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XXXVIII *. REACTIONS BETWEEN $M(C_2R)(PR'_3)$ (M = Cu, Ag, Au; R = Ph, C_6F_5; R′ = Me, Ph) AND $H_2Os_3(CO)_{10}$: X-RAY STRUCTURES OF $Os_3Au(\mu$-CH=CHR)$(CO)_{10}(PPh_3)$ (R = Ph AND C_6F_5)

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Summary

The reactions of $Os_3(\mu\text{-}H)_2(CO)_{10}$ with a series of Group IB metal acetylide-tertiary phosphine complexes are described. Whereas the compounds $M(C_2C_6F_5)(PPh_3)$ (M = Cu, Ag, Au) afforded the complexes $MOs_3(\mu\text{-}CH{=}CHC_6F_5)(CO)_{10}(PPh_3)$ cleanly and in high yield, complex mixtures of products were obtained from reactions of the analogous phenylacetylides. The complexes $MOs_3(\mu\text{-}CH{=}CHPh)(CO)_{10}(PPh_3)$, $MOs_3(\mu\text{-}CH{=}CHPh)(CO)_9(PPh_3)_2$ and $MOs_3(\mu\text{-}H)(CO)_{10}(PPh_3)$ (of known structure), and $MOs_3(\mu\text{-}CH{=}CHPh)(CO)_9(PPh_3)_2$ and $HMOs_3(CH{=}CPh)(CO)_8$ (of unknown structure) were characterised; $Au(C_2Ph)(PMe_3)$ afforded similar derivatives. The reactions proceed by oxidative-addition and hydrogen migration steps; M–P bond cleavage reactions also occur to a small extent. The molecular structures of $AuOs_3(\mu\text{-}CH{=}CHC_6R_5)(CO)_{10}(PPh_3)$ (R = F or H) were determined by X-ray analyses. For R = F, crystals are triclinic, space group $P\bar{1}$, with a 9.081(2), b 13.291(2), c 17.419(2) Å, α 84.49(1), β 76.20(2), γ 75.81(2)° and $Z = 2$; 4622 observed data $[I > 2.5\sigma(I)]$ were refined to $R = 0.027$, $R_w = 0.031$. For R = H, crystals are triclinic, space group $P\bar{1}$, with a 9.403(4), b 13.448(3), c 13.774(4) Å, α 83.34(2), β 88.66(3), γ 70.21(3)°, and $Z = 2$; 4405 observed data $[I > 2.5\sigma(I)]$ were refined to $R = 0.030$, $R_w = 0.033$. The two molecules differ in the orientation of the Ph rings of the PPh_3 groups, but are otherwise similar to $Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CHBu^t)(CO)_{10}$ with the μ-H ligand replaced by the isolobal $\mu\text{-}Au(PPh_3)$ group.

Introduction

The synthesis of gold-containing heterometallic cluster compounds has benefitted from the introduction of new synthetic routes. Those which have been employed

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* For Part XXXVII, see ref. 26.

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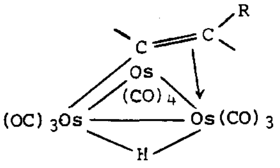
with a wide variety of substrated include (a) reactions of anionic metal cluster complexes with $AuCl(PR_3)$ (R = Et, Ph), often in the presence of thallium(I) [1], (b) elimination of methane in reactions of $AuMe(PPh_3)$ with hydrido-cluster complexes [2], (c) addition of up to three $Au(PPh_3)$ moieties by reactions of anionic complexes with $[\{Au(PPh_3)\}_3O]^+$ [3]. The first cluster complexes containing gold, however, were made by oxidative addition of $AuX(PPh_3)$ (X = halide, SCN, etc.) to $Os_3(CO)_{12}$ [4], and these reactions have recently been reinvestigated [5], and extended to the pentanuclear complex $Ru_5C(CO)_{15}$ [6].

Reactions between $Os_3(\mu\text{-}H)_2(CO)_{10}$ or $Os_3(CO)_{12}$ and 1-alkynes have given complexes containing μ-η^1,η^2-vinyl (**1**), μ_3-η^1,2η^2-alkynyl (**2**), μ_3-2η^1,η^2-alkyne (**3**) and μ_3-η^1,η^2-vinylidene (**4**) ligands [7]. These derivatives are related by thermal rearrangement, hydrogen-migration or -elimination reactions. In the particular case of HC_2Ph, the first-formed products are (**1**; R = Ph) and (**2**; R = Ph); the vinylidene complex (**4**; R = Ph) is formed by heating the former in refluxing octane [8]. Similar results were recently described for reactions of t-butylacetylene (3,3-dimethylbut-1-yne) [9].



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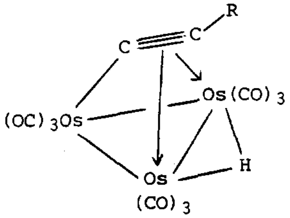

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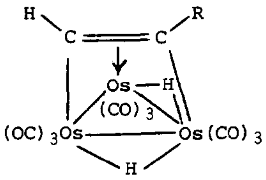

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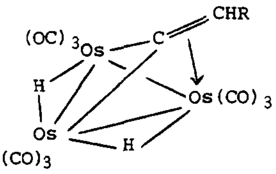

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This paper reports some results of a study of the reactions which occur between $M(C_2R)(PR'_3)$ (M = Au, Ag, Cu; R = Ph, C_6F_5; R′ = Me, Ph) and $Os_3(\mu\text{-}H)_2(CO)_{10}$, which might be expected to proceed by both oxidative addition of the $RC_2\text{-}M(PR'_3)$ complex, and addition of the cluster-bound hydrogen to the acetylide moiety. Oxidative addition of $Au(C_2Ph)(PPh_3)$ to $Os_3(CO)_{10}(NCMe)_2$ was reported to give a 28% yield of $AuOs_3(\mu_3\text{-}C_2Ph)(CO)_9(PPh_3)$ [10]. X-ray crystal structures of the two title complexes were determined during the course of this work, which offered a rare opportunity to compare chemically the behaviour of derivatives of the three Group IB metals.

Results

Reactions between $H_2Os_3(CO)_{10}$ and $M(C_2C_6F_5)(PPh_3)$

In toluene at −11°C, a rapid reaction occurs between $Os_3(\mu\text{-}H)_2(CO)_{10}$ and $Au(C_2C_6F_5)(PPh_3)$ to give $Os_3Au(\mu\text{-}CH{=}CHC_6F_5)(CO)_{10}(PPh_3)$ (**5**) in quantitative yield. This deep red complex was fully characterised by X-ray methods (see below), and its spectroscopic properties are consistent with the solid state structure. The ν(CO) spectrum is given in Table 1, and the NMR data in Table 2. A weak ν(C=C) absorption was found at 1618 cm^{-1}. There is no high-field ^1H resonance, but the appearance of two resonances at δ 8.63 and 5.57 ppm, assigned to the two protons on the C=C double bond, is characteristic; a 14 Hz coupling confirms the *trans* stereochemistry. The CO groups are not fluxional in **5**.

The structure of **5**, which is entirely analogous to other complexes of type **1** obtained from 1-alkynes and $Os_3(\mu\text{-}H)_2(CO)_{10}$, results from a formal *trans* addition of the two H atoms to the C≡C triple bond, and oxidative addition of the Au–C bond to the Os=Os bond in the hydrido complex. This is a familiar reaction pattern with $AuX(PR_3)$ complexes; we cannot say for certain which reaction occurs first, nor indeed, whether they are concerted.

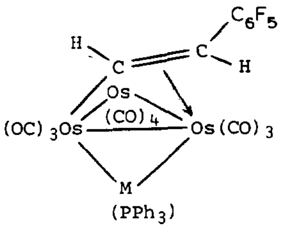
Analogous complexes **6** and **7** were obtained in 99 and 98% yield, respectively, from reactions between the corresponding silver or copper complexes and $H_2Os_3(CO)_{10}$, which were carried out in toluene below 0°C. The ν(CO) spectra of **6** and **7** were similar to that of **5**, but the ^{13}C NMR spectra revealed that the CO ligands in both complexes are fluxional at room temperature.

TABLE 1

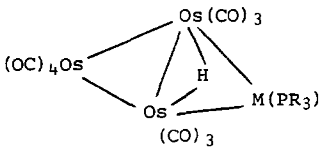
IR ν(CO) AND ν(CC) ABSORPTIONS (cm^{-1}) [a]

Complex	ν(CO)	ν(C=C)
5	2094s,2072m,2063m,2040vs,2037vs,2017vs,1992s,1987s,1971s, 1960s	1618w
6	2097w,2078s,2063vs,2033m,2013m,1998m,1979m,1958m	1602w
7	2099w,2076s,2063(sh),2055vs,2033vs,2018s,2033s,1985m, 1977m,1948vw	1608w
8	2095m,2050s,2047m,2015s,2001s,1981m	
9	2090m,2047s,2040m,2008s,1996m,1977m	
10	2092w,2052m,2046m,2012s,2000ms,1986m	
11	2094w,2052m,2047m,2015s,2001m,1986m	
12	2090m,2070m,2060s,2047s,2041vs,2020m,1999s,1989s,1963m	1610w
13	2087m,2068m,2058s,2045vs,2040vs,2017m,1998s,1985s, 1971(sh),1960m	1604w
14	2096w,2070m,2055s,2046vs,2037vs,2018s,2006s,1996(sh), 1979m,1961m	1615w
15	2100w,2071m,2059s,2048vs,2040vs,2020s,2005s,1996(sh), 1980m,1966(sh)	1621w
16	2092m,2073m,2065s,2050s,2047vs,2040s,2020m,1997s,1972m	1563w
17	2094m,2075m,2066s,2055m,2038s,2015s,1985vs,1945m	1604w
18	2094w,2072s,2066vs,2045vs,2040vs,2036s,1985s,1949m	1617w
19	2090w,2069vs,2049s,2041s,2037s,2017vs,1988(sh),1955(sh)	1681w
20	2091m,2077m,2063vs,2046s,2037m,2018s,2009s,1892m	1607m
21	2095m,2073s,2069vs,2044vs,2017vs,1999s,1983s,1943m	1561w
22	2084w,2072s,2066vs,2045vs,2018vs,2001s,1985s,1949m	1592w
24	2116w,2070vs,2054w,2037s,2023m,2015m,1800m	1513m
25	2120w,2075vs,2058m,2040s,2025m,2019m,1825m	1540m
26	2121w,2077vs,2060m,2043s,2029m,2021m,1817m	1542m

[a] Cyclohexane solution.



(5) M = Au
(6) M = Ag
(7) M = Cu



	M	R
(8)	Au	Me
(9)	Au	Ph
(10)	Ag	Ph
(11)	Cu	Ph

Reactions between $H_2Os_3(CO)_{10}$ and $M(C_2Ph)(PR_3)$

The reactions of Group IB phenylacetylide complexes containing tertiary phosphine ligands are not as specific as those of $M(C_2C_6F_5)(PPh_3)$ (M = Cu, Ag or Au). As described in detail in the Experimental section, complexes of the following types were isolated: $HOs_3M(CO)_{10}(PR_3)$, $Os_3M(\mu\text{-}CH{=}CHPh)(CO)_{10}(PR_3)$, $Os_3M(\mu\text{-}CH{=}CHPh)(CO)_9(PR_3)$, $HOs_3M(\mu_3\text{-}HCCPh)(CO)_8$ and $Os_3M(\eta\text{-}CH{=}CHPh)(CO)_9(PR_3)_2$ (M = Cu, Ag or Au; R = Me or Ph; but not all combinations). It is

TABLE 2

^{1}H NMR CHEMICAL SHIFTS (δ,ppm) AND COUPLING CONSTANTS (Hz)

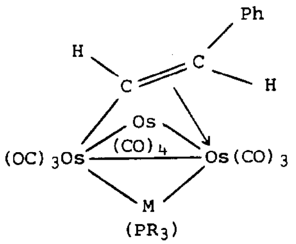
Complex	C*H*CHR	CHC*H*R	Ph	Other	Solvent [a]
5	5.57d(14)	8.63d(14)	7.51m		A
6	5.51d(14.2)	8.42d(14.5)	7.35m		A
7	5.41d(14.7)	8.41d(15.5)	6.87m,7.26m		A
8			7.58s	P*Me* 1.71d(12) Os*H* −15.3s	B
9			7.52m	Os*H* −22.1s	B
10			7.50m	Os*H* −14.6s	C
11			7.59m	Os*H* −13.4s	B
12	5.11d(13)	[b]	7.55m	P*Me* 8.31d(12)	A
13	5.27d(14)	[b]	7.61m		A
14	5.38d(14)	7.91d(14)	7.48m		A
15	4.30d(9)	8.19d(10)	7.25m		A
16	5.09d(14)	7.99d(14)	7.59m	P*Me* 1.75d(12)	B
17	5.26d(14)	8.16d(14)	7.44m		A
18	5.09d(14)	8.35d(14)	7.55m		B
19	5.01d(14)	8.20d(14)	7.54m		B
20	4.98s		7.48m	P*Me* 8.26d(12) Os*H* −17.6s	A
21	5.24d(14)	8.12d(14)	7.43m		A
22	5.09d(14)	7.98d(14)	7.55m		A
24	5.10s		7.58m	Os*H* −21.6s	A
25	4.88s		7.54m	Os*H* −19.8s	A
26	4.69s		7.49m	Os*H* −17.3s	B

[a] Solvents: A, $(CD_3)_2CO$; B, $CDCl_3$; C, CCl_4. [b] Under Ph resonance.

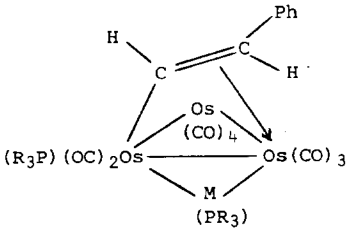
convenient to discuss each type of complex individually.

(a) $HOs_3M(CO)_{10}(PR_3)$ (M = Au, R = Me (8), Ph (9); M = Ag (10), Cu (11), R = Ph). These complexes were isolated in low yield, and were identified by their ν(CO) spectra, which are similar, and by comparison with that of $HOs_3Au(CO)_{10}(PPh_3)$ [5]. The ^1H NMR spectra all contain high-field resonances, and the mass spectrum of $HOs_3Au(CO)_{10}(PMe_3)$ (**9**) contains a molecular ion centred on m/z = 1124, and fragment ions corresponding to stepwise loss of the CO ligands at lower m/z values.

(b) $Os_3M(\mu\text{-}CH{=}CHPh)(CO)_{10}(PR_3)$ (M = Au, R = Me (12), Ph (13); M = Ag (14), Cu (15), R = Ph). These complexes are the major products formed in these reactions, and their ν(CO) spectra are closely similar to those of **5**–**7**. In addition, a weak ν(C=C) band was present in their IR spectra. The ^1H NMR spectra also contained resonances assigned to the CH=CH protons in a *trans* arrangement, as well as signals from the Ph protons (and Me, if present). A molecular ion centred on m/z = 1227 was found in the mass spectrum of $Os_3Au(\mu\text{-}CH{=}CHPh)(CO)_{10}(PMe_3)$ (**12**). Finally, the X-ray structure of $Os_3Au(\mu\text{-}CH{=}CHPh)(CO)_{10}(PPh_3)$ (**13**) (see below) confirmed the analogy with **5**.



	M	R
(12)	Au	Me
(13)	Au	Ph
(14)	Ag	Ph
(15)	Cu	Ph



	M	R
(16)	Au	Me
(17)	Au	Ph
(18)	Ag	Ph
(19)	Cu	Ph

(c) $Os_3M(\mu\text{-}CH{=}CHPh)(CO)_9(PR_3)_2$ (M = Au, R = Me (16), Ph (17); M = Ag (18), Cu (19), R = Ph). These complexes were obtained as minor products from these reactions, although they are apparently not formed if the reactions are carried out above 30°C. The ν(CO) bands in their IR spectra show a close correspondence (Table 1). In their ^1H NMR spectra (Table 2), the appropriate resonances show that addition of 2H to the C≡C triple bond has occurred to give a *trans*-CH=CH moiety. The mass spectrum of **16** contains a molecular ion cluster centred on m/z = 1275. The most likely structure for these compounds is analogous to those of complexes **12**–**15**, with a second tertiary phosphine ligand replacing one of the CO groups on osmium. We note that a previous study of replacement of CO by PR_3 in hydrocarbon complexes of ruthenium found that substitution occurred at the ruthenium bearing a σ-bonded (rather than π-bonded) organic ligand [11]. If this behaviour is emulated by our complexes, the second PR_3 ligand will be on one of the $M(PR_3)$-bridged osmiums; interconversion of the μ-η^1,η^2-vinyl ligand is reported to occur with $Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CH_2)(CO)_{10}$ [12]. As the only source of the second PR_3

ligand is the Au(PR_3) moiety, it follows that Au–P bond cleavage must occur to a limited extent during these reactions (but see below).

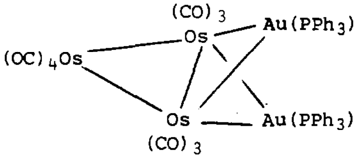
(d) $Os_3M(\mu\text{-}CH{=}CHPh)(CO)_9(PR_3)$ (M = Au, R = Me (20), Ph (21); M = Ag, R = Ph (22)). The identities of these compounds were established by comparison of their IR ν(CO) spectra with that of $Os_3Au(\mu\text{-}CH{=}CHPh)(CO)_9(PMe_3)$, which gave a molecular ion centred on $m/z = 1199$, and fragment ions formed by loss of CO ligands. Their ^{1}H NMR spectra are consistent with the presence of a μ-CH=CHPh moiety (Table 2) but their formulation must include another 2e donor if the cluster electron count is precise. The absence of any detectable high-field resonance in their ^{1}H NMR spectra rules out their formulation as hydridoalkyne complexes of type **3** (with one μ-H ligand replaced by an M(PR_3) group) or as hydrido-*o*-styryl complexes formed by an intramolecular cyclometallation reaction. One possibility is that they are formally unsaturated 46e cluster complexes, stabilised by interaction of the aryl group in a manner similar to that found for $Ru_3(\mu\text{-}H)(\mu\text{-}PPh_2)(CO)_9$ [13]; unfortunately, no crystals suitable for X-ray study have been obtained.

$Os_3M(\mu\text{-}CH{=}CHPh)(CO)_9(PR_3)$

	M	R
(20)	Au	Me
(21)	Au	Ph
(22)	Ag	Ph

$HOs_3M(CH{=}CPh)(CO)_8$

	M
(24)	Au
(25)	Ag
(26)	Cu



(23)

(e) $Os_3Au_2(CO)_{10}(PPh_3)_2$ (23). This complex was obtained, together with complexes **9**, **13**, **17**, **20** and **24**, from a single reaction between $Os_3(\mu\text{-}H)_2(CO)_{10}$ and $Au(C_2Ph)(PPh_3)$ carried out in refluxing benzene. It was identified by analysis and a comparison of its ν(CO) spectrum with that reported by Johnson, Lewis and their coworkers [14].

(f) $HOs_3M(\mu\text{-}CH{=}CPh)(CO)_8$ (M = Au (24), Ag (25), Cu (26)). These unusual complexes do not contain a teriary phosphine ligand, so that cleavage of the Group IB element–P bond has occurred, as mentioned in (c) above. The presence of the Group IB element in these minor products has not been unambiguously established, and the formulation is based on the close similarity of their ν(CO) and ν(C=C) bands and of their ^{1}H NMR spectra, together with microanalytical data which change appropriately along the series M = Au, Ag, Cu. In their ^{1}H NMR spectra, the single resonance between δ 4.5–5.5 ppm is assigned to a C*H* proton, the chemical shift being similar to those found for other μ_3-η^2-alkynes. A band between 1800 and 1825 cm^{-1} suggests the presence of at least one μ-CO ligand, while the high energy ν(CO) absorption at 2120 cm^{-1} may indicate some Group IB metal–CO interaction.

Crystal structures of $Os_3Au(\mu\text{-}CH{=}CHC_6X_5)(CO)_{10}(PPh_3)$ (X = H or F)

The molecular structures of complexes **5** and **13** are essentially identical, differing only in the orientation of the phenyl rings of the PPh_3 ligands. Crystals contain

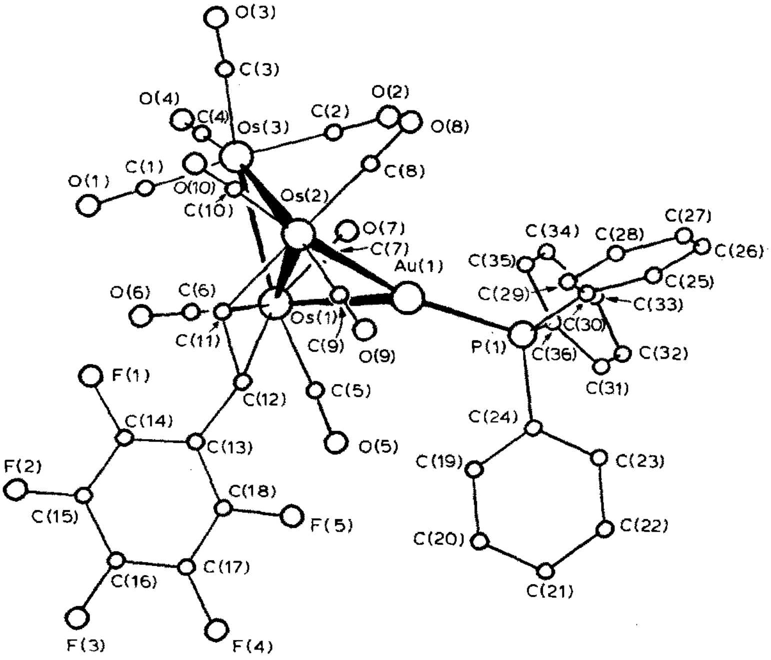


Fig. 1. PLUTO-plot of one molecule of $AuOs_3(\mu\text{-}CH{=}CHC_6F_5)(CO)_{10}(PPh_3)$ (**5**), showing atom-numbering scheme.

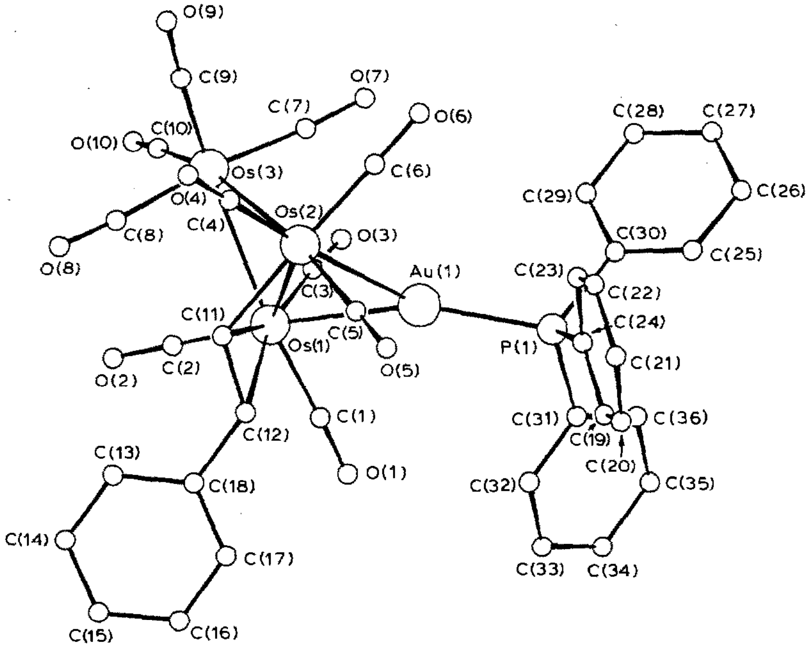


Fig. 2. PLUTO-plot of one molecule of $AuOs_3(\mu\text{-}CH{=}CHPh)(CO)_{10}(PPh_3)$ (**13**), showing atom-numbering scheme.

discrete molecules of the complex, with no intermolecular contacts less than the sum of Van der Waals radii. Plots of the molecular structures are given in Fig. 1 (X = F) and 2 (X = H). Some details of the heavy atom cores are given in Table 3.

The Au(PPh_3) group bridges one edge of the Os_3 triangle, the four metal atoms forming a 'butterfly' arrangement similar to those found in several related complexes. The μ-η^1,η^2-vinyl ligand, formed by transfer of the two cluster-bound H atoms from the precursor $Os_3(\mu\text{-}H)_2(CO)_{10}$ to the acetylide unit, bridges the other side of the Os–Os hinge of the Os_3Au core. The ten CO ligands are distributed three to each Os attached to Au and four to the unique Os atom.

The Os–Os bond lengths comprise a set of one short (2.854(1), 2.864(1) Å; values for **5** given first), one medium (2.894(1), 2.882(1) Å), and one longer bond (2.922(1), 2.924(1) Å). The short bonds are somewhat shorter than the average values found in $Os_3(CO)_{12}$ (2.877(3) Å [15]) but considerably longer than the similar bond in $Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CHBu^t)(CO)_{10}$ (2.814(2) Å [9]). The longest bonds are from the $Os(CO)_4$ group to the Os bearing the π-vinyl group, while the intermediate Os–Os separation is that bridged by the Au(PPh_3) and vinyl carbon C(11). The average Os–Os separation is the same for both complexes. Comparison with the μ-hydrido derivatives in Table 3 shows that the presence of the Au(PPh_3) group results in a lengthening of the average Os–Os separations by some 0.03–0.045 Å; this enlarging effect on replacing μ-H by the isolobal μ-Au(PR_3) group has been observed previously, e.g. in $Ru_3(\mu\text{-}X)(\mu\text{-}COMe)(CO)_{10}$ (average Ru–Ru separations 2.811 Å (X = H) [16], 2.854 Å (X = Au(PPh_3)) [17]).

The Au–Os separations differ, the shorter being that to Os(1) with the π-vinyl ligand (2.766(1), 2.738(1) Å, for (**5**) and (**13**), respectively). The range (2.738(1)–2.795(1) Å) is similar to values found for other gold-osmium complexes. The observed variations, together with the dihedral angles found for the Os_3/Os_2Au planes (126.9 and 125.8°), further demonstrate the tendency of the Au(PPh_3) group to accommodate differences in crystal packing requirements by a bending of the metal skeleton [18,19].

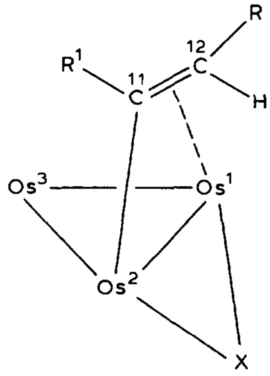
Coordination of the vinyl ligands to Os(1) and Os(2) in (**5**) and (**13**) is essentially identical within experimental error, with an Os(1)–C(11) σ-bond of 2.13, 2.11 Å, and unequal bonds to Os(1) (Os(1)–C(11) 2.276(6), 2.25(1); Os(1)–C(12) 2.40(1), 2.45(1) Å). Within the vinyl ligands, the C(11)–C(12) separations are identical within experimental error. The orientations of the C_6F_5 and Ph groups with respect to the C(11)–C(12) vectors are also similar (angles between C(11)C(12)C(13) (or C(18)) and C(14)C(13)C(18) (or C(13)C(18)C(17)) planes are 11.8 and 11.7°, respectively). The only difference is found in the C(12)–C(13) (or C(12)–C(18)) distances, which are 1.488(12) and 1.516(17) Å, respectively. These parameters are similar to those found in other structurally characterised μ-η^1,η^2-vinyl complexes, such as $Os_3(\mu\text{-}H)(\mu\text{-}CH{=}CHBu^t)(CO)_9$ [9] or $Os_3(\mu\text{-}H)(\mu\text{-}CPh{=}CHPh)(CO)_9$ [20] (Table 3).

Discussion

The major product obtained from reactions between $H_2Os_3(CO)_{10}$ and $M(C_2Ph)(PR_3)$ (M = Cu, Ag, Au; R = Me, Ph) is, in each case, the μ-η^1,η^2-vinyl complex exemplified by **5** and **13**, which were structurally characterised. These complexes are analogous to the hydrido complexes $HOs_3(\mu\text{-}CH{=}CHR)(CO)_{10}$ formed from $Os_3(\mu\text{-}H)_2(CO)_{10}$ and 1-alkynes, and the isolobal relationship between

TABLE 3

SELECTED BOND DISTANCES (Å) AND ANGLES (deg) IN SOME $Os_3(\mu$-vinyl) COMPLEXES



Bond	X =	$Au(PPh_3)$	$Au(PPh_3)$	H [a]	H [b]
or angle	R =	C_6F_5	Ph	Bu^t	Ph
	R′ =	H	H	H	Ph
Os(1)–Os(2)		2.894(1)	2.882(1)	2.814(2)	2.821(3)
Os(1)–Os(3)		2.922(1)	2.924(1)	2.876(3)	2.884(3)
Os(2)–Os(3)		2.854(1)	2.864(1)	2.841(2)	2.877(3)
Os(1)–Au(1)		2.766(1)	2.738(1)		
Os(2)–Au(1)		2.777(1)	2.795(1)		
Au(1)–P(1)		2.315(2)	2.307(4)		
Os(1)–C(11)		2.276(6)	2.251(14)	2.27(2)	2.28(4)
Os(1)–C(12)		2.403(7)	2.448(16)	2.43(2)	2.45(4)
Os(2)–C(11)		2.133(8)	2.107(15)	2.10(2)	2.15(4)
C(11)–C(12)		1.396(10)	1.393(24)	1.38(4)	1.36(5)
C(12)–C(R)		1.488(12)	1.516(17)		
Os(1)–C(11)–C(12)		120.3(6)	123.3(10)	124(2)	128(3)
C(11)–C(12)–C(R)		127.2(7)	127.5(12)	122(2)	130(3)

[a] Ref. 19. [b] Average values for two independent molecules; ref. 14.

H and the $M(PPh_3)$ moiety, particularly well-studied for M = Au, underlines this similarity. Their formation is best interpreted in terms of an initial oxidative-addition of RC_2–$M(PPh_3)$ across the Os=Os double bond in $Os_3(\mu\text{-}H)_2(CO)_{10}$, followed by migration of the cluster hydride ligands to the μ-C_2R group.

It is interesting to find clean reactions occurring between the pentafluorophenyl derivatives and $Os_3(\mu\text{-}H)_2(CO)_{10}$, which proceed quantitatively. This may be related to the molecular structures of these Group IB derivatives, which for M = Au we have recently shown to be monomeric, without any of the extended interactions found in other Group IB acetylide complexes which have been studied [21]. The reactions of the phenylacetylide complexes are more complex, up to five different complexes being characterised, including examples containing two PR_3 ligands per Group IB atom (16–19), and others containing no PR_3 ligands. Although the solid state structures of $M(C_2Ph)(PPh_3)$ (M = Cu, Ag, Au) have not yet been described, related complexes are known to adopt oligomeric or polymeric $\{[M(PR'_3)_3][M(C_2R_2)]\}_n$ zwitter-ionic structures [22], and it is easy to envisage formation of the PR_3-rich or -poor complexes by reaction with the cationic or anionic components, respectively.

The results described in this paper show that complexes formed by the three

Group IB metal derivatives in reactions with $Os_3(\mu\text{-}H)_2(CO)_{10}$ are very similar, and although structural studies were only performed on the Au–Os complexes, the close similarities in the spectra of the silver and copper analogous allow us to assign their structures with confidence.

Experimental

All reactions were carried out in oven-dried glassware under an atmosphere of nitrogen although subsequent work-up was carried out with no special precautions to exclude air. Reagent-grade solvents were dried and distilled before use. IR spectra were obtained with a Perkin–Elmer 683 double-grating spectrometer; ^1H and ^{13}C NMR spectra were recorded on a Bruker WP80 instrument; mass spectra were obtained with an AEI/GEC MS3074 spectrometer. Microanalyses were by the Canadian Microanalytical Service, Vancouver.

The Group IB-acetylide complexes were obtained as described previously [21]; $Os_3(\mu\text{-}H)_2(CO)_{10}$ was made by the literature procedure [23]. Melting points, microanalytical data and molecular weights are collected in Table 4, while selected IR and ^1H NMR data appear in Tables 1 and 2, respectively.

Reactions between $H_2Os_3(CO)_{10}$ and $M(C_2C_6F_5)(PPh_3)$

(a) $Au(C_2C_6F_5)(PPh_3)$. A mixture of $H_2Os_3(CO)_{10}$ (500 mg, 0.59 mmol) and $Au(C_2C_6F_5)(PPh_3)$ (380 mg, 0.58 mmol) in toluene (10 ml) was stirred for 15 min at −11°C. The solvent was removed in vacuo, and recrystallisation of the residue (toluene/n-octane) gave an initial crop of red-crystals (755 mg). Addition of n-hexane to the mother liquor afforded a further 123 mg of red $AuOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHC_6F_5)(CO)_{10}(PPh_3)$ (**5**) (total yield, 878 mg, 98%).

(b) $Ag(C_2C_6F_5)(PPh_3)$. A mixture of $H_2Os_3(CO)_{10}$ (50 mg, 0.06 mmol) and $Ag(C_2C_6F_5)(PPh_3)$ (33 mg, 0.06 mmol) in toluene (30 ml) was stirred for 45 min at 0°C. The solvent was then removed in vacuo, and the residue recrystallised from toluene/n-octane. Two subsequent crystallisations gave red crystalline $AgOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHC_6F_5)(CO)_{10}(PPh_3)$ (**6**) (83 mg, 99%).

(c) $Cu(C_2C_6F_5)(PPh_3)$. A mixture of $H_2Os_3(CO)_{10}$ (50 mg, 0.06 mmol) and $Cu(C_2C_6F_5)(PPh_3)$ (30 mg, 0.06 mmol) in toluene (30 ml) was stirred for 2 h at −23°C. The solvent was then removed in vacuo, and the residue recrystallised from toluene/n-octane to give $CuOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHC_6F_5)(CO)_{10}(PPh_3)$ (**7**) (80 mg, 98%).

Reactions between $H_2Os_3(CO)_{10}$ and $Au(C_2Ph)(PPh_3)$

(a) A mixture of $H_2Os_3(CO)_{10}$ (203 mg, 0.24 mmol) and $Au(C_2Ph)(PPh_3)$ (133 mg, 0.24 mmol) in toluene (50 ml) was stirred at −18°C for 30 min. The solvent was then removed in vacuo. Preparative TLC (15% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent) gave the following bands:

(i) green $HAuOs_3(CO)_{10}(PPh_3)$ (**9**) (28 mg, 9%), R_f 0.61. Recrystallised from benzene/n-pentane as its benzene solvate.

(ii) red $AuOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_{10}(PPh_3)$ (**13**) (118 mg, 35%), R_f 0.56. Recrystallised from toluene/n-octane.

(iii) yellow-brown $AuOs_3(CO)_9(PPh_3)(CH{=}CHPh)$ (**21**) (23 mg, 7%), R_f 0.52. Recrystallised from toluene/n-octane.

(iv) yellow $HAuOs_3(CO)_8(CHCPh)$ (**24**) (13 mg, 5%), R_f 0.49. Recrystallised from acetone/n-pentane.

(v) yellow, R_f 0.75 (uncharacterised). Infrared (C_6H_{12}): ν(CO) 2106m, 2086s, 2078vs, 2069m, 2052vs, 2022m, 2009m, 2000m, 1985w cm^{-1}.

(vi) yellow, R_f 0.68 (uncharacterised). Infrared (C_6H_{12}): ν(CO) 2108m, 2080vs, 2056vs, 2034s, 2014s, 1987m, 1967w cm^{-1}.

TABLE 4

ANALYTICAL DATA

Complex (Formula)	M.p. (°C)	Analysis (Found (calcd.) (%))			
		C	H	Other	M [a]
5		28.67	0.90	(F) 5.44(6.32)	1489(A)
$C_{36}H_{17}AuF_5O_{10}Os_3P$		(28.77)	(1.14)	(P) 2.83(2.06)	(1502)
6		29.80	1.49		1410(A)
$C_{36}H_{17}AgF_5O_{10}Os_3P$		(30.58)	(1.21)		(1413)
7		31.64	0.68		1369(B)
$C_{36}H_{17}CuF_5O_{10}Os_3P$		(31.57)	(1.25)		(1369)
8 C_6H_6		18.54	1.87		1124(MS)
$C_{13}H_{10}AuO_{10}Os_3P.C_6H_6$		(18.97)	(1.34)		(1124)
9 C_6H_6	169–172	29.33	1.12		
$C_{28}H_{16}AuO_{10}Os_3P.C_6H_6$		(29.40)	(1.59)		
10		28.44	1.17		
$C_{28}H_{16}AgO_{10}Os_3P$		(27.51)	(1.40)		
11		27.67	1.54		1204(A)
$C_{28}H_{16}CuO_{10}Os_3P$		(28.51)	(1.54)		(1177)
12	59–62	19.83	1.63		1227(MS)
$C_{21}H_{16}AuO_{10}Os_3P$		(20.56)	(1.31)		(1227)
13	66–69	30.55	1.38	(P) 2.37(2.19)	1425(A)
$C_{36}H_{22}AuO_{10}Os_3P$		(30.58)	(1.57)		(1412)
14	104(dec)	33.72	2.07		
$C_{36}H_{22}AgO_{10}Os_3P$		(32.66)	(1.67)		
15	96–99	33.00	1.47		1296(A)
$C_{36}H_{22}CuO_{10}Os_3P$		(33.79)	(1.73)		(1279)
16		21.93	2.14		1275(MS)
$C_{23}H_{25}AuO_9Os_3P_2$		(21.67)	(1.97)		(1275)
17 C_6H_6	130(dec)	41.17	2.22		1629(B)
$C_{53}H_{37}AuO_9Os_3P_2.C_6H_6$		(41.08)	(2.51)		(1646)
18	251–255	39.65	2.39		1563(A)
$C_{53}H_{37}AgO_9Os_3P_2$		(40.85)	(2.71)		(1557)
19		42.13	2.86		1521(A)
$C_{53}H_{37}CuO_9Os_3P_2$		(42.02)	(2.53)		(1513)
20		19.46	1.95		1199(MS)
$C_{20}H_{16}AuO_9Os_3P$		(20.04)	(1.34)		(1199)
21	130(dec)	30.15	1.50		1369(A)
$C_{35}H_{22}AuO_9Os_3P$		(30.35)	(1.60)		(1384)
22 C_6H_6	262(dec)	35.71	1.71		
$C_{35}H_{22}AgO_9Os_3P.C_6H_6$		(35.84)	(2.05)		
23		30.81	1.55		1812(A)
$C_{46}H_{30}Au_2O_{10}Os_3P_2$		(31.23)	(1.71)		(1768)
24	186(dec)	17.85	0.92	(O)11.55(11.69)	1125(A)
$C_{16}H_7AuO_8Os_3$		(17.55)	(0.64)		(1094)
25 C_6H_6	122(dec)	24.34	1.18		
$C_{16}H_7AgO_8Os_3.C_6H_6$		(24.38)	(1.18)		
26		19.50	0.56		1003(A)
$C_{16}H_7CuO_8Os_3$		(19.99)	(0.73)		(961)

[a] Method: (A) osmometry (acetone); (B) osmometry (benzene); (MS) mass spectrometry.

(vii) light red, R_f 0.36 (uncharacterised). Infrared (C_6H_{12}): ν(CO) 2069s, 2057m, 2045s, 2018vs, 2002(sh), 1999s, 1982m, 1963s, 1955w, 1721m cm^{-1}.

(b) A mixture of $H_2Os_3(CO)_{10}$ (102 mg, 0.12 mmol) and $Au(C_2Ph)(PPh_3)$ (65 mg, 0.12 mmol) in benzene (50 ml) was heated at reflux point for 18 h. The solvent was removed in vacuo, and preparative TLC (15% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent) separated the following products:
(i) green $HAuOs_3(CO)_{10}(PPh_3)$ (**9**) (3 mg, 2%), R_f 0.61.
(ii) red $AuOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_{10}(PPh_3)$ (**13**) (61 mg, 36%), R_f 0.56.
(iii) yellow-brown $AuOs_3(CO)_9(PPh_3)(CH{=}CHPh)$ (**20**) (5 mg, 3%), R_f 0.52.
(iv) yellow $HAuOs_3(CO)_8(CHCPh)$ (**24**) (17 mg, 13%), R_f 0.49.
(v) purple $AuOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_9(PPh_3)_2$ (**17**) (12 mg, 6%), R_f 0.40. Recrystallised from benzene/n-hexane as its benzene solvate.
(vi) red-black $Au_2Os_3(CO)_{10}(PPh_3)_2$ (**23**) (6 mg, 3%), R_f 0.18. Recrystallised from CH_2Cl_2/n-hexane. IR ν(CO) (cyclohexane): 2067m, 2055(sh), 2015vs, 1988(sh), 1979s, 1967m, 1943w cm^{-1} (lit. [13] ν(CO) ($CHCl_3$): 2067w, 2012s, 1977m, 1965w, 1937m cm^{-1}). ^1H NMR δ [$(CD_3)_2CO$]: 7.71m ppm, Ph. Found: C, 30.81; H, 1.55, *M* (acetone) 1812; $C_{46}H_{30}Au_2Os_3O_{10}P_2$ calcd.: C, 31.23; H, 1.71%; *M* 1769.
(vii) five other products were obtained in trace quantities only.

Reaction between $H_2Os_3(CO)_{10}$ and $Au(C_2Ph)(PMe_3)$

A mixture of $H_2Os_3(CO)_{10}$ (200 mg, 0.23 mmol) and $Au(C_2Ph)(PMe_3)$ (176 mg, 0.47 mmol) in benzene (20 ml) was stirred at room temperature for 16 h. The solvent was then removed in vacuo, and preparative TLC (45% diethyl ether/cyclohexane developer, Kieselgel H adsorbent) separated the following complexes:
(i) green $HAuOs_3(CO)_{10}(PMe_3)$ (**8**) (11 mg, 4%), R_f 0.89. Recrystallised from benzene/n-octane as its benzene solvate.
(ii) red $AuOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_{10}(PMe_3)$, (**12**) (78 mg, 27%) R_f 0.73. Recrystallised from dichloromethane/cyclohexane.
(iii) yellow $HAuOs_3(CO)_9(PMe_3)(CHCPh)$ (**20**) (8 mg, 3%), R_f 0.66.
(iv) deep crimson $AuOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_9(PMe_3)_2$ (**16**) (18 mg, 6%), R_f 0.39. Recrystallised from benzene/n-heptane.

Reaction between $H_2Os_3(CO)_{10}$ and $Ag(C_2Ph)(PPh_3)$

(a) A mixture of $H_2Os_3(CO)_{10}$ (210 mg, 0.25 mmol) and $Ag(C_2Ph)(PPh_3)$ (120 mg, 0.25 mmol) in toluene (50 ml) was stirred for 2.5 h at −20°C. The solvent was then removed in vacuo, and preparative TLC (15% diethyl ether/cyclohexane developer, Kieselgel H adsorbent, conducted under nitrogen) separated four complexes:
(i) red $HAgOs_3(CO)_{10}(PPh_3)$ (**10**) (21 mg, 7%), R_f 0.76. Complex **10** is light-sensitive and must be isolated with minimal exposure to light.
(ii) red $AgOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_{10}(PPh_3)$ (**14**) (170 mg, 52%), R_f 0.60. Recrystallised from benzene/n-hexane. Complex **14** decomposes slowly in light, but can be stored indefinitely in the dark under nitrogen.
(iii) orange $HAgOs_3(CO)_8(CHCPh)$ (**25**) (15 mg, 6%), R_f 0.51. Recrystallised from benzene/n-hexane as its benzene solvate.
(iv) dark orange $AgOs_3(CO)_9(PPh_3)(CH{=}CHPh)$ (**22**) (22 mg, 7%), R_f 0.47.

(b) A mixture of $H_2Os_3(CO)_{10}$ (150 mg, 0.18 mmol) and $Ag(C_2Ph)(PPh_3)$ (90 mg, 0.19 mmol) in benzene (35 ml) was stirred at room temperature for 15 min. The solvent was then removed in vacuo, and preparative TLC (15% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent, under nitrogen) separated 12 brightly coloured bands:

(i) red $HAgOs_3(CO)_{10}(PPh_3)$ (**10**) (9 mg, 4%), R_f 0.76.

(ii) red $AgOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_{10}(PPh_3)$ (**14**) (98 mg, 42%), R_f 0.61.

(iii) orange $HAgOs_3(CO)_8(CHCPh)$ (**25**) (16 mg, 9%), R_f 0.51.

(iv) orange $AgOs_3(CO)_9(PPh_3)(CHCHPh)$ (**22**) (9 mg, 4%), R_f 0.47.

(v) crimson $AgOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_9(PPh_3)_2$ (**18**) (16 mg, 6%), R_f 0.30. Recrystallised from CH_2Cl_2/benzene/n-heptane.

(vi) seven other products were observed, but remain uncharacterised.

Reaction between $H_2Os_3(CO)_{10}$ and $Cu(C_2Ph)(PPh_3)$

(a) A mixture of $H_2Os_3(CO)_{10}$ (100 mg, 0.12 mmol) and $Cu(C_2Ph)(PPh_3)$ (42 mg, 0.10 mmol) in toluene (60 ml) was stirred for 3.5 h at −30°C. The solvent was removed in vacuo, and preparative TLC (25% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent) isolated two products:

(i) yellow $HCuOs_3(CO)_{10}(PPh_3)$ (**11**) (18 mg, 13%), R_f 0.56. Recrystallised from diethyl ether/cyclohexane.

(ii) yellow $CuOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_{10}(PPh_3)$ (**15**) (104 mg, 69%), R_f 0.51. Recrystallised from toluene/n-octane.

(b) A mixture of $H_2Os_3(CO)_{10}$ (100 mg, 0.12 mmol) and $Cu(C_2Ph)(PPh_3)$ (50 mg, 0.12 mmol) in benzene (40 ml) was stirred for 19 h at room temperature. The solvent was removed in vacuo, and preparative TLC (25% diethyl ether/cyclohexane developer, Kieselgel GF_{254} adsorbent) separated eight products:

(i) yellow $HCuOs_3(CO)_{10}(PPh_3)$ (**11**) (4 mg, 3%), R_f 0.56.

(ii) yellow $CuOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_{10}(PPh_3)$ (**15**) (62 mg, 41%), R_f 0.51.

(iii) yellow $HCuOs_3(CO)_8(CHCPh)$ (**26**) (9 mg, 8%), R_f 0.42. Recrystallised from benzene/n-heptane.

(iv) orange-red $CuOs_3(\mu\text{-}\eta^2\text{-}CH{=}CHPh)(CO)_9(PPh_3)_2$ (**19**) (5 mg, 3%), R_f 0.23. Recrystallised from diethyl ether/n-pentane.

(v) four other products were observed, but remain uncharacterised.

Crystal structures of 5 and 13

In the account that follows, values for complex **13** are enclosed in square brackets after the corresponding values for **5**.

A crystal of dimensions 0.08 × 0.69 × 0.81 mm [0.06 × 0.13 × 0.84 mm] was mounted on a glass fibre and coated with cyanoacrylate super-glue. Lattic parameters were determined by a least-squares fit to the setting angles of 25 independent reflections, measured and refined from scans performed on an Enraf–Nonius CAD4 four-circle diffractometer employing graphite-monochromated Mo-K_α radiation.

Crystal data. **5**: $C_{36}H_{18}AuF_5O_{10}Os_3P$, mol. wt. 1504.1; triclinic, space group $P\bar{1}$, a 9.081(2), b 13.291(2), c 17.419(2) Å, α 84.49(1), β 76.20(2), γ 75.81(2)°; U 1977.8 Å^3; $Z = 2$, D_c 2.52 g cm^{-3}; $F(000)$ 1362 electrons; λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 134.0 cm^{-1}.

13: $C_{36}H_{23}AuO_{10}Os_3P$, mol. wt. 1254.1; triclinic, space group $P\bar{1}$; a 9.403(4), b 13.448(3), c 13.774(4) Å, α 83.34(2), β 88.66(3), γ 70.21(3)°; U 1863.9Å^3, $Z = 2$, D_c 2.23 g cm^{-1}; $F(000)$ 1280 electrons; λ(Mo-K_α) 0.7107 Å, μ(Mo-K_α) 141.9 cm^{-1}.

Intensity data were collected in the range $1.5 < \theta < 23°$ [$1.2 < \theta < 20°$] using an

(Continued on p. 286)

TABLE 5. POSITIONAL PARAMETERS FOR NON-HYDROGEN ATOMS IN $AuOs_3(\mu\text{-}CHCH\text{-}C_6F_5)(CO)_{10}(PPh_3)$ (5) (Au,Os × 10^5; other atoms × 10^4)

Atom	*x*	*y*	*z*
Au(1)	3624(4)	39150(2)	25967(2)
Os(1)	−8806(3)	22417(2)	24963(2)
Os(2)	24436(3)	20931(2)	20385(2)
Os(3)	12917(4)	6599(2)	32186(2)
P(1)	−246(2)	5650(1)	2894(1)
F(1)	−765(6)	462(3)	783(3)
F(2)	−2674(6)	356(4)	−131(3)
F(3)	−4219(7)	2099(5)	−792(4)
F(4)	−3733(8)	3977(5)	−564(4)
F(5)	−1727(6)	4102(4)	313(3)
O(1)	1437(9)	−823(5)	1927(4)
O(2)	1230(9)	2278(6)	4383(4)
O(3)	4396(10)	−588(6)	3531(7)
O(4)	−1006(11)	−382(8)	4401(5)
O(5)	−3467(8)	4036(6)	2139(5)
O(6)	−2719(8)	575(5)	2550(4)
O(7)	−2247(8)	2551(7)	4257(4)
O(8)	4311(8)	2685(7)	3114(4)
O(9)	3375(9)	3695(6)	763(4)
O(10)	5075(8)	295(6)	1372(4)
C(1)	1364(10)	−244(7)	2408(5)
C(2)	1260(10)	1702(7)	3945(5)
C(3)	3240(12)	−113(8)	3423(6)
C(4)	−156(12)	4(8)	3966(6)
C(5)	−2427(10)	3384(7)	2250(5)
C(6)	−2021(9)	1202(7)	2518(5)
C(7)	−1677(11)	2426(7)	3604(5)
C(8)	3577(11)	2479(7)	2742(5)
C(9)	3005(10)	3100(7)	1241(5)
C(10)	4083(10)	964(7)	1638(5)
C(11)	967(8)	1685(5)	1393(4)
C(12)	−107(8)	2456(6)	1083(4)
C(13)	−1171(8)	2311(6)	593(4)
C(14)	−1451(9)	1361(6)	457(4)
C(15)	−2457(9)	1265(6)	−8(5)
C(16)	−3202(10)	2162(7)	−353(5)
C(17)	−2992(10)	3107(7)	−231(5)
C(18)	−1956(9)	3162(6)	223(5)
C(19)	−1525(7)	6050(3)	1573(3)
C(20)	−2150(7)	6671(3)	983(3)
C(21)	−2252(7)	7738(3)	940(3)
C(22)	−1729(7)	8185(3)	1486(3)
C(23)	−1103(7)	7564(3)	2076(3)
C(24)	−1001(7)	6496(3)	2120(3)
C(25)	1140(5)	6901(4)	3593(3)
C(26)	2382(5)	7326(4)	3627(3)
C(27)	3805(5)	7040(4)	3088(3)
C(28)	3986(5)	6329(4)	2514(3)
C(29)	2743(5)	5904(4)	2480(3)
C(30)	1320(5)	6191(4)	3019(3)
C(31)	−2824(7)	6830(4)	3931(3)
C(32)	−3938(7)	6970(4)	4642(3)
C(33)	−3944(7)	6174(4)	5225(3)
C(34)	−2836(7)	5236(4)	5097(3)
C(35)	−1722(7)	5096(4)	4386(3)
C(36)	−1716(7)	5892(4)	3803(3)

TABLE 6

POSITIONAL PARAMETERS FOR NON-HYDROGEN ATOMS IN AuOs$_3$(μ-CH=CHPh)(CO)$_{10}$(PPh$_3$) (13) [a]

Atom	*x*	*y*	*z*
Au(1)	4830(6)	13006(4)	73933(4)
Os(1)	−473(6)	33862(4)	67792(4)
Os(2)	−20729(6)	28157(4)	79834(4)
Os(3)	−7883(7)	43660(5)	83661(4)
P(1)	1646(4)	−512(3)	7407(3)
O(1)	1373(14)	2256(9)	5238(9)
O(2)	−271(13)	5587(11)	5958(8)
O(3)	3101(14)	2796(10)	7541(9)
O(4)	−4962(15)	4208(11)	8737(8)
O(5)	−3484(16)	1296(11)	7319(10)
O(6)	−869(14)	1349(10)	9634(8)
O(7)	1601(15)	2450(12)	9323(9)
O(8)	−3415(16)	6129(11)	7381(10)
O(9)	−2373(16)	4965(12)	10013(9)
O(10)	1293(17)	5714(11)	8172(9)
C(1)	750(19)	2649(14)	5836(13)
C(2)	−183(18)	4759(17)	6270(10)
C(3)	1908(22)	3040(12)	7280(11)
C(4)	−3872(25)	3689(14)	8469(12)
C(5)	−2942(19)	1839(17)	7545(12)
C(6)	−1284(19)	1928(14)	9003(12)
C(7)	721(25)	3177(16)	8924(11)
C(8)	−2450(28)	5456(16)	7729(12)
C(9)	−1715(22)	4767(15)	9386(14)
C(10)	553(20)	5269(16)	8266(11)
C(11)	−2573(15)	3786(11)	6806(11)
C(12)	−2287(15)	3386(12)	6019(10)
C(13)	−3219(10)	5132(7)	5053(5)
C(14)	−3665(10)	5691(7)	4248(5)
C(15)	−3605(10)	5141(7)	3543(5)
C(16)	−3099(10)	4031(7)	3644(5)
C(17)	−2653(10)	3472(7)	4450(5)
C(18)	−2713(10)	4023(7)	5155(5)
C(19)	−243(11)	−1576(8)	6888(5)
C(20)	−1444(11)	−1962(8)	7015(5)
C(21)	−2189(11)	−1896(8)	7793(5)
C(22)	−1734(11)	−1443(8)	8443(5)
C(23)	−533(11)	−1058(8)	8315(5)
C(24)	212(11)	−1124(8)	7538(5)
C(25)	3275(10)	−2290(7)	8506(6)
C(26)	4266(10)	−2817(7)	9187(6)
C(27)	4923(10)	−2254(7)	9646(6)
C(28)	4590(10)	−1163(7)	9424(6)
C(29)	3598(10)	−636(7)	8744(6)
C(30)	2941(10)	−1200(7)	8285(6)
C(31)	1938(8)	−307(6)	5651(6)
C(32)	2714(8)	−490(6)	4889(6)
C(33)	4187(8)	−1210(6)	4898(6)
C(34)	4883(8)	−1748(6)	5670(6)
C(35)	4107(8)	−1565(6)	6432(6)
C(36)	2634(8)	−845(6)	6423(6)

[a] Au, Os $\times 10^5$; other atoms $\times 10^4$.

ω-θ scan mode [for **13**, an ω-$n/3\theta$ scan mode, where $n(=2)$ was optimised by profile analysis of a typical reflection, was used]. The ω scan angle was $(1.05 + 0.35 \tan\theta)°$ and the horizontal counter aperture employed was $(2.40 + 0.50 \tan\theta)$ mm. Three standard reflections, monitored after every 60 min [58 min] of data collection, indicated that no decomposition occurred during data collection. Of a total of 5262 [5569] unique reflections collected, those 4622 [4405] with $I > 2.5\sigma(I)$ were considered observed and used in the structure refinements. Data reduction, including Lorentz and polarisation corrections, was performed using programme SUSCAD, and absorption corrections were applied using programme ABSORB [24].

Solution and refinement. The Os and Au atoms were located using the direct method routine of programme SHELX [24]. In the first difference Fourier calculations, all heavy metal atoms were modelled as Os, the Au atom then being identified by the associated P atom. All remaining non-hydrogen atoms were located by successive Fourier difference maps of full-matrix least-squares refinements. All H atoms were included at calculated positions (C–H, 0.97 Å) with group temperature factors; the phenyl groups were refined as rigid planar groups (C–C, 1.395 Å). In the final blocked-matrix least-square calculation, the Os, Au, P, F and O atoms, and most carbonyl C atoms, were refined anisotropically, and all other atoms isotropically. The weighting scheme converged at $w = 1.113/(\sigma^2(F_0) + 0.00033\ F_0^2)$ [$w = 4.05/(\sigma^2(F_0) + 0.00042F_0^2)$]. The refinements converged at $R = 0.027$, $R_w = 0.031$ for **5**, and $R = 0.030$, $R_w = 0.033$ for **13**.

Final atomic coordinates for the two complexes are given in Tables 5 and 6. Supplementary material includes tables of observed and calculated structure factors, hydrogen atom coordinates, thermal parameters for all atoms, and complete listings of bond distances and angles for non-hydrogen atoms. Calculations used scattering factors for the respective neutral atoms taken from the International Tables [25]. The atomic coordinates for these compounds are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this paper.

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