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XXXIII *. REACTIONS OF $[\{Au(PPh_3)\}_3O]^+$ WITH $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$: X-RAY STRUCTURE OF $[Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2]$, CONTAINING A t-BUTYLVINYLIDENE LIGAND ATTACHED TO A TRIGONAL-BIPYRAMIDAL Ru_3Au_2 CORE

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Summary

Deprotonation ($K[HBBu_3^s]$) of $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$, followed by reaction of the anion with $[O\{Au(PPh_3)\}_3][BF_4]$, afforded the known complex $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9$ (9%), the vinylidene cluster $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2$ (16%) and the hexanuclear $Ru_3Au_3(C_2Bu^t)(CO)_8(PPh_3)_3$ (3%). The X-ray structure of the pentanuclear complex shows an asymmetric trigonal-bipyramidal Ru_3Au_2 core (Ru, Au at the apices) with the Ru_3 face bridged by a t-butylvinylidene ligand, being σ-bonded to Ru(1) and Ru(3), and η^2-coordinated to Ru(2). Crystals are monoclinic, space group $P2_1/n$ with *a* 19.121(3), *b* 13.109(3), *c* 23.649(4) Å, β 106.76(2)° and $Z = 4$. The structure was solved using 4405 observed diffractometer data, and refined to *R* 0.044, R_w 0.047.

Introduction

We have recently described the use of the trigold-oxonium reagent $[O\{Au(PPh_3)\}_3]^+$ to introduce up to three $Au(PPh_3)$ moieties on to cluster anions of ruthenium. In this way, complexes $H_{4-n}Ru_4Au_n(CO)_{12}(PPh_3)_n$ ($n = 1$–3) [1], $Ru_3CoAu_n(CO)_{13}(PPh_3)_n$ ($n = 1$–3) [2], and $Ru_3Au_n(\mu_3\text{-}S)(CO)_9(PPh_3)_n$ [3] ($n =$ 1,2) have been obtained. This paper describes the reaction between the anion $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ and this reagent, carried out to determine whether the $Au(PPh_3)$ moiety would add to the cluster core or to the bridging hydrocarbon. In previous accounts, $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ (**1**) (Scheme 1) is reported to react with

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* For Part XXXII, see ref. 18.

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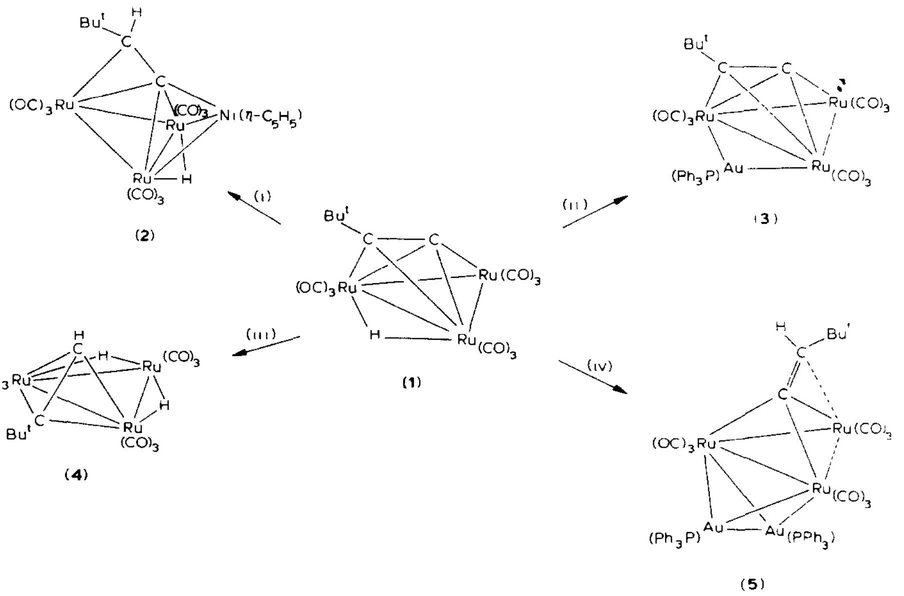
$[Ni(CO)(\eta\text{-}C_5H_5)]_2$ to give $HRu_3Ni(\mu_4\text{-}C{=}CHBu^t)(CO)_9(\eta\text{-}C_5H_5)$ (**2**) [4], and the anion with $AuCl(PPh_3)$ to give $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$ (**3**) [5]. Hydrogenation of complex **1** affords $H_2Ru_3(HC{\equiv}CBu^t)(CO)_9$ (**4**) [6], and we were interested to compare the formal addition of "$Au_2(PPh_3)_2$", observed in this reaction, with the addition of the isolobal equivalent H_2.



SCHEME 1. Some reactions of $(\mu\text{-H})Ru(\mu_3\text{-}C_2Bu^t)(CO)_9$ (**1**). Reagents: (i) $[Ni(CO)(\eta\text{-}C_5H_5)]_2$; (ii) KOH/MeOH, then $AuCl(PPh_3)$; (iii) H_2, refluxing heptane; (iv) $K[HBBu^s_3]$, then $[O\{Au(PPh_3)\}_3][BF_4]$

Results

The hydrido-alkynyl complex $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ (**1**) reacts readily with K-Selectride ($K[HB(CHMeEt)_3]$) to generate the anion $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$. This derivative has been obtained previously by reaction of the parent hydrido cluster with KOH/MeOH [7]; we have found the present method to be experimentally more convenient, as the cluster-bound hydride can be titrated off with the complex hydride reagent. Addition of $[O\{Au(PPh_3)\}_3][BF_4]$ to a solution of the anion, followed by thin-layer chromatographic separation of the products, afforded two major products, the known $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$ (**3**), which was identified by comparison of its IR and NMR spectra with those reported in the literature [5], and the digold adduct $Ru_3Au_2(\mu_3\text{-}C_2HBu^t)(CO)_9(PPh_3)_2$ (**5**). The latter was formulated on the basis of analytical and NMR spectrometric measurements; the IR spectrum contains only terminal $\nu(CO)$ absorptions, while the ^1H NMR spectrum has resonances at δ 1.38 and 7.46 ppm, assigned to the Bu^t and Ph protons, respectively, together with a singlet at δ 6.30 ppm, of relative intensity 1. A single-crystal X-ray study was carried out to determine the molecular structure, and hence the nature of the C_2HBu^t ligand.

Structure of $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2$ (5)

A molecule of **5** is shown in Fig. 1; sketches of the metal cores in **3** and **5** are given in Fig. 2. The complex contains a trigonal pyramidal Ru_3Au_2 core, with Ru(2) and Au(1) as apical atoms. The nine CO ligands are distributed to three to each ruthenium, while each gold atom carries one PPh_3 ligand. The hydrocarbon ligand no longer interacts with the Ru_3 core in the μ_3-η^1,$2\eta^2$ mode found in $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$; instead, C(10) interacts with all three rutheniums, but C(11) is attached only to Ru(2). The C(10)–C(11) separation (1.41(2) Å) is consistent with the presence of a C=C double bond, which is π-bonded to Ru(2). The C(12)–C(11) vector forms an angle of 130(1)° with the C=C bond, and the ^1H NMR spectrum confirms the presence of the hydrogen attached to C(11) suggested by the geometry around that atom. This hydrogen was not located in the difference map. In **2**, the vinylidene proton resonates at δ 4.80 ppm [4].

The metal–metal separations are of three types: three Ru–Ru (2.837(2)–2.918(2) Å), five Ru–Au (2.781(1)–2.916(1) Å), and one Au–Au (3.033(1) Å). These values fall within the ranges already reported for complexes containing ruthenium–gold cores. However, there is an interesting asymmetry of the Ru_3Au_2 core, as indicated by individual atom separations, such as Ru(2)–Ru(1) (2.903(2) Å) and Ru(2)–Ru(3) (2.837(2) Å), Au(1)–Ru(1) (2.826(2) Å) and Au(1)–Ru(3) (2.781(1) Å), Au(2)–Ru(1)

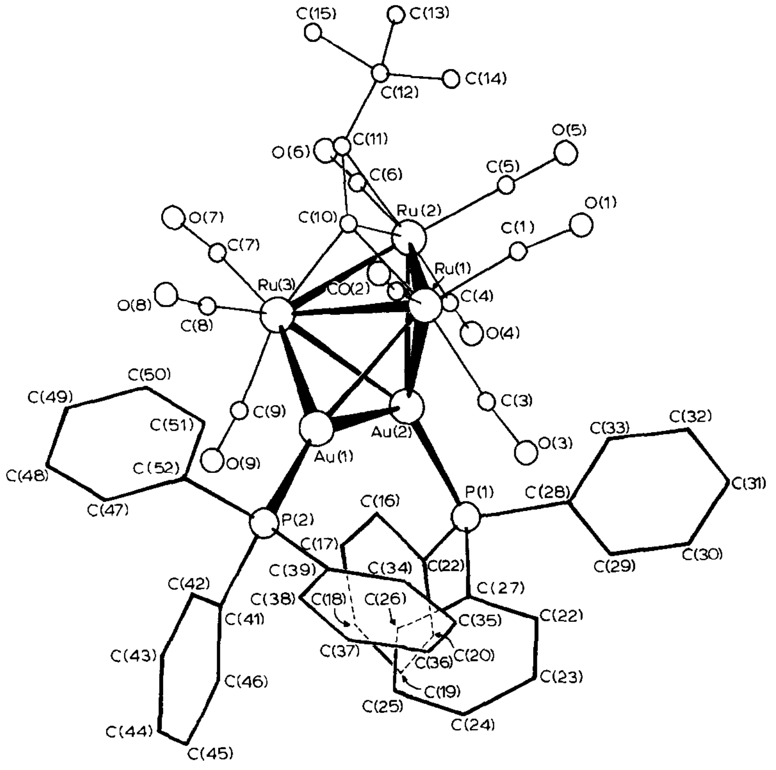


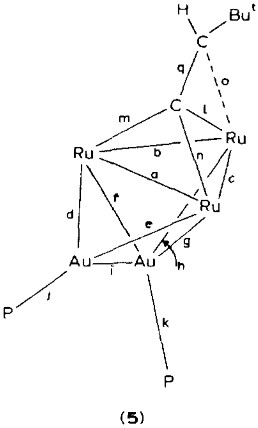
Fig. 1. PLUTO plot of one molecule of $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2$ (5), showing atom numbering system.

(2.829(2) Å) and Au(2)–Ru(3) (2.800(2) Å). Although the vinylidene ligand lies across the Ru_3 face so that the C(10)–C(11) bond leans towards the Ru(2)–Ru(3) edge, we suggest that the main origin of these differences is to be found in the mode of attachment of the $Au(PPh_3)$ moieties of the Ru_3 cluster. Thus the P(1)–Au(2) vector points towards the Ru(2)–Ru(3) edge rather than to the centre of the Ru_3 face, while the P(2)–Au(1) vector intersects the Ru(1)Ru(3)Au(2) face near its centre. This feature is further emphasised by the torsion angle P(2)Au(1)Au(2)/Au(1)Au(2)P(1) (15.7°), which indicates the degree of skewing of the $Au_2(PPh_3)_2$ group about the Au–Au bond when bonded to this cluster.

Comparison of the cores of the Ru_3Au (**3**) and Ru_3Au_2 (**5**) complexes shows that the addition of the second $Au(PPh_3)$ moiety results in considerable lengthening of the Au–Ru and Ru–Ru separations. In **5**, only Au(1)–Ru(3) approaches the values found for Au(1)–Ru(2) and Au(1)–Ru(3) in **3** (2.757, 2.763(1) Å, respectively), other separations all being > 2.80 Å.. In the two complexes, the Ru(2)–Ru(3) separations, bridged by the hydrocarbon as well as by $Au(PPh_3)$, differ little (2.820(1) in **3**, 2.837(2) Å in **5**), while the other two separations increase from 2.79 (av.) in **3** to 2.91 Å (av.) in **5**. In the hydrido analogue, $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$, all Ru–Ru separations are equal at 2.80 Å [8]. These observations are in accord with previous observations of bond lengthening which occurs on addition of more than one $Au(PPh_3)$ moiety to cluster complexes [1,2,9].

Comparison of the modes of attachment of the hydrocarbon ligands in the two complexes shows that the acetylide is bonded to the Ru_3 cluster in **3** by one short (1.95(1) Å) and four long (2.22 Å (av.)) Ru–C interactions, while the vinylidene ligand in **5** is attached via three short bonds (2.11 Å (av.)) from C(10), one to each Ru, and the long and rather weak C(11)–Ru(2) interaction (2.42(1) Å).

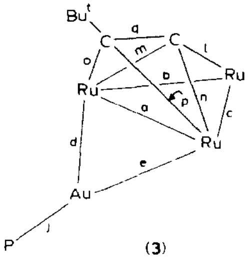
The major point of interest in this reaction is the transformation of the μ_3-acetylide unit found in the anion $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$, and the mono-gold complex **3**, to the μ_3-vinylidene ligand concomitantly with the introduction of the second $Au(PPh_3)$



(**5**)

	5	**3**^{a}
a	2 918(2)	2 820(1)
b	2 837(2)	2 786(2)
c	2.903(2)	2 800(1)
d	2 781(1)	2.757(1)
e	2.826(2)	2 763(1)
f	2 800(2)	–
g	2 829(2)	–
h	2 916(1)	–
i	3.033(1)	–
j	2 299(4)	2 276(3)
k	2 309(4)	–
l	2 190(14)	1.95(1)
m	2 102(17)	2 19(1)
n	2.040(14)	2.22(1)
o	2 423(15)	2 27(1)
p	–	2 21(1)
q	1 406(19)	1 29(2)

^{a} Ref. **5**.



(**3**)

Fig. 2. Heavy-atom cores of $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$ (**3**) and $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2$ (**5**), showing modes of attachment of hydrocarbon ligands

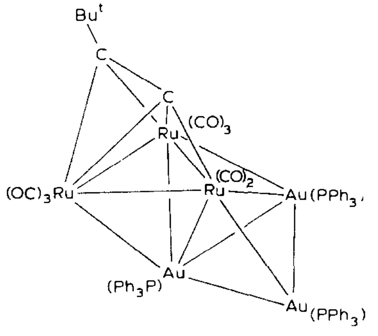
group. We have carried out separate experiments and find (i) stoichiometric generation of the anion $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ followed by protonation (H_3PO_4) results in a 60% recovery of $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$; (ii) addition of excess K-Selectride to a solution of the anion, followed by protonation (HPF_6) afforded a mixture of four neutral complexes, of which only $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ (7% yield) was identified; (iii) addition of K-Selectride to a solution of **1**, followed by addition of HPF_6, gave a complex mixture of products, among which was identified $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ (15%). The low recovery of hydrido-cluster in experiment (i) was not unexpected: the anion $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ is reported [7] to decompose slowly under CO, and we find it rapidly decomposes under N_2. While these experiments are generally inconclusive, it does not seem likely that any vinylidene complex is formed in significant amount in reactions that parallel the synthesis of **5**, nor is the hydrogen added to a mono-gold complex, followed by addition of a second $Au(PPh_3)$ moiety. However, we cannot preclude a reaction which proceeds by initial addition of hydride to the α-carbon, followed by isomerisation of the resulting acetylene to the vinylidene ligand found in **5**.

The isolobal replacement of H by $Au(PPh_3)$ in cluster carbonyl hydrides is now a well established process; reaction (i), for example, has its isolobal equivalent in the formation of $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$ from the anion and $AuCl(PPh_3)$ [5]. We have shown that addition of three $Au(PPh_3)$ units to a mono-hydrido cluster can occur with loss of the hydrogen atom and a CO ligand, as found in the synthesis of $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$ from $HRu_3(\mu_3\text{-}C_{12}H_{15})(CO)_9$ [10]. In the present example, however, addition of two $Au(PPh_3)$ units does not result in loss of CO. Instead a formal migration of H from the Ru_3 cluster to the μ_3-acetylide (a 5*e*-donor) occurs to give a μ_3-vinylidene ligand (a 4*e*-donor). This reaction contrasts with the reaction between H_2 (formally isolobal with $Au_2(PPh_3)_2$) and $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ which affords the complex $H_2Ru_3(HC{\equiv}CBu^t)(CO)_9$ [6]. In this, one hydrogen adds to the Ru_3 cluster in an edge-bridging position, while the second adds to the α-carbon of the acetylide function to give a μ-alkyne ligand.

This difference can be rationalised in terms of the tendency for the formation of Au–Au bonds where more than one $Au(PR_3)$ group is attached to the same triangular face of a cluster complex. In **1**, the two $Au(PPh_3)$ moieties are similar to μ_2-H (Au(2)P(1)) and μ_3-H (Au(1)P(2)) ligands, while also being involved in a long Au–Au interaction, probably because steric interaction with the CO ligands results in the two $Au(PPh_3)$ groups moving to within mutual bonding distance. Addition of H to the β-carbon may then be the result of the steric requirements of a μ_3-vinylidene vs. a μ_3-alkyne ligand on this particular cluster. Conversion of μ_3-vinylidene to μ_3-alkyne ligands has been observed on an Os_3 cluster [11], while formation of a vinylidene complex has also been found in the reaction between $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ and $[Ni(CO)(\eta\text{-}C_5H_5)]_2$, which affords $HRu_3Ni(\mu_4\text{-}C{=}CHBu^t)(CO)_9(\eta\text{-}C_5H_5)$ [4].

Bonding in gold–ruthenium clusters

The isolobal replacement of H by $Au(PPh_3)$ in $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ is consistent with the arguments advanced by Lauher and Wald [12] in their initial account which drew attention to this area. A formal extension of that work is the consideration of $Au_2(PR_3)_2$ as a 2*e*-donor ligand, and in the present instance such a ligand might be considered to bridge the Ru(1)–Ru(3) bond. If considered as a pseudoolefin, one might anticipate bond-lengthening as a result of electronic interactions of Ru electron density with σ^* orbitals of the Au–Au bond. In any case, the geometry of this interaction (including steric effects of associated ligands) also forces one gold to approach within bonding distance of Ru(2); we have commented above on the apparent preference of the orbital lying along the extension of the Au(2)P(1) vector for overlap in the Ru(2)–Ru(3) bond region.



(**6**)

We note here that a third product from this reaction is the hexanuclear product $Ru_3Au_3(C_2Bu^t)(CO)_8(PPh_3)_3$ (**6**), which has been characterised from microanalytical and NMR data only, no crystals of X-ray quality having been obtained at this time. We could not detect any hydrogens other than those of the Bu^t and Ph groups. Addition of the $Au_3(PPh_3)_3$ unit to the original hydrido cluster requires formal loss of (H + CO), and we consider it likely that this complex contains a *cyclo*-$Au_3(PPh_3)_3$ ligand attached to the Ru_3 cluster on the face opposite to that occupied by the C_2Bu^t ligand. By similar arguments to those advanced in the case of $Ru_3Au_3(\mu_3\text{-}C_{12}H_{15})(CO)_8(PPh_3)_3$, we suggest that an axial CO is lost from Ru(3), allowing the compact $Au_3(PPh_3)_3$ unit to become attached at this point, i.e. the original Ru–CO vector would point to the centre of the Au_3 triangle.

Conclusion

We have shown that a further type of reactivity associated with the generation of cluster anions and their poly-auration is the addition of hydrogen to a cluster-bound ligand. In the present case, this occurs in a manner different from the addition of molecular hydrogen, but this may result from steric or electronic factors, the interconversion of alkyne and vinylidene ligands on metal aggregates being a facile process [13].

Experimental

General experimental conditions and instrumentation were the same as reported in other papers in this series. The complexes $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ [14] and $[O\{Au(PPh_3)\}_3][BF_4]$ [15] were made according to the literature procedures.

Reaction between $[Ru_3(\mu_3\text{-}C_2Bu^t)(CO)_9]^-$ *and* $[O\{Au(PPh_3)\}_3][BF_4]$

A solution of $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ (100 mg, 0.157 mmol) in dry deoxygenated tetrahydrofuran (THF) (15 ml) was treated with K-Selectride (0.31 ml of a 0.5 mol l^{-1} solution in THF) for 15 min. Solid $[O\{Au(PPh_3)\}_3][BF_4]$ (232 mg, 0.157 mmol) was added and the mixture stirred for 3 h. After removal of the solvent, the residue was separated by preparative thin-layer chromatography (silica gel, acetone/cyclohexane (35/65)). Four bands developed:

Band 1: orange, R_f 0.57, was recrystallised from n-hexane to give orange crystals, identified as $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$ (**3**) (15 mg, 9%) m.p. 140°C (dec.). Found: C, 35.92; H, 2.15. $C_{33}H_{24}AuO_9PRu_3$ calcd.: C, 36.16; H, 2.19%. IR: $\nu(CO)$ (cyclohexane) 2076s, 2054vs, 2036vs, 1999vs, 1990sh, 1970m cm^{-1} (lit. 5: $\nu(CO)$ (hexane) 2074m, 2051s, 2036vs, 1996vs, 1968m cm^{-1}); ^1H NMR: δ ($CDCl_3$) 7.46, m, 15H, Ph; 1.38, s, 9H, Bu^t.

Band 2: red, R_f 0.51, was recrystallized from dichloromethane/petroleum spirit (1/2) to give deep red crystals, identified (X-ray crystallography) as $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2$ (**5**) (40 mg, 16%) m.p. 150°C (dec.). Found: C, 40.03; H, 2.77. $C_{51}H_{40}Au_2O_9P_2Ru_3$ calcd.: C, 39.36; H, 2.51%. IR: $\nu(CO)$ (cyclohexane) 2048 m, 2039w, 2018vs, 1978m, 1962s cm^{-1}; ^1H NMR: δ ($CDCl_3$) 7.27, m, 30H, Ph; 6.30, s, 1H, =CH; 1.42, s, 9H, Bu^t.

Band 3: red, R_f 0.46, traces only, IR: $\nu(CO)$ (cyclohexane) 2047m, 2037s, 2008s(br), 1972s, 1958(sh), 1930w, 1910w cm^{-1}, not further investigated.

Band 4: orange, R_f 0.42, was recrystallised from CH_2Cl_2/n-heptane (1/2) to give orange crystals, identified as $Ru_3Au_3(C_2Bu^t)(CO)_8(PPh_3)_3$ (**6**) (10 mg, 3%) m.p. 150°C (changes colour). Found: C, 41.55; H, 2.54. $C_{68}H_{54}Au_3O_8P_3Ru_3$ calcd.: C, 41.12; H, 2.74%. IR: $\nu(CO)$ (cyclohexane) 2048vs, 2018vs, 1982s, 1971m, 1964s, 1956w, 1912m cm^{-1}; ^1H NMR: δ ($CDCl_3$) 7.44, m, 45H, Ph; 1.50, s, 9H, Bu^t.

Sequential reactions of $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ with H^- and H^+

(i) K-Selectride (0.16 mmol, 0.32 ml of 0.5 *M* solution is tetrahydrofuran) was added to a solution of $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ (100 mg) in the same solvent (10 ml). The colour darkened immediately, and H_3PO_4 (5 drops) was added after one minute. After stirring (1 h), the solution was evaporated, the residue dissolved in CH_2Cl_2 (10 ml), and washed with water (3 × 10 ml). Evaporation and purification by preparative TLC (acetone/X4 10/90) afforded $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ (60 mg, 60%); a considerable amount of material was left as a dark-coloured base-line.

(ii) Excess K-Selectride (0.48 mmol) was added to $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ (150 mg, 0.24 mmol) in tetrahydrofuran (20 ml). After 5 min, solvent was removed and the residue taken up in CH_2Cl_2 (10 ml). Addition of $HPF_6 \cdot OEt_2$ (5 drops) and separation (preparative TLC, acetone/X4 10/90) afforded four fractions: (a) yellow unknown (9 mg), R_f 0.84, $\nu(CO)$ (cyclohexane) 2107w, 2100(sh), 2079s, 2074s, 2057vs, 2042s, 2024vs, 1996m cm^{-1}; (b) $HRu_3(\mu_3\text{-}C_2Bu^t)(CO)_9$ (11 mg, 7%); (c) orange unknown (trace), R_f 0.46, $\nu(CO)$ (cyclohexane) 2070m, 2053m, 2040w, 2025m, 2009w cm^{-1}; (d) orange-brown unknown (trace), R_f 0.24.

Sequential reactions of $Ru_3Au(\mu_3\text{-}C_2Bu^t)(CO)_9(PPh_3)$ with H^- and H^+

Addition of K-Selectride (0.064 mmol) to the Ru_3Au complex **3** (70 mg, 0.064 mmol) in tetrahydrofuran (10 ml), was followed by solvent removal (after 2 min), and protonation ($HPF_6 \cdot OEt_2$) of a solution of the residue in CH_2Cl_2. After 2 h, evaporation and preparative TLC (acetone/X4 30/70) afforded ten multi-coloured bands, of which only two were obtained in more than trace amounts: (a) $HRu_3(\mu_3\text{-}$

$C_2Bu^t)(CO)_9$ (6 mg, 15%), and (b) bright yellow unknown (8 mg), R_f 0.61, ν(CO) (cyclohexane) 2075s, 2038vs, 1991vs, 1982(sh), 1970s cm^{-1}.

Structure of $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2 \cdot 0.5CHCl_3$ *(5)*

Crystals of **5** suitable for X-ray analysis were obtained by slow diffusion of heptane into a concentrated solution in chloroform. A crystal of dimensions 0.08 × 0.10 × 0.19 mm^3 was mounted on a glass fibre and coated with cyano-acrylate super glue. Lattice parameters at 27°C were determined by a least-squares fit to the setting angles of 25 independent reflections, measured and refined by scans performed on an Enraf-Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo-K_α radiation.

Crystal data. $C_{51}H_{40}Au_2O_9P_2Ru_3 \cdot 0.5CHCl_3$, mol.wt 1615.65, Monoclinic, space group $P2_1/n$, a 19.121(3), b 13.109(3), c 23.649(4) Å; β 106.763(15)°; D_c

TABLE 1

FINAL ATOMIC COORDINATES FOR $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2 \cdot 0.5CHCl_3$ (**5**)

Atom^a	x	y	z	Atom	x	y	z
Au(1)	6175	4620(1)	3614	C(19)	4582(6)	−529(8)	4209(5)
Au(2)	5329	2888	2874	C(20)	5117(6)	−81(8)	3995(5)
Ru(1)	6022(1)	4432(1)	2394(1)	C(21)	4925(6)	678(8)	3564(5)
Ru(2)	4548(1)	3828(1)	1752(1)	C(22)	7085(6)	850(9)	3855(4)
Ru(3)	4783(1)	4876(1)	2841(1)	C(23)	7711(6)	896(9)	4337(4)
P(1)	5604(2)	1283(3)	3278(2)	C(24)	7680(6)	1353(9)	4862(4)
P(2)	6890(2)	5015(3)	4549(2)	C(25)	7025(6)	1764(9)	4905(4)
O(1)	6526(9)	3846(14)	1340(7)	C(26)	6400(6)	1718(9)	4423(4)
O(2)	7203(7)	2838(11)	3006(7)	C(27)	6430(6)	1260(9)	3898(4)
O(3)	6993(8)	6302(12)	2668(8)	C(28)	5799(7)	389(9)	2756(5)
O(4)	4145(10)	1629(14)	1875(7)	C(29)	5812(7)	−659(9)	2862(5)
O(5)	4897(10)	3154(11)	641(7)	C(30)	6020(7)	−1330(9)	2482(5)
O(6)	2905(8)	4100(17)	1288(7)	C(31)	6215(7)	−953(9)	1995(5)
O(7)	3206(8)	5540(12)	2414(6)	C(32)	6202(7)	95(9)	1891(5)
O(8)	5262(7)	6932(10)	3374(6)	C(33)	5993(7)	766(9)	2271(5)
O(9)	4375(7)	3760(11)	3852(6)	C(34)	8070(6)	3869(9)	4478(5)
C(1)	6276(11)	4112(17)	1721(8)	C(35)	8800(6)	3564(9)	4650(5)
C(2)	6746(11)	3409(13)	2805(8)	C(36)	9317(6)	4125(9)	5072(5)
C(3)	6662(10)	5578(15)	2597(8)	C(37)	9104(6)	4992(9)	5322(5)
C(4)	4343(14)	2461(15)	1867(9)	C(38)	8374(6)	5298(9)	5150(5)
C(5)	4773(11)	3424(14)	1059(9)	C(39)	7857(6)	4736(9)	4728(5)
C(6)	3526(12)	4022(15)	1461(8)	C(41)	6618(6)	4394(9)	5144(4)
C(7)	3798(10)	5278(15)	2549(7)	C(42)	5890(6)	4106(9)	5043(4)
C(8)	5092(10)	6125(13)	3185(8)	C(43)	5672(6)	3598(9)	5482(4)
C(9)	4573(10)	4127(15)	3487(9)	C(44)	6182(6)	3377(9)	6022(4)
C(10)	5090(8)	5269(11)	2084(7)	C(45)	6910(6)	3665(9)	6123(4)
C(11)	4591(8)	5641(12)	1566(7)	C(46)	7128(6)	4174(9)	5683(4)
C(12)	4728(10)	6113(14)	1013(8)	C(47)	6517(6)	6796(9)	5076(5)
C(13)	4099(10)	5847(16)	470(9)	C(48)	6505(6)	7850(9)	5157(5)
C(14)	5435(9)	5859(14)	860(8)	C(49)	6811(6)	8498(9)	4824(5)
C(15)	4682(13)	7260(16)	1085(10)	C(50)	7128(6)	8093(9)	4411(5)
C(16)	4199(6)	990(8)	3349(5)	C(51)	7140(6)	7040(9)	4331(5)
C(17)	3664(6)	542(8)	3563(5)	C(52)	6834(6)	6391(9)	4663(5)
C(18)	3856(6)	−217(8)	3994(5)				

^{a} All coordinates $\times 10^4$

1.893 g cm^{-3}; U 5675.60; Z 4; μ(Mo-K_α) 61.63 cm^{-1}; λ(Mo-K_α) 0.7107 Å; F(000) 3076 electrons.

Intensity data were collected in the range $1.5 < \theta < 22°$ using an ω–$n/3\theta$ scan, where n ($= 3$) was optimized by profile analysis of a typical reflection. The ω scan angles and horizontal counter apertures employed were $(1.00 + 0.35\tan\theta)°$ and $(2.40 + 0.5\tan\theta)$ mm, respectively. Three standard reflections, monitored after every 58 min of data collection, indicated that on completion of the data collection no decomposition had occurred. Data reduction and application of Lorentz and polarization corrections were performed using program SUSCAD [16]. Absorption corrections were applied with program ABSORB [16]. Maximum and minimum transmission factors were estimated to be 0.69 and 0.40, respectively. Of the 5569 reflections collected, 4405 with $I > 2.5\sigma(I)$ were considered observed and used in the calculations.

Solution and refinement. The ruthenium and gold atom locations were determined using the direct method routine of the SHELX [16] programme. All other non-hydrogen atoms were located in the Fourier difference maps of successive full-matrix least-square refinements. The remaining electron density at this stage was modelled as one half of a disordered chloroform molecule. All hydrogen atoms were included at calculated positions (C–H, 0.97 Å) with group temperature factors. The methyl and phenyl entities were refined as rigid groups (C–C, 1.395 Å). In the final blocked-matrix least-square calculation the gold, ruthenium, phosphorus and carbonyl atoms were modelled anisotropically and all others isotropically. The refinement converged with $R = 0.044$ and $R_w = 0.047$. The weighting scheme employed converged at $w = 1.00/(\sigma^2F_0 + 0.0026F_0^2)$. The largest peak remaining in the

TABLE 2

BOND LENGTHS (Å) IN $Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2 \cdot 0.5CHCl_3$ (5)

Au(2)–Au(1)	3.033(1)	Ru(1)–Au(1)	2.826(2)
Ru(3)–Au(1)	2.781(1)	P(2)–Au(1)	2.299(4)
Ru(1)–Au(2)	2.829(2)	Ru(2)–Au(2)	2.916(1)
Ru(3)–Au(2)	2.800(2)	P(1)–Au(2)	2.309(4)
Ru(2)–Ru(1)	2.903(2)	Ru(3)–Ru(1)	2.918(2)
C(1)–Ru(1)	1.840(22)	C(2)–Ru(1)	1.970(17)
C(3)–Ru(1)	1.909(19)	C(10)–Ru(1)	2.040(14)
Ru(3)–Ru(2)	2.837(2)	C(4)–Ru(2)	1.870(21)
C(5)–Ru(2)	1.888(22)	C(6)–Ru(2)	1.889(21)
C(10)–Ru(2)	2.190(14)	H(2)–Ru(2)	1.731(15)
C(11)–Ru(2)	2.423(15)	C(7)–Ru(3)	1.884(18)
C(8)–Ru(3)	1.847(17)	C(9)–Ru(3)	1.954(22)
C(10)–Ru(3)	2.102(17)	H(2)–Ru(3)	1.361(16)
C(21)–P(1)	1.811(13)	C(27)–P(1)	1.819(10)
C(28)–P(1)	1.816(14)	C(39)–P(2)	1.810(12)
C(41)–P(2)	1.826(13)	C(52)–P(2)	1.832(12)
C(1)–O(1)	1.190(29)	C(2)–O(2)	1.145(22)
C(3)–O(3)	1.126(25)	C(4)–O(4)	1.155(28)
C(5)–O(5)	1.138(29)	C(6)–O(6)	1.142(26)
C(7)–O(7)	1.138(24)	C(8)–O(8)	1.157(22)
C(9)–O(9)	1.142(27)	C(11)–C(10)	1.406(19)
C(12)–C(11)	1.536(26)	C(13)–C(12)	1.525(24)
C(14)–C(12)	1.511(29)	C(15)–C(12)	1.518(28)

final difference map (height, 1.3e Å^{-3}) was associated with the disordered chloroform molecule. All calculations were performed using scattering factors for the respective neutral atoms as tabulated in the International Tables [17].

The final least-square positional parameters of $\mathrm{Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2}$ are given in Table 1, and bond distances are collected in Table 2. The chloroform and hydrogen atom coordinates, thermal parameters for all atoms and the structure factor amplitudes are available from the authors.

All atomic coordinates, and complete tables of bond lengths and angles have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, England. Any request should be addressed to the Director, and accompanied by the full literature citation for this paper.

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References

1 M.I. Bruce and B.K. Nicholson, J. Organomet. Chem., 252 (1983) 243.

2 M.I. Bruce and B.K. Nicholson, Organometallics, 3 (1984) 101.

3 M.I. Bruce, B.K. Nicholson and O. bin Shawkataly, unpublished results.

4 A.J. Carty, N.J. Taylor, E. Sappa and A. Tiripicchio, Inorg. Chem., 22 (1983) 1871. This complex was first described as $\mathrm{Ru_3Ni(\mu_4\text{-}C{=}CHBu^t)(CO)_9(\eta\text{-}C_5H_5)}$ by E. Sappa, A. Tiripicchio and M Tiripicchio-Camellini, J. Chem. Soc., Chem. Commun., (1979) 254; Inorg. Chim Acta, 41 (1980) 11.

5 P Braunstein, G. Predieri, A. Tiripicchio and E Sappa, Inorg. Chim Acta, 63 (1982) 113

6 S. Aime, G. Gervasio, L. Milone, E Sappa and M. Frachini-Angela, Inorg Chim Acta, 26 (1978) 223

7 C. Barner Thorsen, K.I Hardcastle, E Rosenberg, J. Siegel, A.M. Manotti Lanfredi, A Tiripicchio and M. Tiripicchio-Camellini, Inorg Chem., 20 (1981) 4306.

8 M. Catti, G. Gervasio and S.A. Mason, J. Chem. Soc., Dalton Trans., (1977) 2260.

9 L.W. Bateman, M. Green, J.A.K. Howard, K.A. Mead, R.M. Mills, I.D. Salter, F.G A. Stone and P Woodward, J. Chem. Soc., Chem. Commun., (1982) 773; L.W. Bateman, M. Green, K.A. Mead, R M Mills, I.D. Salter, F.G.A. Stone and P. Woodward, J. Chem. Soc., Dalton Trans., (1983) 2599.

10 M.I. Bruce, B.K. Nicholson and O. bin Shawkataly, paper in preparation.

11 C.J. Cooksey, A.J. Deeming and I.P. Rothwell, J. Chem. Soc., Dalton Trans., (1981) 1718.

12 J.W. Lauher and K. Wald, J. Am Chem. Soc., 103 (1981) 7648.

13 M.I. Bruce and A.G. Swincer, Adv Organomet. Chem., 22 (1983) 59.

14 S. Aime, L. Milone and E. Sappa, Inorg. Chim. Acta, 13 (1975) 67.

15 A N Nesmeyanov, E.G. Perevalova, Yu.T. Struchkov, M.Yu. Antipin, K.I. Grandberg and V.P. Dyadchenko, J. Organomet. Chem, 201 (1980) 343.

16 Programmes used in this structure determination and refinement included: SUSCAD and ABSORB, Data reduction programs for the CAD4 diffractometer, University of Sydney, 1976; SHELX, Program for crystal structure determination, G.M. Sheldrick, University of Sydney, 1976; PLUTO, Program for plotting molecular structures, W.D.S. Motherwell, University of Cambridge, 1977.

17 International Tables for X-ray Crystallography, Vol. 4, pp. 99, 149, Kynoch Press, Birmingham, 1974.

18 M.I. Bruce, M.L. Williams, J.M. Patrick and A.H. White, J. Chem Soc, Dalton Trans., in press.

Addendum

In our discussion of the complex formed by hydrogenation of $\mathrm{Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9}$ (**1**), which was originally described as having the illustrated structure **4**, we inadvertently overlooked the paper by M. Castiglioni, G. Gervasio and E. Sappa (Inorg. Chim. Acta, 49 (1981) 217), which describes its X-ray characterisation as the alkylidene complex $\mathrm{Ru_3(\mu\text{-}H)_3(\mu_3\text{-}CCH_2Bu^t)(CO)_9}$. The auration and hydrogenation reactions are thus closely related, since the isolobal analogue of $\mathrm{Ru_3Au_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9(PPh_3)_2}$, namely $\mathrm{Ru_3(\mu\text{-}H)_2(\mu_3\text{-}C{=}CHBu^t)(CO)_9}$, can be considered to be a likely intermediate in the conversion of **1** to the alkylidene complex.