despite some twinning problems, the data from the low-temperature CCD determination permitted location and refinement of all hydrogen atoms except that associated with the Ru$_3$ core. For **3**, $(x, y, z, U_{iso})_H$ were included constrained at estimated values, CCH$_2$ hydrogen atoms being observable in difference maps. For **4**, all reflections were used in a refinement on F^2; $(x, y, z, U_{iso})_H$ were refined for all hydrogen atoms.

CCDC reference number 186/1494.

See http://www.rsc.org/suppdata/dt/1999/2777/ for crystallographic files in .cif format.

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