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XXX *. REACTION OF A TRIRUTHENIUM ANION WITH $[O\{Au(PPh_3)\}_3][BF_4]$: SYNTHESIS AND STRUCTURE OF $Ru_3Au_3(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$

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Summary

The cluster $HRu_3(\mu_3\text{-}C_{12}H_{15})(CO)_9$ is rapidly deprotonated by $K[HBBu_3{}^{sec}]$ in tetrahydrofuran, generating the anion $[Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_9]^-$ in high yield. Reaction between this anion and $[O\{Au(PPh_3)\}_3][BF_4]$ gives $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (**2**) as the main product, shown by an X-ray study to contain a capped trigonal-bipyramidal Ru_3Au_3 core in which the $C_{12}H_{15}$ ligand is bonded in the $\mu_3\text{-}2\eta^1,\eta^3$ fashion to the Ru_3 face. An alternative formulation involving the cyclo-$Au_3(PPh_3)_3$ moiety acting as a three-electron donor to the Ru_3 cluster is discussed. Crystals of **2** are monoclinic, space group $P2_1/c$, a 13.574(1), b 40.634(4), c 14.617(2) Å, β 92.58(1)°, $Z = 4$; 3233 data with $I > 3\sigma(I)$ were refined to $R = 0.078$, $R_w = 0.084$.

Introduction

Much interest in gold-containing heterometallic clusters has been aroused by the proposal that the $Au(PR_3)$ moiety is isolobal with H, and that as a consequence, structures of complexes containing such groups might be useful indicators of the geometries of related hydrido compounds [1]. However, a feature of the gold derivatives which is not shown by the corresponding cluster hydrides is the tendency towards formation of gold–gold interactions in systems containing more than one gold atom [2–11]. Some examples are $HRu_3Au_2(\mu_3\text{-}COMe)(CO)_9(PPh_3)_2$ [2],

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* For Part XXIX, see ref. 27.

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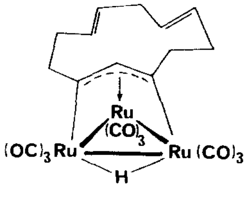
$Ru_3Au_2(\mu_3\text{-}S)(CO)_8(L)(PPh_3)_2$ ($L = CO$ or PPh_3 [2]), $Ru_2Co_2Au_2(CO)_{12}(PPh_3)_2$ [10], $HRu_4Au_3(CO)_{12}(PPh_3)_3$ [4,8], $H_2Os_4Au_2(CO)_{12}(PPh_3)_2$ [6] and $Ru_3CoAu_3(CO)_{12}(PPh_3)_3$ [8,9]. While the majority of these can be obtained from reactions between the appropriate cluster anions and $AuCl(PPh_3)$, or by methane elimination reactions between the poly-hydrido clusters and $AuMe(PPh_3)$, we have found that up to three $Au(PPh_3)$ units per cluster may be added in reactions of the anions with the trigold-oxonium ion, $[O\{Au(PPh_3)\}_3]^+$ [8,9]. In this paper we describe the synthesis of the new cluster anion $[Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_9]^-$ and its reactions with $[O\{Au(PPh_3)\}_3][BF_4]$.

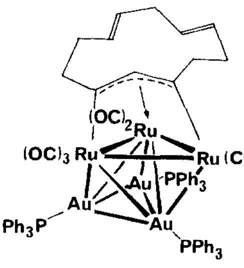
Results

Several methods have been used to generate anionic species from cluster carbonyl hydrides. A favoured reagent used to deprotonate these complexes is an alkali-metal hydroxide, often KOH, in an appropriate solvent, usually MeOH or tetrahydrofuran [12]. More recently, the use of potassium hydride has been described [10]. We find that addition of the readily available solutions of alkali metal alkyl-substituted borohydride reagents, such as $Li[HBEt_3]$ or $K[HBBu_3^{sec}]$ * in tetrahydrofuran, to the cluster hydride results in rapid (minutes) formation of the cluster anion. In some cases, but not all, a colour change accompanies the reaction. Although these reagents have been used to generate anionic species from binuclear metal carbonyl derivatives, [13] and via cleavage of the S–S bond in $Fe_2(\mu\text{-}S_2)(CO)_6$ [14], we are not aware of any examples of their use to deprotonate metal cluster hydrides apart from our earlier reports.

Using this approach, we have obtained the anion from the cluster $HRu_3(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_9$ (**1**), which is formed in high yield in the reaction between $Ru_3(CO)_{12}$ and 1,5,9-cyclododecatriene [15]. Addition of a solution of $K[HBBu_3^{sec}]$ dropwise to one of **1**, both in tetrahydrofuran, results in immediate darkening of the solution; addition of $[O\{Au(PPh_3)\}_3][BF_4]$ then gave a purple compound as the major product, which was characterised as the novel hexanuclear cluster $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (**2**) by analysis and a single-crystal X-ray structure determination (see below). The IR spectrum of **2** showed only four bands in the $\nu(CO)$ region, and the ^1H NMR spectrum was similar to that of the parent hydride **1**, with the addition of resonances from the PPh_3 ligands. The allylic CH proton in **2**



(1)



(2)

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* These reagents are available under the proprietary names Superhydride ($Li[HBEt_3]$) and K-Selectride ($K[HBBu_3^{sec}]$) from Aldrich Chemical Company, Milwaukee, Wisconsin (U.S.A.).

resonated as a singlet at δ 6.1 while in **1**, coupling between this proton and the cluster-bound μ-H atom is found [15].

Description of the structure of $Ru_3Au_3(\mu_3\text{-}2\eta^1,\eta^3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$

The metal framework in **2** has the capped trigonal bipyramidal geometry, formed conceptually by the addition of an Au atom to an Ru_2Au face of an Ru_3Au tetrahedron, followed by capping of an Au_2Ru face of the resulting trigonal bipyramid. The $C_{12}H_{15}$ ligand remains attached to the Ru_3 face by the same μ_3-$(2\eta^1,\eta^3)$ interaction found in the parent hydrido complex. Both Ru(1) and Ru(2) are bonded to three CO groups, but Ru(3) has only two; each gold atom carries one PPh_3 ligand (Fig. 1).

In **2**, there are twelve metal–metal bonds: three Au–Au, 2.840–2.911(3) Å; six Au–Ru, 2.737–2.943(4) Å, and three Ru–Ru, 2.845–2.929(5) Å. The Au–Au separations in heterometallic clusters containing three interacting gold atoms range from 2.784(1) Å in $Ru_3CoAu_3(CO)_{12}(PPh_3)_3$ [8,9] to 3.010(1) Å in $Ru_3Au_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3$ [4]; in these complexes, the three $Au(PPh_3)$ moieties form an open, bent array, if considered in isolation from the remainder of the metal core (Fig. 2a). In contrast, **2** contains a triangular $Au_3(PPh_3)_3$ system (Fig. 2b), the three Au–Au distances being within the range mentioned above. The longer edge of the Au_3 face is common with the Ru(1)Au(1)Au(3) face. The Au–Ru distances separate into three short (between 2.737–2.775 Å, involving Ru(3)), two longer ones, which are the "opposite" edges of the $Au(1)Au(3)Ru_3$ trigonal bipyramid not involved with

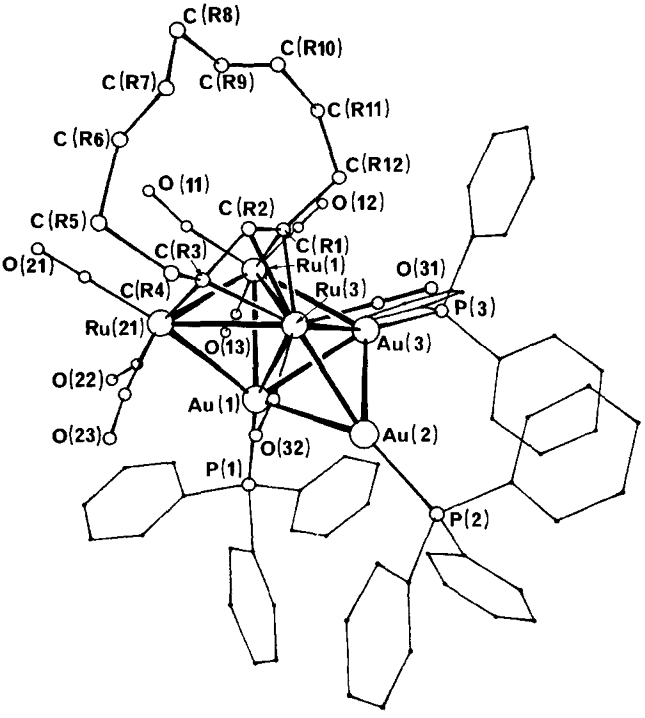

Figure 1. A view of $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (**2**) showing atom labelling scheme.

the capping Au(2) atom (2.882, 2.896(4) Å), and the equatorial edge of the same trigonal bipyramid (2.929(5) Å).

The Au–P distances are normal. One of the Au–P vectors (Au(2) ← P(2)) intersects an $RuAu_2$ face, while the other two intersect the Ru(1)–Ru(3) and Ru(3)–Au(1) edges, respectively.

In $HRu_3(\mu_3\text{-}C_{12}H_{15})(CO)_9$, the Ru_3 triangle has two short edges, (average 2.777 Å) and one long edge (2.929(4) Å); the latter links the two metal atoms which are η^1-bonded to the C_{12} ring, and is assumed to be bridged by the cluster-bound hydrogen atom [16]. The analogous separations in **2** are 2.922, 2.929, and 2.845 Å respectively: the short/long pattern of the parent hydride complex is reversed in the poly-gold derivative.

The C_{12} ring does not differ significantly from that found in **1**, attachment being via η^1 interactions of Ru(1) and Ru(2) with C(R1) and C(R3), respectively; these two carbons are the terminal atoms of an allylic C_3 function which is η^3-bonded to Ru(3). As for **1**, atoms C(1)C(2)C(3)Ru(1)Ru(2) are essentially coplanar, and with Ru(3) form a considerably distorted pentagonal pyramid. Standard deviations in the individual C–C bond distances are too high for the latter to be used as unambiguous indicators of the locations of the two carbon–carbon double bonds. However, the coplanarity of C(R5)C(R6)C(R7)C(R8) and of C(R8)C(R9)C(R10)C(R11), taken with the short C(R6)–C(R7) and C(R9)–C(R10) distances strongly suggest that these latter are the uncoordinated double bonds. The ligand thus has the same conformation as found in the parent hydrido complex [16].

Discussion

The electronic equivalence of H and $Au(PPh_3)$ has been discussed widely and, formally at least, it has proved possible to replace up to three H atoms in hydrido-clusters with $Au(PPh_3)$ groups. Thus, the monohydride $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ affords $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$ [17]; the dihydride $H_2Ru_3(\mu_3\text{-}S)(CO)_9$ gives $H_{2-n}Ru_3Au_n(\mu_3\text{-}S)(CO)_9(PPh_3)_n$ ($n = 1$, 2) [2]; and the trihydride $H_3Ru_3(\mu_3\text{-}COMe)(CO)_9$ affords $H_{3-n}Ru_3Au_n(\mu_3\text{-}COMe)(CO)_9(PPh_3)_n$ ($n = 1$–3) [4]; with $H_4Ru_4(CO)_{12}$, up to three $Au(PPh_3)$ groups can replace H to give the

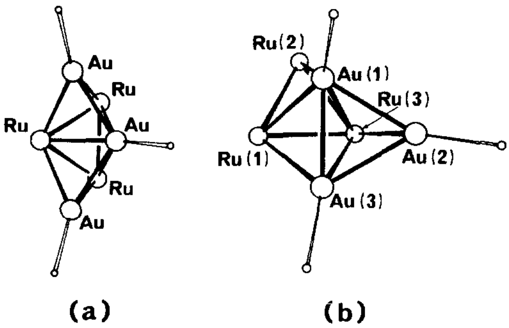

Fig. 2. Projections of the Au_3P_3 sub-units onto the capped triangular Ru_3 faces. (a) The open arrangement found for $Au_3Ru_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3$, $HAu_3Ru_4(CO)_{12}(PPh_3)_3$ and for $Au_3CoRu_3(CO)_{11}(PPh_3)_3$. (b) The closed triangular arrangement found for $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (**2**).

series $H_{4-n}Ru_4Au_n(CO)_{12}(PPh_3)_n$ ($n = 1$–3) [8]. Although the mono-gold complexes have the $Au(PPh_3)$ occupying the same position as the H in the corresponding hydride, the analogy appears to break down in the poly–gold clusters as a result of the tendency towards the formation of Au–Au bonds, the gold atoms occupying adjacent sites in the metal core. There are no similar H–H interactions in metal polyhydride complexes, although the recently described $M(H_2)(CO)_3(PR_3)_2$ (M = Mo, W; R = Cy, Pr^i), containing dihydrogen as a ligand [18], has a related digold derivative in $Os[Au(PPh_3)]_2(CO)_4$ [19].

The synthesis of poly-gold clusters has been developed using reactions 1–3 [4,5,8,20]:

$$[M_nL_m]^- + XAu(PR_3) \rightarrow L_mM_nAu(PR_3) + X^- \qquad (1)$$

$$(X = Cl, NO_3)$$

$$H_xM_nL_m + x\,MeAu(PR_3) \rightarrow L_mM_n[Au(PR_3)]_x + x\,CH_4 \qquad (2)$$

$$(x = 1, 2, 3)$$

$$[M_nL_m]^- + [O\{Au(PPh_3)\}_3]^+ \rightarrow L_mM_n[Au(PPh_3)] + HL_{m-1}M_n[Au(PPh_3)]_2 + L_{m-1}M_n[Au(PPh_3)]_3 \qquad (3)$$

The efficiency of reaction **1** is often increased when it is carried out in the presence of thallium(I), which removes chloride ion from the reaction medium. Both reactions **1** and **2** appear to be limited to the introduction of the same number of $Au(PR_3)$ units as there are charges or hydrides on the cluster, up to a present limit of three. The trigold-oxonium cation can also introduce up to three $Au(PPh_3)$ units, but can achieve this with mono-anionic clusters. Reactions 3 proceed smoothly at room temperature, and often give the M_nAu_3 cluster as the major product.

The isolobal equivalence of H and $Au(PPh_3)$ requires that another ligand be lost if three $Au(PPh_3)$ moieties add to a cluster anion derived from a mono-hydride. In the case of **2**, the $Au_3(PPh_3)_3$ unit functions as a three electron donor, displacing one H and one CO ligand from the precursor hydride. The formation of the hexanuclear cluster **2** from $[Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_9]^-$ and a deficit of $[O\{Au(PPh_3)\}_3]^+$ with no more than traces, if any, of intermediate $AuRu_3$ or Au_2Ru_3 species, demonstrates again that the trigold-oxonium reagent efficiently adds three $Au(PPh_3)$ moieties simultaneously.

The Ru_3Au_3 core of **2** does not exhibit the common octahedral M_6 arrangement; rather a capped trigonal bipyramidal geometry is found. This geometry has been noted previously in $Ru_3Au_3(\mu_3\text{-}COMe)(CO)_9(PPh_3)_3$ [4], $H_2Ru_4Au_2(CO)_{12}(PPh_3)_2$, and $HRu_3CoAu_2(CO)_{12}(PPh_3)_2$ [8,9] and in the homometallic $Os_6(CO)_{18}$ [21]. In all cases this geometry is predicted by Wade's rules, and by other more sophisticated treatments of the electronic structures of metal clusters [22]. There is however, one significant difference between the cores of **2** and those of all other clusters containing three $Au(PPh_3)$ groups. The formation of the Ru_3Au_3 skeleton may be considered formally to result from the addition of the first $Au(PPh_3)$ group to the opposite face of the Ru_3 triangle to that occupied by the C_{12} hydrocarbon, followed by capping of an Ru_2Au face by the second gold group. This generates a trigonal bipyramid, which is capped on a $RuAu_2$ face by the third $Au(PPh_3)$ group. This leads to a *closo* $Au_3(PPh_3)_3$ unit (Fig. 2b). For the other Au_3M_3 clusters mentioned above, a different sequence involves (formal) successive addition of the three Au(PPh$_3$) groups to a M$_3$ triangle on the Ru$_3$, Ru$_2$Au and Ru$_2$Au faces to produce an open Au$_3$(PPh$_3$)$_3$ sub-unit (Fig. 2a).

The reasons for the different geometries are not clear at present. A recent theoretical study [23] of poly-gold clusters indicated that *closo*-Au$_3$ units are particularly stable, suggesting that the less-common geometry found for **2** is in fact electronically favoured. Previously, this triangular sub-unit has been observed for the simple clusters VAu$_3$(CO)$_5$(PPh$_3$)$_3$ [24], MnAu$_3$(CO)$_4$(PPh$_3$)$_3$ [24] and ReAu$_3$(CO)$_4$(PPh$_3$)$_3$ [25], and for homonuclear gold clusters. The different geometry in the other clusters may be determined by steric factors, and we note that in **2**, only eight CO ligands are associated with the Ru$_3$ face, which is thus less sterically constrained than those in Ru$_3$Au$_3$(μ_3-COMe)(CO)$_9$(PPh$_3$)$_3$ and related species which have nine CO groups on the equivalent face. Furthermore, the "bond vector" used for the third, axial CO ligand of Ru(3) in the parent hydride **1** points to the centre of the triangular Au$_3$ unit (or alternatively, to the centre of the Au$_3$Ru tetrahedron.) Superficially the two Au$_3$ geometries are similar to the cyclopropenyl (*closo*-C$_3$) and allyl (open, bent C$_3$) shapes for three-carbon organic ligands, but the analogy does not appear to have any useful consequences. It is probable that the two arrangements differ little in energy since both lead to the same total number of metal–metal bonds.

There seems to be no pattern for the Au–Au bond lengths in **2** or in other cluster complexes containing Au$_3$(PR$_3$)$_3$ groups. The Au–Au separation in gold metal is 2.884 Å, whereas the reported range of Au–Au distances is 2.60–3.10 Å. This conformational softness is echoed in solution: ^{31}P NMR studies of the dynamic behaviour of Ru$_3$Au$_2$(μ_3-S)(CO)$_8$(PPh$_3$)$_3$ suggest that both Ru–Au and Au–Au interactions are sufficiently labile to allow facile rearrangements of the metal core [2]. If this is a general feature of heterometallic clusters containing gold, the solid state geometry of the metal core may be determined by a delicate balance of electronic, steric and crystal packing effects, with no one dominating.

Experimental

General experimental conditions have been described previously. HRu$_3$(μ_3-C$_{12}$H$_{15}$)(CO)$_9$ [15] and [O{Au(PPh$_3$)}$_3$][BF$_4$] [26] were prepared by literature methods; K-Selectride (K[HBBu$_3^{sec}$], 0.5 *M* in tetrahydrofuran) was supplied by Aldrich, and used as received.

Reaction between [Ru$_3$(μ_3-C$_{12}$H$_{15}$)(CO)$_9$]$^-$ and [O{Au(PPh$_3$)}$_3$][BF$_4$]

K-Selectride (0.28 mmol) was added dropwise to a solution of HRu$_3$(μ_3-C$_{12}$H$_{15}$)(CO)$_9$ (200 mg, 0.28 mmol) in dry, deoxygenated tetrahydrofuran (15 ml), and the solution was stirred for 10 min. Solid [O{Au(PPh$_3$)}$_3$][BF$_4$] (138 mg, 0.093 mmol) was then added, and the mixture was stirred for 18 h at room temperature. After removal of solvent in vacuo, excess K-Selectride was destroyed by addition of ethanol; after evaporation, the solid remaining was dissolved in acetone. Preparative TLC (2/3 acetone/cyclohexane) of the filtered solution gave four bands: Band 1 (R_f = 0.83) contained HRu$_3$(μ_3-C$_{12}$H$_{15}$)(CO)$_9$ (47 mg, 24%) (IR identification); Band 2 (R_f = 0.71) contained a trace of orange material, with ν(CO) (cyclohexane) at 2064w, 2044vs, 2032m, 2002s, 1994s, 1976(sh), 1956(sh), 1907(sh) cm^{-1}; Band 3

(R_f 0.65) afforded only a trace of red solid with ν(CO) (cyclohexane) 2072w, 2044w, 2020m, 1998vs, 1966m, 1928m cm^{-1}; Band 4 ($R_f = 0.60$) contained the major product, purple $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (**2**) (56 mg, 29%), m.p. 223°C (dec.), which was recrystallised from 1/4 benzene/cyclohexane (Found: C, 43.85; H,

TABLE 1

FINAL POSITIONAL PARAMETERS FOR $Au_3Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)$ ($\times 10^4$)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Au(1)	6563(1)	4081(1)	2797(1)	C(124)	3913(24)	5236(7)	2868(21)
Au(2)	7394(1)	3651(1)	1483(1)	C(125)	4893(24)	5247(7)	3198(21)
Au(3)	8594(1)	3854(1)	3022(1)	C(126)	5585(24)	5033(7)	2850(21)
Ru(1)	7455(3)	3935(1)	4624(2)	C(131)	5531(20)	4344(7)	0754(18)
Ru(2)	5447(3)	3772(1)	4205(2)	C(132)	5554(20)	4487(7)	−0.113(18)
Ru(3)	6994(2)	3439(1)	3221(2)	C(133)	5035(20)	4343(7)	−0.855(18)
P(1)	6139(10)	4498(3)	1784(8)	C(134)	4494(20)	4056(7)	−0.731(18)
P(2)	7659(9)	3553(3)	−0009(7)	C(135)	4471(20)	3913(7)	0.135(18)
P(3)	0183(12)	3964(3)	2922(8)	C(136)	4990(20)	4057(7)	0878(18)
C(11)	6776(31)	3936(10)	5678(40)	C(211)	8497(21)	3197(6)	−0087(23)
O(11)	6472(24)	3913(8)	6375(25)	C(212)	8442(21)	2975(6)	−0815(23)
C(12)	8663(39)	4025(12)	5130(74)	C(213)	9114(21)	2716(6)	−0846(23)
O(12)	9404(30)	4077(8)	5441(19)	C(214)	9840(21)	2679(6)	−0147(23)
C(13)	7344(39)	4431(14)	4431(30)	C(215)	9895(21)	2900(6)	0582(23)
O(13)	7312(38)	4693(9)	4396(30)	C(216)	9223(21)	3160(6)	0612(23)
C(21)	4792(27)	3731(10)	5219(44)	C(221)	6531(18)	3398(7)	−0669(20)
O(21)	4205(27)	3715(9)	5797(25)	C(222)	6219(18)	3541(7)	−1499(20)
C(22)	5106(37)	4244(17)	4111(28)	C(223)	5349(18)	3435(7)	−1951(20)
O(22)	4890(42)	4515(9)	4225(36)	C(224)	4791(18)	3185(7)	−1572(20)
C(23)	4458(64)	3691(21)	3352(41)	C(225)	5103(18)	3042(7)	−0741(20)
O(23)	3854(30)	3618(9)	2837(30)	C(226)	5973(18)	3149(7)	−0289(20)
C(31)	7924(34)	3139(14)	2886(23)	C(231)	8146(20)	3859(6)	−0717(17)
O(31)	8506(26)	2945(8)	2673(21)	C(232)	8607(20)	3789(6)	−1528(17)
C(32)	5891(34)	3273(10)	2239(27)	C(233)	8934(20)	4045(6)	−2073(17)
O(32)	5341(30)	3169(9)	1853(27)	C(234)	8800(20)	4371(6)	−1806(17)
C(R1)	5865(39)	3289(11)	4195(33)	C(235)	8338(20)	4441(6)	−0994(17)
C(R2)	6821(43)	3196(11)	4572(22)	C(236)	8011(20)	4185(6)	−0450(17)
C(R3)	7578(35)	3410(11)	4582(30)	C(311)	0588(38)	4369(7)	3355(24)
C(R4)	8654(30)	3271(11)	4938(23)	C(312)	9924(38)	4609(7)	3618(24)
C(R5)	8839(39)	3233(10)	5980(39)	C(313)	0268(38)	4919(7)	3896(24)
C(R6)	8103(73)	2894(39)	6379(65)	C(314)	1275(38)	4988(7)	3912(24)
C(R7)	7440(80)	3002(17)	6700(48)	C(315)	1939(38)	4747(7)	3649(24)
C(R8)	6642(57)	2688(15)	6881(42)	C(316)	1596(38)	4438(7)	3371(24)
C(R9)	6002(93)	2625(22)	6097(67)	C(321)	0681(36)	3948(9)	1812(19)
C(R10)	5352(60)	2880(18)	5951(35)	C(322)	0128(36)	4035(9)	1021(19)
C(R11)	4582(37)	2950(11)	5031(30)	C(323)	0540(36)	4009(9)	0166(19)
C(R12)	5215(37)	3004(12)	4159(30)	C(324)	1505(36)	3896(9)	0103(19)
C(111)	7157(17)	4751(6)	1421(17)	C(325)	2059(36)	3810((9)	0894(19)
C(112)	6930(17)	5039(6)	0935(17)	C(326)	1647(36)	3836(9)	1748(19)
C(113)	7685(17)	5139(6)	0637(17)	C(331)	0892(26)	3644(9)	3672(28)
C(114)	8667(17)	5152(6)	0825(17)	C(332)	1434(26)	3682(9)	4499(28)
C(115)	8894(17)	4864(6)	1310(17)	C(333)	1881(26)	3409(9)	4923(28)
C(116)	8139(17)	4664(6)	1608(17)	C(334)	1786(26)	3099(9)	4520(28)
C(121)	5297(24)	4806(7)	2171(21)	C(335)	1243(26)	3061(9)	3693(28)
C(122)	4318(24)	4795(7)	1841(21)	C(336)	0796(26)	3334(9)	3269(28)
C(123)	3625(24)	5009(7)	2190(21)				

2.64; $C_{74}H_{60}Au_3O_8P_3Ru_3$ calcd.: C, 43.03; H, 2.93%) IR (cyclohexane): ν(CO) at 2040m, 1974vs, 1957(sh), 1918m cm^{-1}; ^1H NMR: δ ($CDCl_3$) 0.88–5.95, m, 14H, C_{12} ring protons; 6.10, s, 1H, allylic C*H*; 7.2, m, 45H, P*Ph*.

Crystal structure determination

A red-brown needle (0.65 × 0.16 × 0.16 mm) of **2** was mounted on a Hilger and Watts four-circle diffractometer. Graphite monochromated Cu-K_α radiation was used; 15 high angle reflections were used to determine accurate cell dimensions.

Crystal data. $C_{74}H_{60}Au_3O_8P_3Ru_3$, $M = 2064.3$, Monoclinic, Space group $P2_1/c$, a 13.574(1), b 40.634(4), c 14.617(2) Å, β 92.58(1)°, U 8054.1 Å^3, D_c 1.70 g cm^{-3} for $Z = 4$, $F(000) = 3928$, μ(Cu-K_α) 157 cm^{-1}, λ(Cu-K_α) 1.5418 Å.

Intensity data were collected in the range $2° < 2\theta < 40°$ to give 4347 unique reflections, which were corrected for Lorentz and polarisation effects, and for absorption (ABSORB; maximum and minimum correction factors were 10.0 and 3.17, respectively). The final calculations used 3233 reflections with $I > 3\sigma(I)$.

The structure was solved by direct methods (SHELX) to give the heavy atom skeleton, and subsequent difference maps located all other non-hydrogen atoms. In the final cycles of blocked full-matrix, least-squares refinement all atoms other than those of the phenyl rings were assigned anisotropic temperature parameters, the

TABLE 2

SELECTED BOND LENGTHS FOR $Au_3Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (Å)

Au(2)–Au(1)	2.865(2)	C(121)–P(1)	1.803(32)
Au(3)–Au(1)	2.911(3)	C(131)–P(1)	1.797(28)
Ru(1)–Au(1)	2.943(4)	C(211)–P(2)	1.846(29)
Ru(2)–Au(1)	2.896(4)	C(221)–P(2)	1.881(28)
Ru(3)–Au(1)	2.737(3)	C(231)–P(2)	1.765(27)
P(1)–Au(1)	2.307(11)	C(311)–P(3)	1.837(35)
Au(3)–Au(2)	2.840(2)	C(321)–P(3)	1.787(35)
Ru(3)–Au(2)	2.761(3)	C(331)–P(3)	1.930(40)
P(2)–Au(2)	2.261(11)	C(11)–O(11)	1.121(68)
Ru(1)–Au(3)	2.882(4)	C(12)–O(12)	1.106(83)
Ru(3)–Au(3)	2.775(4)	C(13)–O(13)	1.068(65)
P(3)–Au(3)	2.215(16)	C(21)–O(21)	1.097(68)
Ru(2)–Ru(1)	2.845(5)	C(22)–O(22)	1.154(78)
Ru(3)–Ru(1)	2.922(4)	C(23)–O(23)	1.128(85)
C(R3)–Ru(1)	2.140(41)	C(31)–O(31)	1.170(61)
C(11)–Ru(1)	1.830(56)	C(32)–O(32)	1.008(58)
C(12)–Ru(1)	1.806(55)	C(R1)–C(R2)	1.437(74)
C(13)–Ru(1)	2.039(55)	C(R2)–C(R3)	1.345(73)
Ru(3)–Ru(2)	2.929(5)	C(R3)–C(R4)	1.628(62)
C(21)–Ru(2)	1.847(58)	C(R4)–C(R5)	1.541(67)
C(22)–Ru(2)	1.976(68)	C(R5)–C(R6)	1.813(115)
C(23)–Ru(2)	1.821(74)	C(R6)–C(R7)	1.149(129)
C(R1)–Ru(2)	2.045(44)	C(R7)–C(R8)	1.693(114)
C(31)–Ru(3)	1.837(50)	C(R8)–C(R9)	1.429(127)
C(32)–Ru(3)	2.136(42)	C(R9)–C(R10)	1.371(94)
C(R1)–Ru(3)	2.224(52)	C(R10)–C(R11)	1.690(88)
C(R2)–Ru(3)	2.230(36)	C(R11)–C(R12)	1.584(66)
C(R3)–Ru(3)	2.111(44)	C(R12)–C(R1)	1.456(68)
C(111)–P(1)	1.819(27)		

phenyl rings were treated as rigid groups and the cyclododecatrienyl group H atoms were included in their calculated positions with a common temperature factor. Refinement converged at $R = 0.078$, $R_w = 0.084$ where $w = 0.955[\sigma^2(F) + 0.008F^2]^{-1}$. Five carbon atoms gave "non-positive definite" thermal ellipsoids, no doubt arising from the imprecise absorption correction; a number of peaks of ca. 2 e Å^{-3} near the heavy metal atoms in the final difference map can be similarly explained.

Atomic coordinates, and selected bond, lengths and angles are given in Tables 1–3; Figure 1 is a plot of a molecule of **2** showing the numbering scheme. Tables of

TABLE 3

SELECTED BOND ANGLES FOR $Au_3Ru_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ (degrees)

Au(3)–Au(1)–Au(2)	58.9(1)	C(23)–Ru(2)–C(21)	96.6(3)
Ru(1)–Au(1)–Au(2)	109.1(1)	C(23)–Ru(2)–C(22)	87.9(3)
Ru(1)–Au(1)–Au(3)	59.0(1)	Au(2)–Ru(3)–Au(1)	62.8(1)
Ru(2)–Au(1)–Au(2)	116.6(1)	Au(3)–Ru(3)–Au(1)	63.8(1)
Ru(2)–Au(1)–Au(3)	107.8(1)	Au(3)–Ru(3)–Au(2)	61.7(1)
Ru(2)–Au(1)–Ru(1)	58.3(1)	Ru(1)–Ru(3)–Au(1)	62.6(1)
Ru(3)–Au(1)–Au(2)	59.0(1)	Ru(1)–Ru(3)–Au(2)	112.7(1)
Ru(3)–Au(1)–Au(3)	58.8(1)	Ru(1)–Ru(3)–Au(3)	60.7(1)
Ru(3)–Au(1)–Ru(1)	61.8(1)	Ru(2)–Ru(3)–Au(1)	61.4(1)
Ru(3)–Au(1)–Ru(2)	62.6(1)	Ru(2)–Ru(3)–Au(2)	118.9(1)
P(1)–Au(1)–Au(2)	96.4(3)	Ru(2)–Ru(3)–Au(3)	110.6(1)
P(1)–Au(1)–Au(3)	120.8(3)	Ru(2)–Ru(3)–Ru(1)	58.2(1)
P(1)–Au(1)–Ru(1)	144.2(3)	C(32)–Ru(3)–C(31)	94.6(1)
P(1)–Au(1)–Ru(2)	130.6(3)	C(111)–P(1)–Au(1)	115.6(1)
P(1)–Au(1)–Ru(3)	152.9(3)	C(121)–P(1)–Au(1)	116.9(1)
Au(3)–Au(2)–Au(1)	61.4(1)	C(131)–P(1)–Au(1)	111.9(1)
Ru(3)–Au(2)–Au(1)	58.2(1)	C(211)–P(2)–Au(2)	108.9(1)
Ru(3)–Au(2)–Au(3)	59.4(1)	C(221)–P(2)–Au(2)	113.1(1)
P(2)–Au(2)–Au(1)	147.0(3)	C(231)–P(2)–Au(2)	121.3(1)
P(2)–Au(2)–Au(3)	134.8(3)	C(311)–P(3)–Au(3)	115.8(2)
P(2)–Au(2)–Ru(3)	151.5(3)	C(321)–P(3)–Au(3)	117.5(2)
Au(2)–Au(3)–Au(1)	59.7(1)	C(331)–P(3)–Au(3)	106.7(1)
Ru(1)–Au(3)–Au(1)	61.1(1)	O(11)–C(11)–Ru(1)	170.1(4)
Ru(1)–Au(3)–Au(2)	111.6(1)	O(12)–C(12)–Ru(1)	152.3(7)
Ru(3)–Au(3)–Au(1)	57.5(1)	O(13)–C(13)–Ru(1)	174.5(4)
Ru(3)–Au(3)–Au(2)	58.9(1)	O(21)–C(21)–Ru(2)	176.3(4)
Ru(3)–Au(3)–Ru(1)	62.2(1)	O(22)–C(22)–Ru(2)	167.5(4)
P(3)–Au(3)–Au(1)	148.1(4)	O(23)–C(23)–Ru(2)	175.0(6)
P(3)–Au(3)–Au(2)	122.1(3)	O(31)–C(31)–Ru(3)	179.1(4)
P(3)–Au(3)–Ru(1)	126.2(3)	O(32)–C(32)–Ru(3)	170.9(4)
P(3)–Au(3)–Ru(3)	154.0(4)	C(R12)–C(R1)–C(R2)	109.9(3)
Au(3)–Ru(1)–Au(1)	60.0(1)	C(R3)–C(R2)–C(R1)	120.8(4)
Ru(2)–Ru(1)–Au(1)	60.0(1)	C(R4)–C(R3)–C(R2)	117.0(4)
Ru(2)–Ru(1)–Au(3)	110.0(1)	C(R5)–C(R4)–C(R3)	117.1(3)
Ru(3)–Ru(1)–Au(1)	55.6(1)	C(R6)–C(R5)–C(R4)	109.1(4)
Ru(3)–Ru(1)–Au(3)	57.1(1)	C(R7)–C(R6)–C(R5)	108.1(1)
Ru(3)–Ru(1)–Ru(2)	61.0(1)	C(R8)–C(R7)–C(R6)	106.7(9)
Ru(1)–Ru(2)–Au(1)	61.7(1)	C(R9)–C(R8)–C(R7)	113.9(5)
Ru(3)–Ru(2)–Au(1)	56.1(1)	C(R10)–C(R9)–C(R8)	110.6(4)
Ru(3)–Ru(2)–Ru(1)	60.8(1)	C(R11)–C(R10)–C(R9)	128.4(5)
C(22)–Ru(2)–C(21)	90.4(2)	C(R12)–C(R11)–C(R10)	109.0(4)
		C(R11)–C(R12)–C(R1)	115.5(3)

thermal parameters and of structure factors can be obtained from the authors (BKN).

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