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Cluster chemistry

LXXXII *. Reactions between $Ru_3(\mu\text{-dppm})(CO)_{10}$ and 1-alkynes and related chemistry. Crystal structures of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2C_6F_5)(\mu\text{-dppm})(CO)_7$, $Ru_3\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}(\mu\text{-}C_4H_2Ph_2)(CO)_6$, $AuRu_3(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_7\{P(C_6H_4Me\text{-}p)_3\}$ and $Ru_2(\mu\text{-I})(\mu\text{-dppm})(\mu\text{-}C_2Ph)(CO)_4$

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Abstract

Reactions between $Ru_3(\mu\text{-dppm})(CO)_{10}$ (**1**) and 1-alkynes, HC_2R (R = Ph, ^tBu, $SiMe_3$, C_6F_5), have given 75–90% yields of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2R)(\mu\text{-dppm})(CO)_7$ (**3–6**); the related complexes $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_6(PPh_3)$ and $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2Ph)(\mu\text{-dpam})(CO)_7$ have also been obtained, while addition of $Au(C_2Ph)(PR_3)$ to **1** gave $AuRu_3(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_7(PR_3)$ (R = Ph, **10**; $C_6H_4Me\text{-}p$, **11**). A reaction between $Ru_3(\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4))(CO)_9$ and HC_2Ph afforded $Ru_3\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}(\mu\text{-}C_4H_2Ph_2)(CO)_6$ (**9**), containing a metallacyclopentadiene unit. The complex $Ru_2(\mu\text{-I})(\mu\text{-dppm})(\mu\text{-}C_2Ph)(CO)_4$ (**12**) was obtained by treating **3** with I_2. The molecular structures of **6**, **9**, **11** and **12** were determined by single-crystal X-ray studies.

Introduction

We have recently described some chemistry resulting from reactions between $Ru_3(\mu\text{-dppm})(CO)_{10}$ (**1**) and $C_2(CO_2Me)_2$ in which complexes containing mono- and di-meric alkyne moieties attached to Ru_3 and Ru_4 clusters were obtained [1].

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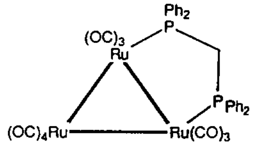
* For Part LXXXI, see ref. 1.

The chemistry of multi-site bonded alkynes is of interest in connection with modelling of the adsorption of alkynes of metal surfaces and also from the point of view of the modification of their reactivity when coordinated to several metal atoms. As described previously, the reactions of **1** proceed readily and generally more cleanly than the corresponding reactions of $Ru_3(CO)_{12}$. In the case of 1-alkynes, however, methods are available for the preparation of hydrido-alkynyl cluster complexes in high yield. In the present study, therefore, we have concentrated on expanding the chemistry of dppm- and dpam-substituted clusters and of a related species, $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(CO)_9$ (**2**), containing a metallated dephenylated dppm ligand.

Results and discussion

The reaction between **1** and HC_2Ph gave a high yield of the corresponding hydrido-alkynyl complex, $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Ph)(\mu\text{-}dppm)(CO)_7$ (**3**), as yellow crystals. This compound was identified by the usual analytical and spectroscopic techniques. The IR spectrum contained seven bands in the terminal $\nu(CO)$ region. In the ^1H NMR spectrum, a doublet at δ -19.26 can be assigned to the cluster-bonded H atom; a small signal is also found close by, at δ -19.25. The methylene protons of the dppm ligand resonate as two doublets of triplets at δ 3.3 and 4.3. We cannot be sure that there are not two sets of CH_2 (of dppm) signals as in all cases these form an extended multiplet and appear at very similar chemical shifts. A multiplet between δ 6.4–7.9 can be assigned to the various Ph protons. The FAB mass spectrum contains a molecular ion at m/z 987, which breaks down by loss of up to seven CO groups; some of these ions also lose C_6H_6, presumably benzene formed by combination of the cluster hydride with a phenyl group.



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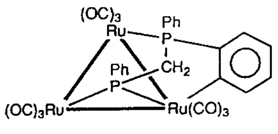


(2)

We have also prepared similar derivatives from HC_2R ($R = {}^tBu$ (**4**), $SiMe_3$ (**5**) and C_6F_5 (**6**)); the PPh_3-substituted complex (**7**) was prepared directly from **1**, HC_2Ph and PPh_3. All of these complexes could be obtained in excellent yields by direct crystallisation of the reaction mixture after removal of the solvent. Their spectroscopic data are in accord with the same general structure as that deduced for the phenyl derivative **3**. For **6**, the $\nu(CO)$ frequencies are about 10 cm^{-1} higher than for the other complexes. However, the ^1H NMR spectra in the hydride region show interesting differences. For **5** and **6**, doublets are found at δ -20 and -19.4, respectively, while for **4**, a triplet is found in this region at 295 K. Recently, a preparation of **4** from $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2{}^tBu)(CO)_9$ and dppm was described [2] together with a detailed variable temperature study of its ^1H, ^{13}C and ^{31}P NMR spectra. The changes observed in these spectra were interpreted as indicating a fluxional process involving acetylide rotation and concomitant hydride transfer. We have so far been unable to determine whether **3**, **5** and **6** exhibit the same dynamic

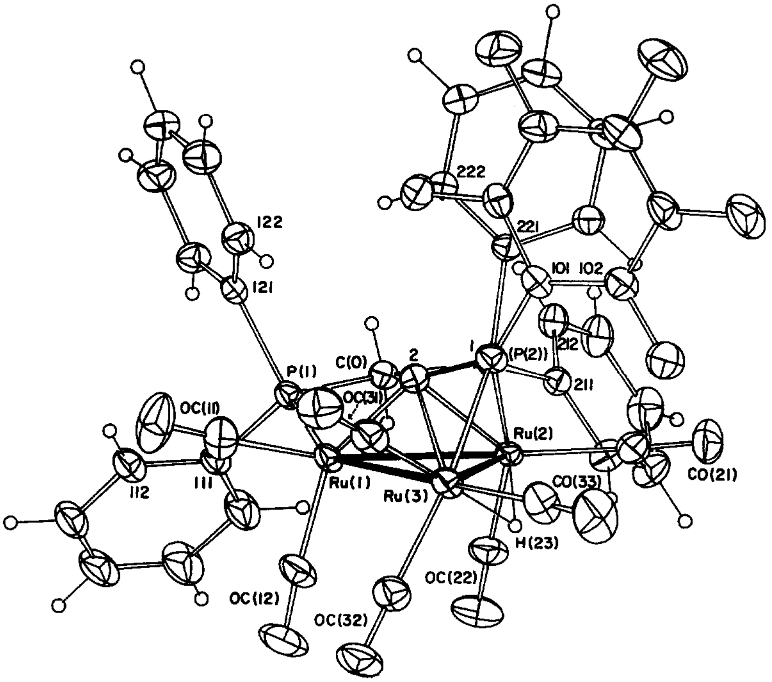
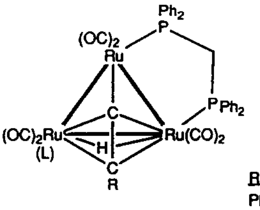


Fig. 1. Computer-generated plot of a molecule of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2C_6F_5)(\mu\text{-}dppm)(CO)_7$ (6), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

processes as 4. We have determined the molecular structure of the fluorinated complex 6 by an X-ray study to compare with the t-butyl analogue [2].



R	L	
Ph	CO	(3)
C_6F_5	CO	(6)
Bu^t	CO	(4)
$SiMe_3$	CO	(5)
Ph	PPh_3	(7)

Molecular structure of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2C_6F_5)(\mu\text{-}dppm)(CO)_7$ *(6)*

A molecule of 6 is depicted in Fig. 1 and selected bond lengths and angles are given in Table 1. The Ru_3 core forms an almost equilateral triangle [Ru–Ru 2.798(1)–2.811(1) Å]. The seven CO groups are distributed so that two are attached to each of Ru(1) and Ru(2) and three to Ru(3). The pentafluorophenylacetylide ligand is π-bonded to Ru(2) and Ru(3) [Ru(2)–C(1,2) 2.226(5), 2.197(4); Ru(3)–C(1,2) 2.245(4), 2.214(4) Å] and σ-bonded to Ru(1) through C(2) [1.924(4)

Table 1

Selected bond lengths (Å) and angles (deg.) for $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2R)(\mu\text{-dppm})(CO)_7$ (R = C_6F_5 (**6**), Ph [2]) and equivalent parameters for $AuRu_3(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_7\{P(C_6H_4Me\text{-}p)_3\}$ (**11**)

Bond	R = C_6F_5 (**6**) [a]	R = Ph [2]	**11**
Ru(1)–Ru(2)	2.811(1)	2.783(4)	2.826(2)
Ru(1)–Ru(3)	2.810(2)	2.781(3)	2.812(2)
Ru(2)–Ru(3)	2.798(1)	2.787(5)	2.826(2)
Au(1)–Ru(2)			2.743(1)
Au(1)–Ru(3)			2.773(2)
Ru(1)–P(1)	2.274(1)	2.266(4)	2.297(4)
Ru(2)–P(2)	2.304(1)	2.303(4)	2.326(5)
Au(1)–P(3)			2.282(5)
Ru(1)–C(2)	1.924(4)	1.964(9)	1.95(2)
Ru(2)–C(1)	2.226(5)	2.309(7)	2.24(2)
Ru(2)–C(2)	2.197(4)	2.197(7)	2.20(2)
Ru(3)–C(1)	2.245(4)	2.286(10)	2.23(2)
Ru(3)–C(2)	2.214(4)	2.215(10)	2.24(2)
P(1)–C(0)	1.842(4)		1.86(2)
P(2)–C(0)	1.827(4)		1.83(2)
C(1′)–C(2′)	1.320(5)	1.285(12)	1.31(2)
Au(1)–C(21)			2.82(2)
Au(1)–C(12)			2.81(2)
Ru–CO	1.854–1.920(6) (av. 1.898)		1.82–1.87(2) (av. 1.84)
C–O	1.132–1.153(7) (av. 1.142)		1.15–1.21(2) (av. 1.18)
P–C(Ph)	1.815–1.827(5) (av. 1.823)		1.817–1.856(13) (av. 1.829)
P(3)–C(Ph)			1.780–1.854(12) (av. 1.811)
Ru(2)–Ru(1)–P(1)	95.79(5)		94.9(1)
Ru(1)–Ru(2)–P(2)	91.57(4)		90.4(1)
Ru(1)–P(1)–C(0)	112.6(1)		112.6(5)
Ru(2)–P(2)–C(0)			111.2(5)
P(1)–C(0)–P(2)			114.0(9)
Ru(1)–C(2)–C(1)			151.7(13)
C(2)–C(1)–C(1)			141.1(15)

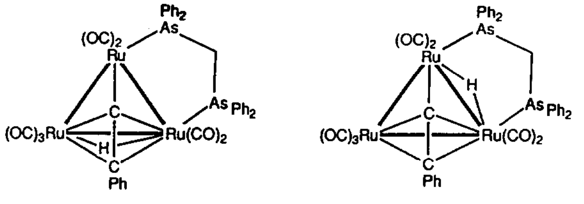
[a] H(23)–Ru(2,3) are 1.78(3), 1.72(4) Å; angles at Ru(1,2,3) (intraring) are 59.70(4), 60.12(4), 60.18(2)°.

Å]. The dppm ligand bridges the Ru(1)–Ru(2) edge [Ru(1)–P(1) 2.274(1), Ru(2)–P(2) 2.304(1) Å].

The cluster-bonded H atom was located in the crystallographic study and bridges the Ru(2)–Ru(3) vector, consistent with the ^1H NMR spectrum, from which it was found to interact with only one ^{31}P nucleus. This location is also the same as has been found in the neutron diffraction study of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2{}^tBu)(CO)_9$ [3] and the X-ray study of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2{}^tBu)(\mu\text{-dppm})(CO)_7$ [2]. In both these compounds, the Ru–Ru edge bridged by the hydride is the longest as a result of the usual lengthening of metal–metal bonds induced by bridging H atoms. In **6**, however, this pattern is not observed; here, the perpendicular arrangement of the C≡C triple bond over the Ru(2)–Ru(3) vector may counter the normal lengthening effect. In this, there is a similarity with the structure of

$Os_3(\mu\text{-}H)(\mu_3\text{-}C_2R)(CO)_9$ (R = CF_3 [4], $SiMe_3$ [5]) where the H-bridged Os–Os vectors [2.828(1), 2.833(1) Å] are shorter than the unbridged bonds [average 2.873(1), 2.845(1) Å].

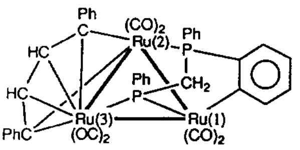
A similar reaction between HC_2Ph and $Ru_3(\mu\text{-dpam})(CO)_{10}$ afforded a 76% yield of orange-yellow $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Ph)(\mu\text{-dpam})(CO)_7$ (**8**). This complex gave a seven-band ν(CO) spectrum and the FAB mass spectrum contained the ions $[M - n\text{CO}]^+$ ($n = 0$–7) and one formed by loss of benzene, as found for **3**. The ^1H NMR spectrum was particularly interesting in that there are two equal intensity hydride resonances around δ 20 and two AB quartets for the CH_2 resonances. These data suggest the presence of two isomers **8a** and **8b** which do not interconvert on the NMR time scale at 295 K.



(a) (b)

(8)

In none of these reactions did we obtain any evidence for the formation of complexes containing oligomeric alkyne-derived ligands. In contrast, the reaction between $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(CO)_9$ (**2**) and excess HC_2Ph afforded a moderate yield of a new cluster identified as $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(\mu\text{-}C_4H_2Ph_2)(CO)_6$ (**9**) by X-ray crystallography. Unfortunately, the structural determination, while enabling us to determine the basic molecular structure, was only of modest quality, allowing a description of the stereochemistry to be given in general terms. The molecule (Fig. 2 and Table 2) contains a triangle of ruthenium atoms, capped by the metallated dephenylated dppm ligand, with each metal atom bonded to two CO ligands. Within the core, the shortest Ru–Ru separation [Ru(2)–Ru(3) 2.714(3) Å] is that bridged by the $C_4H_2Ph_2$ ligand; Ru(1)–Ru(3), bridged by P(1) is 2.827(4) Å, while Ru(1)–Ru(2), spanned by the $P(2)C_6H_4$ group, is considerably lengthened at 2.982(3) Å. This may be a result of the steric demands of the metallated ligand, but in **2**, the corresponding separation is only 2.8618(7) Å [6]. Angles involving the bridging group are: Ru(2)–P(2)–C(211) 112.0(7), P(2)–C(211)–C(212) 118(2), Ru(1)–C(212)–C(211) 116(2)°. The remaining ligand has been formed by dimerisation of the alkyne such that a 2,5-diphenylruthenacyclopentadiene ligand is formed, interacting in an η^5-fashion with Ru(3). Alternatively, a 1,4-diphenylbuta-1,3-diene-1,4-diyl ligand is σ-bonded to Ru(2) [Ru(2)–C(1,2) 2.21(3), 2.07(2) Å] and η^4-bonded to Ru(3) [Ru(3)–C 2.23–2.32(3) Å]. The C_6H_4 group of the metallated dppm ligand is σ-bonded to Ru(1) [Ru(1)–C(212) 2.00(3) Å].



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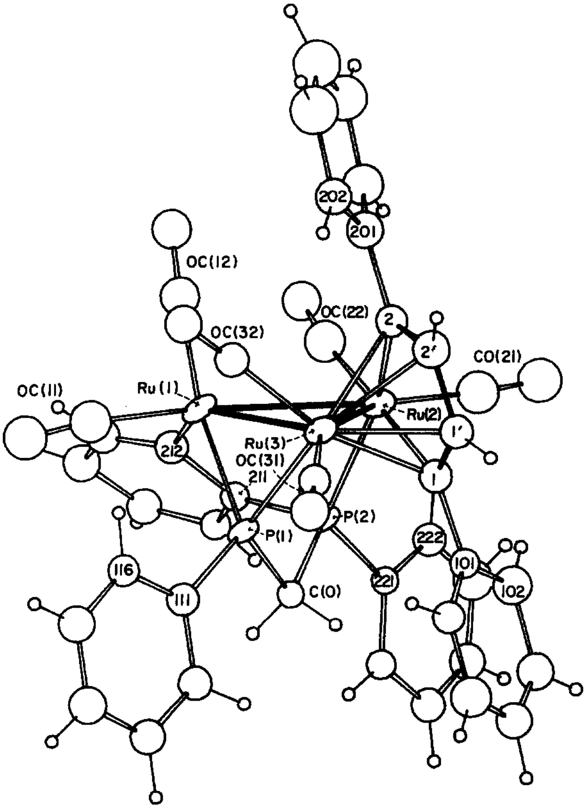


Fig. 2. Computer-generated plot of a molecule of $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(\mu\text{-}C_4H_2Ph_2)(CO)_6$ (9), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

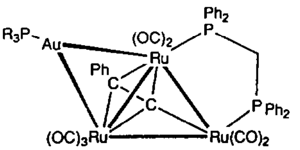
Spectroscopic data support this structure. There are six terminal $\nu(CO)$ bands in the solution IR spectrum. The FAB mass spectrum contains a molecular ion at m/z 983 which loses the six CO ligands sequentially; loss of C_6H_6 is also found. The ^1H NMR spectrum contains resonances centred on $\delta \sim 3$ for the dppm CH_2 groups; other protons resonate as a complex multiplet between δ 5.9 and 7.7.

Table 2

Selected bond lengths (Å) for $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(\mu\text{-}C_4H_2Ph_2)(CO)_6$ (9)

Ru(1)–Ru(2)	2.982(3)	Ru(2)–C(1)	2.21(3)
Ru(1)–Ru(3)	2.827(4)	Ru(2)–C(2)	2.07(2)
Ru(2)–Ru(3)	2.714(3)	Ru(1)–C(212)	2.00(3)
Ru(1)–P(1)	2.288(6)	P(1)–C(0)	1.81(2)
Ru(3)–P(1)	2.352(7)	P(2)–C(0)	1.84(2)
Ru(2)–P(2)	2.360(7)	P(2)–C(211)	1.76(2)
Ru(3)–C(1)	2.23(2)	P–C(Ph)	1.81(2), 1.84(2)
Ru(3)–C(1')	2.23(3)	C(1)–C(1')	1.33(4)
Ru(3)–C(2)	2.32(3)	C(1')–C(2')	1.41(4)
Ru(3)–C(2')	2.25(3)	C(2)–C(2')	1.46(4)

The isolobal analogy between H and Au(PR_3) has been often used to generate new gold-containing complexes [7]. We have studied the addition of Au(C_2Ph)(PR_3) (R = Ph, tol) to **1** to generate new $AuRu_3$ clusters containing μ_3-acetylide ligands. From reactions carried out in tetrahydrofuran, orange crystalline $AuRu_3(\mu_3$-$C_2Ph)(\mu$-dppm)$(CO)_7(PR_3)$ (R = Ph (**10**), tol (**11**)) were obtained in excellent yields. Both complexes were identified by the usual analytical and spectroscopic techniques. The FAB mass spectra contained molecular ions at m/z 1445 (**10**) and 1487 (**11**); in addition, an ion at m/z 1904 in the spectrum of **10** can be assigned to $[M + Au(PPh_3)]^+$, the isolobal analogue of the $[M + H]^+$ ion so often found in FAB mass spectra [8]. As found with **3**, loss of CO groups occurs stepwise, and some ions lose C_6H_6 fragments. Other significant ions are at m/z 459 and 721, assigned to $[Au(PPh_3)_n]^+$ (n = 1, 2, respectively). There are six bands in the terminal ν(CO) region, at frequencies about 20–25 cm^{-1} below those found for **3**, and characteristic resonances for the dppm and Ph groups occur in the ^{1}H NMR spectra. In **11**, the tolyl Me group is found at δ 2.4. It was of interest to compare the structures of the hydrido and aurated clusters, so the X-ray structure of **11** has been determined.



R = Ph (10)

R = C₆H₄Me-*p* (11)

Molecular structure of $AuRu_3(\mu_3$-$C_2Ph)(\mu$-dppm$)(CO)_7\{P(C_6H_4Me$-p$)_3\}$ (11)

A molecule of **11** is shown in Fig. 3 and selected bond parameters are given in Table 1. As expected, the three Ru atoms form a bonded triangle, capped by the C_2Ph ligand which is σ-bonded to Ru(1) [Ru(1)–C(2) 1.95(2) Å] and π-bonded to Ru(2) and Ru(3) [Ru(2)–C(1,2) 2.24(2), 2.20(2); Ru(3)–C(1,2) 2.23(2), 2.24(2) Å]. The dppm ligand bridges the Ru(1)–Ru(2) vector [Ru(1)–P(1) 2.297(4); Ru(2)–P(2) 2.326(5) Å]. The Au{P(tol)$_3$} group bridges Ru(2)–Ru(3) [Ru(2)–Au(1) 2.743(1), Ru(3)–Au(1) 2.773(2) Å] in a somewhat asymmetric fashion. Apart from the obvious differences resulting from the use of different groups on the acetylide, complexes **6** and **11** have virtually identical structures, so that with this pair, the H and Au(PR_3) groups are strictly isolobal, bridging the same Ru–Ru bond.

Replacement of the H atom in **3** by the Au(PR_3) group in **11** has resulted in an expansion of the Ru_3 cluster (average Ru–Ru separations: 2.784 Å in **3**, 2.821 Å in **11**) and a lengthening of the Ru–P bonds to the dppm ligand (average 2.284 Å in **3**, 2.312 Å in **11**). Conversely, the acetylide approaches more closely to the Ru_3 core (average Ru(2,3)–C(1,2) separations: 2.252 Å in **3**, 2.226 Å in **11**), and the average Ru–CO bond length is 0.054 Å shorter in **11**. However, it is interesting to note that this pattern is not found for the related compounds $Ru_3(\mu$-X$)(\mu_3$-$C_2{}^tBu)(CO)_9$ (X = H [3], Cu(PPh_3) [9], Ag(PPh_3) [10] and Au(PPh_3) [11]). In this set, the average Ru–Ru separations are closely similar (2.795, 2.802, 2.806 and 2.796 Å, respectively) as are the Ru–C distances within the C_2Ru_2 tetragonal pyramid (~ 2.23 Å).

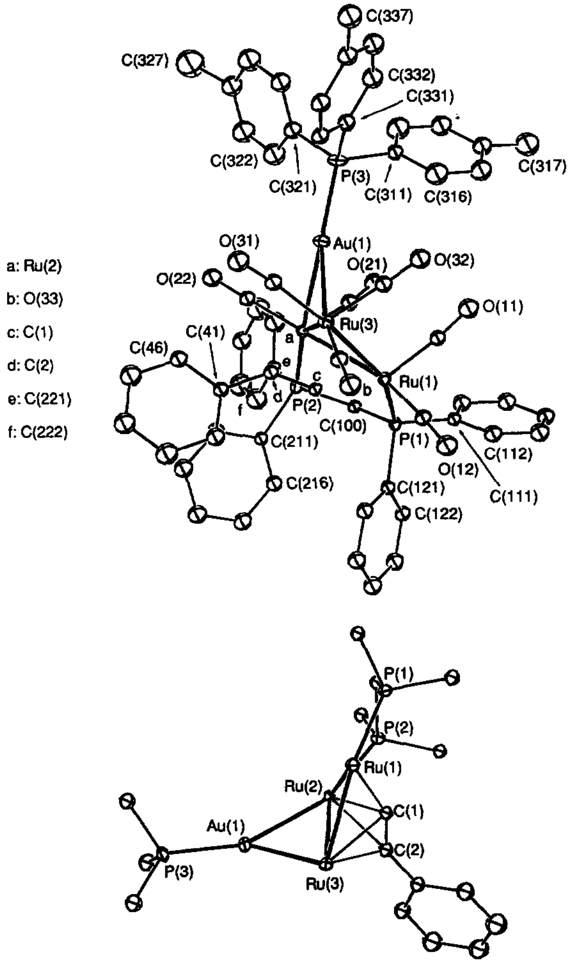
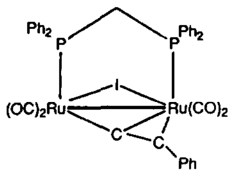


Fig. 3. Computer-generated plot of a molecule of AuRu$_3$(μ_3-C$_2$Ph)(μ-dppm)(CO)$_7${P(C$_6$H$_4$Me-*p*)$_3$} (**11**), showing the atom numbering scheme.

Reaction between $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Ph)(\mu\text{-}dppm)(CO)_7$ *and iodine*

An immediate reaction occurred between **3** and iodine to give as the only isolable product, a red complex identified as Ru$_2$(μ-I)(μ-dppm)(μ-C$_2$Ph)(CO)$_4$ (**12**). The IR spectrum contained four strong bands in the terminal ν(CO) region and the ^{1}H NMR spectrum confirmed the presence of the μ-dppm ligand, the CH$_2$ protons giving rise to the usual two doublets of triplets at δ 3.63 and 4.73. The molecular ion, present in the FAB mass spectrum at *m/z* 928, undergoes competitive loss of CO and I. The X-ray structure of **12** was determined to confirm the arrangement of ligands about the Ru$_2$ centre deduced from the above data.



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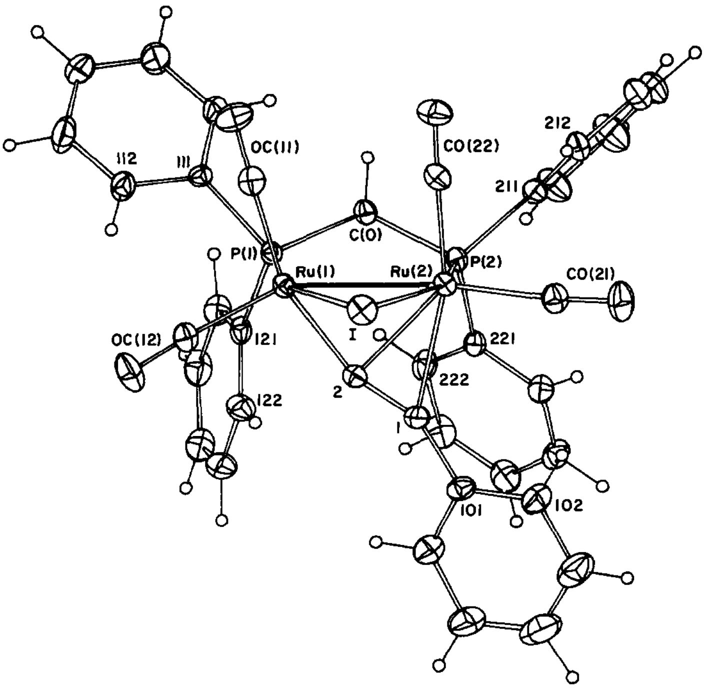


Fig. 4. Computer-generated plot of a molecule of $Ru_2(\mu\text{-}I)(\mu\text{-}dppm)(\mu\text{-}C_2Ph)(CO)_4$ (12), showing the atom numbering scheme. Non-hydrogen are atoms shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

Molecular structure of $Ru_2(\mu\text{-}I)(\mu\text{-}dppm)(\mu\text{-}C_2Ph)(CO)_4$ (12)

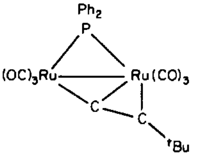
Figure 4 shows a plot of a molecule of **12** and some bond lengths and angles are given in Table 3. The two ruthenium atoms are connected by a single bond [2.713(1) Å] which is bridged by the dppm ligand [Ru(1)–P(1) 2.276(2), Ru(2)–P(2)

Table 3

Selected bond lengths (Å) and angles (deg.) for $Ru_2(\mu\text{-}I)(\mu\text{-}dppm)(\mu\text{-}C_2Ph)(CO)_4$ (12)

Bond		Bond	
Ru(1)–Ru(2)	2.713(1)	Ru(2)–C(1)	2.367(7)
Ru(1)–P(1)	2.276(2)	Ru(2)–C(2)	2.231(8)
Ru(2)–P(2)	2.288(2)	P(1)–C(0)	1.851(9)
Ru(1)–I	2.7646(9)	P(2)–C(0)	1.858(6)
Ru(2)–I	2.804(1)	C(1)–C(2)	1.251(9)
Ru(1)–C(2)	2.021(6)		
Ru–CO	1.869–1.920(6) (av. 1.896)		
C–O	1.13–1.144(8) (av. 1.134)		
P–C(Ph)	1.811–1.835(5) (av. 1.823)		
Ru(2)–Ru(1)–P(1)	95.02(6)	P(1)–C(0)–P(2)	114.9(3)
Ru(1)–Ru(2)–P(2)	95.27(6)	Ru(1)–I–Ru(2)	58.31(3)
Ru(1)–P(1)–C(0)	112.0(2)	Ru(1)–C(2)–C(1)	157.9(6)
Ru(2)–P(2)–C(0)	110.2(2)	C(2)–C(1)–C(Ph)	154.9(8)

2.288(2) Å], the iodine atom [Ru(1,2)–I 2.765, 2.804(1) Å] and the phenylethynyl ligand. The latter is bonded in the σ,η^2-mode [Ru(1)–C(2) 2.021(6); Ru(2)–C(1,2) 2.367, 2.231(8) Å]. The C(1)–C(2) bond length is 1.251(9) Å, very close to that found in uncoordinated ethyne. Coordination about each ruthenium atom is completed by two CO groups each. Comparison with $Ru_2(\mu\text{-}PPh_2)(\mu\text{-}C_2{}^tBu)(CO)_6$ (**13**) [12] shows that the Ru–Ru bond is 0.039 Å shorter in **12**; we note that in $Ru_3(\mu\text{-dppm})(CO)_{10}$, the Ru–Ru bond bridged by the dppm ligand is about 0.02 Å shorter than the others, although the two systems are not strictly comparable [13]. Similarly, the C–C vector of the alkynyl group is not parallel to the Ru–Ru vector; the difference in the Ru(2)–C(1,2) separations in **12** is the same as in **13**, i.e. 0.136 Å.



(13)

The work described here has shown that the reactivity of **1** towards terminal alkynes and the isolobal gold acetylides is high, giving single products in good to excellent yields. The products are similar to those obtained from $Ru_3(CO)_{12}$ [11] and can also be obtained by reactions of the latter complexes with dppm [2]. The molecular structures that we have determined are similar to previously known examples, there being no major structural changes resulting from replacement of Ph by C_6F_5, but an unusual enlargement of the Ru_3 cluster occurs when H is replaced by $Au(PR_3)$.

As shown by other groups [14], the dppm complexes are good sources of binuclear ruthenium carbonyl complexes, such as **12**, the bridging dppm holding the two ruthenium atoms together while allowing the third to be excised out of the cluster. In the present example, addition of iodine has given a μ-iodo derivative (presumably accompanied by $\{Ru(\mu\text{-}I)I(CO)_3\}_2$ or $RuI_2(CO)_4$, neither of which were detected), which can be used as a precursor for other Ru_2 complexes.

In the reactions of **1** with 1-alkynes, no oligomeric products were found. However, when cluster **2**, containing the metallated dephenylated dppm ligand, was used, the only product isolated contained a dimer of the alkyne, forming a ruthenole-$Ru_2(CO)_4$ system, analogous to that found in the product from **2** and $C_2(CO_2Me)_2$ [1]. Evidently the μ_3-capping ligand prevents formation of a μ_3-acetylide; the greater reactivity of a $\mu\text{-}C_2R$ fragment has been documented previously [15].

Experimental

General conditions

All reactions were carried out under dry, high purity nitrogen by use of standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7. TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick).

Reagents. The complexes $Ru_3(\mu\text{-LL})(CO)_{10}$ (LL = dppm [16], dpam [17]) and **2** were prepared by the literature methods. 1-Alkynes were commercial products and were used as received. $Me_3NO \cdot 2H_2O$ (Aldrich) was dehydrated by sublimation (100°C/0.1 mm).

Instrumentation. IR: Perkin–Elmer 1700X FT or 683 double beam, NaCl optics; NMR: Bruker CXP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz). Spectra recorded in non-deuterated solvents used an external concentric tube containing D_2O for field lock. FAB MS: VG ZAB 2HF (FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Reactions of $Ru_3(\mu\text{-dppm})(CO)_{10}$

(a) With HC_2Ph. Phenylethyne (60 mg, 0.59 mmol) was added to a solution of **1** (350 mg, 0.36 mmol) in tetrahydrofuran (25 ml) and the mixture was heated at reflux point for 100 min. After removal of solvent, crystallisation of the residue (CH_2Cl_2/MeOH) gave a yellow powder of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_7$ (**3**) (329 mg, 92%), m.p. > 150°C (dec.). Anal. Found: C, 48.67; H, 2.87; M (mass spectrometry), 987; $C_{40}H_{28}O_7P_2Ru_3$ calc.: C, 48.74; H, 2.86%; M, 987. IR: $\nu(CO)$ (cyclohexane) 2065s, 2011vs, 2003vs, 1994(sh), 1985m, 1958m, 1940w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ -19.26 [d, $J(PH) = 34$, 1H, Ru–H] (a small signal is present at δ -19.25 at 295 K), 3.33 (dt, $J(HH) = 14$, $J(PH) = 12$, 1H, CH_2), 4.31 (dt, $J(HH) = 14$, $J(PH) = 11$, 1H, CH_2), 6.42–7.89 (m, 25H, Ph). FAB MS: 987, M^+, 100; 959, $[M-CO]^+$, 21; 931, $[M-2CO]^+$, 7; 903, $[M-3CO]^+$, 18; 875, $[M-4CO]^+$, 77; 847, $[M-5CO]^+$, 62; 819, $[M-6CO]^+$, 50; 791, $[M-7CO]^+$, 94; 769, $[M-5CO-C_6H_6]^+$, 39; 741, $[M-6CO-C_6H_6]^+$, 16; 713, $[M-7CO-C_6H_6]^+$, 64.

(b) With $HC_2{}^tBu$. The reaction was carried out as described in (a), using **1** (500 mg, 0.52 mmol) and $HC_2{}^tBu$ (60 mg, 0.73 mmol) in tetrahydrofuran (20 ml) for 9 h. Orange crystals (from CH_2Cl_2/MeOH) of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2{}^tBu)(\mu\text{-dppm})(CO)_7$ (**4**) (402 mg, 81%) were obtained, m.p. 133–136°C. Anal. Found: C, 45.68; H, 3.32; M (mass spectrometry), 967. $C_{38}H_{32}O_7P_2Ru_3.0.5CH_2Cl_2$ calc.: C, 45.86; H, 3.30%; M (unsolvated), 967. Complex **4** has identical IR and NMR spectra to those reported in ref. 2.

(c) With HC_2SiMe_3. Similarly, a mixture of **1** (200 mg, 0.21 mmol) and HC_2SiMe_3 (22 mg, 0.22 mmol) was heated in refluxing tetrahydrofuran (20 ml) for 9 h to give orange crystals (from CH_2Cl_2/MeOH) of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2SiMe_3)(\mu\text{-dppm})(CO)_7.0.5CH_2Cl_2$ (**5**) (151 mg, 74%), m.p. 149–152°C. Anal. Found: C, 44.05; H, 3.33; M (mass spectrometry), 983. $C_{37}H_{32}O_7P_2Ru_3Si$ calc.: C, 43.97; H, 3.25%, M (unsolvated), 983. IR: $\nu(CO)$ (cyclohexane) 2062s, 2008s, 1998vs, 1991(sh), 1981m, 1956m, 1938w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ -19.99 (d, $J(PH) = 34$, 1H, Ru–H), 0.05 (s, 9H, Me), 3.38 (dt, $J(HH) = 14$, $J(PH) = 12$, 1H, CH_2), 4.29 (dt, $J(HH) = 14$, $J(PH) = 11$, 1H, CH_2), 5.30 (s, 1H, CH_2Cl_2), 7.39 (m, 20H, Ph). FAB MS; 983, M^+, 22; 955, $[M-CO]^+$, 22; 899, $[M-3CO]^+$, 51; 871, $[M-4CO]^+$, 24; 843, $[M-5CO]^+$, 32; 815, $[M-6CO]^+$, 44; 793, $[M-4CO-C_6H_6]^+$, 72; 787, $[M-7CO]^+$, 61; 765, $[M-5CO-C_6H_6]^+$, 100.

(d) With $HC_2C_6F_5$. Following the method described in (a), a mixture of **1** (249 mg, 0.26 mmol) and $HC_2C_6F_5$ (75 mg, 0.39 mmol) was heated in tetrahydrofuran (25 ml) for 1.5 h. Crystallisation (CH_2Cl_2/MeOH) gave orange crystals of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2C_6F_5)(\mu\text{-dppm})(CO)_7$ (**6**) (214 mg, 77%), m.p. > 200°C (dec.). Anal.

Found: C, 44.65; H, 2.18; *M* (mass spectrometry), 1077; $C_{40}H_{23}F_5O_7P_2Ru_3$ calc.: C, 44.66; H, 2.16%; *M*, 1077. IR: ν(CO) (cyclohexane) 2070s, 2018(sh), 2013vs, 2002m, 1992m, 1965m, 1947w cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) −19.41 (d, *J*(PH) = 33, 1H, Ru–H), 3.21 (dt, *J*(HH) = 14, *J*(PH) = 12, 1H, CH$_2$), 4.19 (dt, *J*(HH) = 14, *J*(PH) = 11, 1H, CH$_2$), 6.29–8.03 (m, 20H, Ph). FAB MS: 1077, M^+, 46; 1049, $[M-\text{CO}]^+$, 20; 1021, $[M-2\text{CO}]^+$, 4; 993, $[M-3\text{CO}]^+$, 52; 965, $[M-4\text{CO}]^+$, 26; 937, $[M-5\text{CO}]^+$, 39; 909, $[M-6\text{CO}]^+$, 70; 881, $[M-7\text{CO}]^+$, 100; 859, $[M-5\text{CO}-C_6H_6]^+$, 41; 831, $[M-6\text{CO}-C_6H_6]^+$, 15; 803, $[M-7\text{CO}-C_6H_6]^+$, 39.

Preparation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_6(PPh_3)$ *(7)*

A mixture of **1** (151 mg, 0.156 mmol), PPh$_3$ (45 mg, 0.17 mmol) and HC$_2$Ph (20 mg, 0.20 mmol) was heated in refluxing tetrahydrofuran (20 ml) for 18 h. After removal of solvent, the residue was recrystallised (CH$_2$Cl$_2$/MeOH) to give a yellow powder of $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_6(PPh_3)$ (**7**) (130 mg, 68%), m.p. > 250°C. Anal. Found: C, 54.92; H, 3.73; *M* (mass spectrometry), 1221. $C_{57}H_{43}O_6P_3Ru_3 \cdot 0.5CH_2Cl_2$ calc.: C, 54.70; H, 3.51%; *M* (unsolvated) 1221. IR: ν(CO)(CH$_2$Cl$_2$) 2072m, 2043vw, 2016vs, 1986s, 1968m, 1953m, 1915w (br) cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 3.32 (m, 1H, CH$_2$), 4.31 (m, 1H, CH$_2$), 5.30 (s, 1H, CH$_2$Cl$_2$), 6.31–7.74 (m, 40H, Ph). No Ru–H resonance was detected in the ^{1}H NMR spectrum. FAB MS: 1221, M^+, 100; 1137, $[M-3\text{CO}]^+$, 21; 1109, $[M-4\text{CO}]^+$, 32; 1081, $[M-5\text{CO}]^+$, 26; 1053, $[M-6\text{CO}]^+$, 26; 1031, $[M-4\text{CO}-C_6H_6]^+$, 17; 1003, $[M-5\text{CO}-C_6H_6]^+$, 23; 975, $[M-6\text{CO}-C_6H_6]^+$, 38.

Preparation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Ph)(\mu\text{-dpam})(CO)_7$ *(8)*

A reaction between $Ru_3(\mu\text{-dpam})(CO)_{10}$ (78 mg, 0.074 mmol) and HC$_2$Ph (11 mg, 0.11 mmol) in refluxing tetrahydrofuran (15 ml) for 1.5 h afforded orange-yellow $Ru_3(\mu\text{-H})(\mu_3\text{-}C_2Ph)(\mu\text{-dpam})(CO)_7$ (**8**) (60 mg, 76%) as a yellow powder, m.p. 208–210°C (from CH$_2$Cl$_2$/MeOH). Anal. Found: C, 43.86; H, 2.65; *M* (mass spectrometry), 1075. $C_{40}H_{28}As_2O_7Ru_3$ calc.: C, 44.75; H, 2.63%; *M*, 1075. IR: ν(CO) (cyclohexane) 2068m, 2062s, 2012vs, 2005(sh), 1992s, 1983m, 1958m, 1937w cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) −20.01, 19.89 (2 × s, 1H, Ru–H) (isomers a and b), 2.01, 2.50 (AB q, *J*(HH) = 11, 1H, CH$_2$, isomer a), 3.05, 3.99 (AB q, *J*(HH) = 12, 1H, CH$_2$, isomer b), 6.72–7.47 (m, 25H, Ph). FAB MS: 1075, M^+, 72; 1047, $[M-\text{CO}]^+$, 13; 1019, $[M-2\text{CO}]^+$, 5; 991, $[M-3\text{CO}]^+$, 20; 963, $[M-4\text{CO}]^+$, 15; 935, $[M-5\text{CO}]^+$, 20; 907, $[M-6\text{CO}]^+$, 33; 879, $[M-7\text{CO}]^+$, 52; 857, $[M-5\text{CO}-C_6H_6]^+$, 38; 829, $[M-6\text{CO}-C_6H_6]^+$, 46; 801, $[M-7\text{CO}-C_6H_6]^+$, 100.

Preparation of $Ru_3\{\mu_3\text{-}PPhCH_2PPh(C_6H_4)\}(\mu\text{-}C_4H_2Ph_2)(CO)_6$ *(9)*

The product from heating **2** (96 mg, 0.11 mmol) and HC$_2$Ph (30 mg, 0.29 mmol) in refluxing tetrahydrofuran (17 ml) for 9 h was separated by preparative TLC (acetone/light petroleum 1:3) into several coloured fractions. Band 2 (R_f 0.69) was crystallised (CH$_2$Cl$_2$/MeOH) to give $Ru_3\{\mu_3\text{-PPhCH}_2\text{PPh}(C_6H_4)\}(\mu\text{-}C_4H_2Ph_2)(CO)_6$ (**9**) (34 mg, 31%) as an orange-red powder, m.p. > 150°C. Anal. Found: C, 49.66; H, 2.89; *M* (mass spectrometry), 983. $C_{41}H_{28}O_6P_2Ru_3$ calc.: C, 50.16; H, 2.87%; *M*, 983. IR; ν(CO) (cyclohexane) 2041s, 2010s, 2000vs, 1970w, 1959s, 1945w cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 2.97 (m, part of ABXY pattern, 2H, CH$_2$), 5.88–7.70 (m, 26H, 2 × CH + Ph + C$_6$H$_4$). FAB MS: 983, M^+, 66; 955,

$[M - CO]^+$, 89; 927, $[M - 2CO]^+$, 37; 899, $[M - 3CO]^+$, 32; 871, $[M - 4CO]^+$, 100; 843, $[M - 5CO]^+$, 32; 815, $[M - 6CO]^+$, 42; 735, $[M - 6CO - C_6H_6]^+$, 37.

Preparation of $AuRu_3(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_7(PR_3)$

(a) R = Ph. A mixture of **1** (102 mg, 0.11 mmol) and $Au(C_2Ph)(PPh_3)$ (59 mg, 0.11 mmol) was heated in refluxing tetrahydrofuran (28 ml) for 1.5 h. After removal of solvent, crystallisation (CH_2Cl_2/MeOH) of the residue afforded orange microcrystals of $AuRu_3(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_7(PPh_3).1.5CH_2Cl_2$ (**10**) (147 mg, 89%), m.p. > 190°C. Anal. Found: C, 45.39; H, 2.75; *M* (mass spectrometry), 1445. $C_{58}H_{42}AuO_7P_3Ru_3.1.5CH_2Cl_2$ calc.: C, 45.48; H, 2.89%; *M* (unsolvated), 1445. IR: ν(CO) (cyclohexane) 2034vs, 1990s, 1971vs, 1957m, 1940m, 1909w cm^{-1}. ^1H NMR: $\delta(CDCl_3)$ 3.34 (dt, J(HH) = 14, J(PH) = 11, 1H, CH_2), 4.25 (dt, J(HH) = 14, J(PH) = 11, 1H, CH_2), 5.30 (s, 3H, CH_2Cl_2), 6.34–7.94 (m, 40H, Ph). FAB MS: 1904, $[M + Au(PPh_3)]^+$, 11; 1876, $[M + Au(PPh_3) - CO]^+$, 20; 1445, M^+, 71; 1417, $[M - CO]^+$, 11; 1389, $[M - 2CO]^+$, 3; 1361, $[M - 3CO]^+$, 100; 1333, $[M - 4CO]^+$, 23; 1305, $[M - 5CO]^+$, 29; 1277, $[M - 6CO]^+$, 21; 1249, $[M - 7CO]^+$, 29; 1227, $[M - 5CO - C_6H_6]^+$, 9; 1199, $[M - 6CO - C_6H_6]^+$, 6; 1171, $[M - 7CO - C_6H_6]^+$, 26; 986, $[M - Au(PPh_3)]^+$, 19; 721, $[Au(PPh_3)_2]^+$, 36; 459, $[Au(PPh_3)]^+$, 86.

Table 4

Crystal data and refinement details for complexes **6**, **9**, **11** and **12**

Compound	**6**	**9**	**11**	**12**
Formula	$C_{40}H_{23}F_5O_7P_2Ru_3$	$C_{41}H_{28}O_6P_2Ru_3 \cdot \sim 0.83\ CH_2Cl_2$	$C_{61}H_{48}AuO_7P_3Ru_3$	$C_{37}H_{28}IO_4P_2Ru_2 \cdot CH_2Cl_2$
MW	1075.8	~ 1054.7	1486.1	1012.6
Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	$P\bar{1}$, No. 2	*Pbcn*, No. 60	*C*2/*c*, No. 15	*Cc*, No. 9
a (Å)	16.54(1)	13.012(8)	40.846(3)	22.951(3)
b (Å)	11.735(5)	23.555(7)	12.587(2)	10.825(4)
c (Å)	10.816(8)	26.828(5)	22.642(2)	18.309(5)
α (deg.)	74.67(5)			
β (deg.)	80.22(6)		92.599(6)	121.84(2)
γ (deg.)	84.56(5)			
U ($Å^3$)	1993	8223	11629.2	3864.1
Z	2	8	8	4
D_c ($g\ cm^{-3}$)	1.79	~ 1.70	1.698	1.74
F(000)	1052	~ 4151	5808	1980
Crystal size (mm)	0.26×0.35×0.18	0.46×0.40×0.07	0.11×0.15×0.44	0.20×0.28×0.42
A^* (min, max)	1.22, 1.35	1.08, 1.45	[a]	1.35, 1.63
μ (cm^{-1})	11.4	11.9	33.61	16.8
$2\theta_{max}$ (deg.)	50	50	45	55
T (K)	295	295	298	295
N	6810	6439	7249	4433
N_0	5338	2346	3472	4031
R	0.029	0.087	0.050	0.029
R_w	0.029	0.070	0.054	0.032

[a] See text.

Table 5

Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters for $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2C_6F_5)(\mu\text{-dppm})(CO)_7$ (**6**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.81623(2)	0.18709(3)	0.39146(3)	0.0481(2)
Ru(2)	0.68600(2)	0.35995(3)	0.36924(3)	0.0441(2)
Ru(3)	0.65689(2)	0.12903(3)	0.51719(3)	0.0540(3)
C(11)	0.8755(3)	0.0442(4)	0.3963(4)	0.089(5)
O(11)	0.9106(3)	−0.0450(3)	0.3957(4)	0.148(5)
C(12)	0.8698(3)	0.2232(5)	0.5171(4)	0.085(5)
O(12)	0.8993(2)	0.2485(4)	0.5941(3)	0.132(5)
C(21)	0.5883(3)	0.4598(4)	0.3610(4)	0.068(4)
O(21)	0.5309(2)	0.5209(3)	0.3509(4)	0.105(4)
C(22)	0.7459(3)	0.4359(4)	0.4529(4)	0.074(4)
O(22)	0.7813(2)	0.4837(4)	0.5056(3)	0.113(4)
C(31)	0.6741(3)	−0.0302(4)	0.5080(4)	0.073(4)
O(31)	0.6871(2)	−0.1263(3)	0.5004(3)	0.103(4)
C(32)	0.7093(3)	0.0964(4)	0.6678(4)	0.076(4)
O(32)	0.7390(2)	0.0771(3)	0.7586(3)	0.102(4)
C(33)	0.5441(3)	0.1172(5)	0.5972(5)	0.087(5)
O(33)	0.4785(2)	0.1051(4)	0.6482(4)	0.136(5)
P(1)	0.90398(6)	0.29040(9)	0.22274(9)	0.0463(8)
C(111)	1.0013(2)	0.3175(4)	0.2653(4)	0.052(3)
C(112)	1.0579(3)	0.2224(4)	0.2876(4)	0.069(4)
C(113)	1.1302(3)	0.2342(5)	0.3309(5)	0.081(5)
C(114)	1.1459(3)	0.3380(5)	0.3518(5)	0.095(6)
C(115)	1.0914(3)	0.4305(5)	0.3303(6)	0.111(7)
C(116)	1.0177(3)	0.4210(5)	0.2876(5)	0.089(5)
C(121)	0.9359(2)	0.2283(3)	0.0833(3)	0.045(3)
C(122)	0.8926(2)	0.1428(4)	0.0626(4)	0.061(4)
C(123)	0.9139(3)	0.1041(4)	−0.0482(5)	0.080(5)
C(124)	0.9782(3)	0.1500(4)	−0.1399(4)	0.080(5)
C(125)	1.0227(3)	0.2340(5)	−0.1193(4)	0.078(4)
C(126)	1.0014(2)	0.2743(4)	−0.0090(4)	0.058(4)
C(0)	0.8614(2)	0.4394(3)	0.1506(3)	0.048(3)
P(2)	0.74974(6)	0.46349(9)	0.17031(9)	0.0432(8)
C(211)	0.7444(2)	0.6249(3)	0.1327(4)	0.050(3)
C(212)	0.7747(2)	0.6885(3)	0.0084(4)	0.057(3)
C(213)	0.7781(3)	0.8092(4)	−0.0202(5)	0.072(4)
C(214)	0.7519(3)	0.8692(4)	0.0716(5)	0.086(5)
C(215)	0.7212(3)	0.8092(4)	0.1935(5)	0.087(5)
C(216)	0.7166(3)	0.6868(4)	0.2263(4)	0.072(4)
C(221)	0.7163(2)	0.4363(3)	0.0298(3)	0.044(3)
C(222)	0.7649(3)	0.3859(4)	−0.0591(4)	0.064(4)
C(223)	0.7342(3)	0.3683(5)	−0.1629(4)	0.082(5)
C(224)	0.6551(3)	0.4013(4)	−0.1798(4)	0.075(4)
C(225)	0.6060(3)	0.4537(5)	−0.0934(4)	0.076(5)
C(226)	0.6360(2)	0.4695(4)	0.0114(4)	0.063(4)
C(1)	0.6393(2)	0.2132(4)	0.3109(3)	0.053(3)
C(2)	0.7187(2)	0.1919(3)	0.3150(3)	0.049(3)
C(101)	0.5797(2)	0.2013(3)	0.2316(4)	0.054(3)
C(102)	0.4968(2)	0.2317(4)	0.2570(4)	0.065(4)
F(102)	0.4681(1)	0.2728(3)	0.3613(3)	0.096(3)
C(103)	0.4416(3)	0.2209(4)	0.1802(4)	0.076(4)
F(103)	0.3625(2)	0.2491(3)	0.2100(3)	0.112(3)
C(104)	0.4686(3)	0.1792(5)	0.0735(5)	0.086(5)

Table 5 (continued)

Atom	x	y	z	U_{eq} (Å^2)
F(104)	0.4166(2)	0.1699(4)	−0.0055(3)	0.136(4)
C(105)	0.5492(3)	0.1478(4)	0.0431(5)	0.079(5)
F(105)	0.5765(2)	0.1101(3)	−0.0638(3)	0.121(4)
C(106)	0.6034(2)	0.1587(4)	0.1226(4)	0.060(4)
F(106)	0.6825(1)	0.1298(2)	0.0892(3)	0.081(3)
H(23)	0.644(2)	0.274(3)	0.525(3)	0.07(1)

(b) $R = C_6H_4Me$-p. A similar reaction using **1** (74 mg, 0.076 mmol) and $Au(C_2Ph)\{P(tol)_3\}$ (46 mg, 0.076 mmol) gave orange crystals of $AuRu_3(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_7\{P(tol)_3\}.0.5CH_2Cl_2$ (**11**) (107 mg, 92%), m.p. > 200°C (dec.). Anal. Found: C, 48.38; H, 3.24; M (mass spectrometry), 1487. $C_{61}H_{48}AuO_7P_3Ru_3 \cdot 0.5CH_2Cl_2$ calc.: C, 48.32; H, 3.23%; M (unsolvated), 1487. IR: ν(CO) 2034vs, 1990s, 1970vs, 1957m, 1939m, 1909w cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 2.39 (s, 9H, Me), 3.34 (dt, J(HH) = 14, J(PH) = 11, 1H, CH$_2$), 4.25 (dt, J(HH) = 14, J(PH) = 11, 1H, CH$_2$), 5.30 (s, 1H, CH$_2$Cl$_2$), 6.38–8.54 (m, 37H, Ph + C$_6$H$_4$). FAB MS: 1988, $[M + Au\{P(tol)_3\}]^+ \equiv [M']^+$, 1; 1960, $[M' - CO]^+$, 17; 1932, $[M' - 2CO]^+$, 1; 1487, M^+, 9; 1459, $[M - CO]^+$, 4; 1431, $[M - 2CO]^+$, 3; 1403, $[M - 3CO]^+$, 51; 1375, $[M - 4CO]^+$, 18; 1347, $[M - 5CO]^+$, 22; 1319, $[M - 6CO]^+$, 20; 1291, $[M - 7CO]^+$, 25; 1213, $[M - 7CO - C_6H_6]^+$, 21; 1199, $[M - 7CO - C_7H_8]^+$, 9; 986, $[M - Au\{P(tol)_3\}]^+$, 9; 805, $[Au\{P(tol)_3\}_2]^+$, 45; 501, $[Au\{P(tol)_3\}]^+$, 100.

Reaction of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_7$ with iodine

Iodine (36 mg, 0.14 mmol) in tetrahydrofuran (17 ml) was added dropwise to a solution of $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_7$ (130 mg, 0.13 mmol) in the same solvent (15 ml) over a period of 30 min. The colour of the solution deepened to orange. Separation by preparative TLC (acetone/light petroleum 3:7) gave a major fraction (band 2, R_f 0.44) which afforded red crystals of $Ru_2(\mu\text{-}I)(\mu\text{-}C_2Ph)(\mu\text{-dppm})(CO)_4 \cdot 0.5CH_2Cl_2$ (**12**) (42 mg, 34%), m.p. > 180°C, from CH$_2$Cl$_2$/MeOH. Anal. Found: C, 45.86; H, 2.96; M (mass spectrometry) 928. $C_{37}H_{27}IO_4P_2Ru_2 \cdot 0.5CH_2Cl_2$ calc.: C, 46.48; H, 2.91%; M (unsolvated), 928. IR: ν(CO) (cyclohexane) 2025s, 2002m, 1991s, 1969vs, 1954w, 1947w cm^{-1}. ^{1}H NMR: δ(CDCl$_3$) 3.63 (dt, J(HH) = 13, J(PH) = 12, 1H, CH$_2$), 4.73 (dt, J(HH) = 13, J(PH) = 12, 1H, CH$_2$), 5.30 (s, 1H, CH$_2$Cl$_2$), 6.89–7.54 (m, 25H, Ph). FAB MS: 928, M^+, 32; 900, $[M - CO]^+$, 46; 844, $[M - 3CO]^+$, 100; 816, $[M - 4CO]^+$, 40; 745, $[M - 2CO - I]^+$, 80; 717, $[M - 3CO - I]^+$, 46; 689, $[M - 4CO - I]^+$, 88. The other fractions contained only trace amounts of complexes which were not identified.

Crystallography

Unique data sets were measured for **6**, **9** and **12** at room temperature within the specified $2\theta_{max}$ limits using an Enraf–Nonius CAD4 diffractometer (2θ–θ scan mode; monochromatic Mo-K_α radiation, λ 0.71073 Å); N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered "observed" and used in the full matrix least squares refinement on $|F|$ after gaussian absorption correction.

Table 6

Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters for $Ru_3\{\mu_3\text{-}PPhCH_2\text{-}PPh(C_6H_4)\}(\mu\text{-}C_4H_2Ph_2)(CO)_6$ (**9**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.3589(2)	0.32128(7)	0.42294(8)	0.0611(9)
Ru(2)	0.3162(2)	0.40220(8)	0.33998(8)	0.0620(9)
Ru(3)	0.1608(2)	0.36050(7)	0.39666(8)	0.0564(8)
C(11)	0.375(3)	0.275(1)	0.478(1)	0.11(1)
O(11)	0.394(2)	0.2539(8)	0.5143(8)	0.125(9)
C(12)	0.400(2)	0.260(1)	0.382(1)	0.10(1)
O(12)	0.436(1)	0.2272(7)	0.3549(7)	0.100(7)
C(21)	0.321(3)	0.448(1)	0.287(1)	0.12(1)
O(21)	0.338(2)	0.4763(8)	0.2503(8)	0.125(7)
C(22)	0.435(3)	0.363(1)	0.326(1)	0.11(1)
O(22)	0.517(2)	0.3448(7)	0.3117(7)	0.098(7)
C(31)	0.040(2)	0.363(1)	0.4343(9)	0.067(8)
O(31)	−0.034(2)	0.3632(7)	0.4575(7)	0.101(7)
C(32)	0.168(2)	0.280(1)	0.4104(9)	0.076(8)
O(32)	0.158(1)	0.2347(7)	0.4206(6)	0.089(6)
P(1)	0.2679(5)	0.3917(2)	0.4618(2)	0.048(3)
C(111)	0.216(2)	0.388(1)	0.5245(9)	0.068(8)
C(112)	0.211(2)	0.437(1)	0.553(1)	0.074(9)
C(113)	0.167(2)	0.433(1)	0.603(1)	0.079(8)
C(114)	0.144(2)	0.382(1)	0.621(1)	0.09(1)
C(115)	0.155(2)	0.336(1)	0.593(1)	0.088(9)
C(116)	0.188(2)	0.3377(9)	0.5447(9)	0.066(8)
C(0)	0.331(2)	0.4599(8)	0.4567(8)	0.048(6)
P(2)	0.4115(5)	0.4521(2)	0.4007(3)	0.051(3)
C(211)	0.517(2)	0.4126(9)	0.4223(8)	0.053(7)
C(212)	0.500(2)	0.352(1)	0.4348(9)	0.071(8)
C(213)	0.586(2)	0.326(1)	0.453(1)	0.076(9)
C(214)	0.681(2)	0.345(1)	0.463(1)	0.09(1)
C(215)	0.700(2)	0.403(1)	0.4478(9)	0.079(9)
C(216)	0.619(2)	0.4349(9)	0.4308(9)	0.059(7)
C(221)	0.463(2)	0.5238(8)	0.3900(9)	0.048(7)
C(222)	0.515(2)	0.534(1)	0.3459(9)	0.071(8)
C(223)	0.564(2)	0.586(1)	0.335(1)	0.11(1)
C(224)	0.559(2)	0.625(1)	0.372(1)	0.083(9)
C(225)	0.504(2)	0.618(1)	0.414(1)	0.076(9)
C(226)	0.461(2)	0.5657(9)	0.4259(9)	0.057(7)
C(101)	0.165(2)	0.5040(9)	0.3804(9)	0.059(8)
C(102)	0.219(2)	0.549(1)	0.360(1)	0.10(1)
C(103)	0.202(2)	0.603(1)	0.385(1)	0.09(1)
C(104)	0.140(2)	0.608(1)	0.423(1)	0.084(9)
C(105)	0.090(2)	0.565(1)	0.440(1)	0.11(1)
C(106)	0.101(2)	0.513(1)	0.4174(9)	0.068(8)
C(1)	0.170(2)	0.445(1)	0.3589(9)	0.070(8)
C(1′)	0.088(2)	0.418(1)	0.341(1)	0.073(9)
C(2)	0.204(2)	0.347(1)	0.3136(9)	0.065(8)
C(2′)	0.096(2)	0.364(1)	0.319(1)	0.09(1)
C(201)	0.221(2)	0.289(1)	0.288(1)	0.09(1)
C(202)	0.154(2)	0.244(1)	0.297(1)	0.087(9)
C(203)	0.173(3)	0.192(2)	0.270(1)	0.15(2)
C(204)	0.253(3)	0.183(2)	0.240(1)	0.15(1)
C(205)	0.320(3)	0.227(2)	0.233(1)	0.13(1)
C(206)	0.309(3)	0.280(1)	0.260(1)	0.11(1)

Table 6 (continued)

Atom	x	y	z	U_{eq} (Å^2)
Cl(1) [a]	−0.102(2)	0.526(1)	0.2639(9)	0.37(2)
C(01) [a]	0	0.581(5)	1/4	0.30(7)
Cl(21) [b]	0.826(2)	0.396(1)	0.323(1)	0.26(2)
Cl(22) [b]	0.862(2)	0.290(1)	0.352(1)	0.26(2)
C(02) [b]	0.742(9)	0.336(5)	0.349(4)	0.29(6)

[a] Site occupancy factor = 0.67(2). [b] Site occupancy factor = 0.5.

Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system [18] implemented by S.R. Hall; neutral atom complex scattering factors were employed [19]. Pertinent results are given in the Figures and Tables 4–8.

Abnormal features / variations in procedure

In **6**, the core hydrogen atom H(23) was located and refined in (x, y, z, U_{iso}).

In **9**, the crystal deteriorated substantially (approx. 25%) during data collection, with hindsight apparently as a result of solvent loss or reaction, with progressive loss/deterioration in the high angle data accessed; regrettably, no better material came to hand for recollection and accordingly the data already obtained was processed in the spirit that it was better than nothing. The resulting structure is sensible and unambiguous in the light of the associated chemistry and seemingly not disordered in spite of apparent loss of solvent: two independent CH_2Cl_2 molecules are found in the lattice, one located about a symmetry element. Site occupancy factors were estimated by refinement. In view of the limited quantity of data, anisotropic thermal parameters were refined for Ru, P, Cl only.

In **12**, residuals for the opposite hand were R 0.031, R_w 0.035.

Intensity data for **11** were measured at room temperature on an Enraf–Nonius CAD4 diffractometer fitted with Mo-K_α radiation, $\lambda = 0.7107$, with the ω–2θ scan technique. The data set was corrected for Lorentz and polarization effects and for absorption employing an analytical procedure [20] such that the maximum and minimum transmission factors were 0.695 and 0.594, respectively. Of the 7677 reflections measured, 7249 were unique and 3472 satisfied the $I \geq 2.5\sigma(I)$ criterion of observability and were used in the subsequent analysis. Relevant crystal data are listed in Table 4.

The structure of **11** was solved by direct methods [21] and refined by a full matrix least squares procedure based on F [20]. The Au, Ru and P atoms were refined anisotropically and the phenyl groups were modeled as hexagonal rigid groups; H atoms were included in the model at their calculated positions. After the inclusion of a weighting scheme of the form, $w = k/[\sigma^2(F) + |g|F^2]$, the refinement was continued until convergence. At convergence $R = 0.050$, $k = 2.02$, $g = 0.0011$ and $R_w = 0.054$. The maximum residual electron density peak in the final difference map was 1.44 e Å^{-3} located in the vicinity of the Au atom. Neutral scattering factors for Au and Ru (corrected for f' and f'') were from ref. 19 and those for the remaining atoms were as incorporated in SHELX76 [20]; all calcula-

Table 7

Non-hydrogen atomic coordinates for $AuRu_3(\mu_3\text{-}C_2Ph)(\mu\text{-dppm})(CO)_7\{P(C_6H_4Me\text{-}p)_3\}$ (11)

Atom	x	y	z
Au(1)	0.10210(2)	0.27648(6)	0.09970(3)
Ru(1)	0.1790(1)	0.2861(1)	0.2272(1)
Ru(2)	0.1229(1)	0.4052(1)	0.1917(1)
Ru(3)	0.1674(1)	0.3379(1)	0.1073(1)
P(1)	0.1742(1)	0.3170(3)	0.3266(2)
P(2)	0.1223(1)	0.4832(3)	0.2848(2)
P(3)	0.0633(1)	0.1693(4)	0.0550(2)
O(11)	0.1556(4)	0.0583(12)	0.2259(6)
O(12)	0.2498(4)	0.2252(12)	0.2380(7)
O(21)	0.0864(4)	0.2220(12)	0.2424(7)
O(22)	0.0667(3)	0.5356(12)	0.1366(7)
O(31)	0.1436(3)	0.4354(12)	−0.0092(7)
O(32)	0.1662(3)	0.0992(12)	0.0833(6)
O(33)	0.2390(4)	0.3375(12)	0.0808(6)
C(1)	0.1645(4)	0.4951(13)	0.1523(7)
C(2)	0.1762(4)	0.4283(12)	0.1914(7)
C(100)	0.1360(4)	0.3895(12)	0.3430(7)
C(11)	0.1656(4)	0.1467(15)	0.2295(8)
C(12)	0.2220(5)	0.2459(14)	0.2329(8)
C(21)	0.1024(5)	0.2892(16)	0.2242(9)
C(22)	0.0896(5)	0.4843(15)	0.1584(8)
C(31)	0.1513(5)	0.3951(15)	0.0353(8)
C(32)	0.1655(5)	0.1910(16)	0.0956(9)
C(33)	0.2107(5)	0.3389(16)	0.0905(8)
C(42)	0.2009(3)	0.6483(10)	0.1377(6)
C(43)	0.2067(3)	0.7493(10)	0.1151(6)
C(44)	0.1820(3)	0.8017(10)	0.0819(6)
C(45)	0.1516(3)	0.7532(10)	0.0713(6)
C(46)	0.1459(3)	0.6522(10)	0.0940(6)
C(41)	0.1705(3)	0.5997(10)	0.1272(6)
C(111)	0.1734(3)	0.1975(10)	0.3719(5)
C(112)	0.2015(3)	0.1345(10)	0.3708(5)
C(113)	0.2039(3)	0.0425(10)	0.4050(5)
C(114)	0.1783(3)	0.0134(10)	0.4404(5)
C(115)	0.1503(3)	0.764(10)	0.4415(5)
C(116)	0.1478(3)	0.1685(10)	0.4073(5)
C(121)	0.2061(3)	0.03943(9)	0.3659(5)
C(122)	0.2069(3)	0.3959(9)	0.4276(5)
C(123)	0.2298(3)	0.4588(9)	0.4588(5)
C(124)	0.2520(3)	0.5202(9)	0.4284(5)
C(125)	0.2512(3)	0.5186(9)	0.3668(5)
C(126)	0.2283(3)	0.4557(9)	0.3355(5)
C(211)	0.1456(3)	0.6043(10)	0.2975(4)
C(212)	0.1417(3)	0.6799(10)	0.2527(4)
C(213)	0.1578(3)	0.7775(10)	0.2581(4)
C(214)	0.1777(3)	0.7995(10)	0.3084(4)
C(215)	0.1815(3)	0.7239(10)	0.3532(4)
C(216)	0.1654(3)	0.6263(10)	0.3478(4)
C(222)	0.0805(3)	0.5964(12)	0.3591(7)
C(223)	0.0503(3)	0.6239(12)	0.3810(7)
C(224)	0.0216(3)	0.5780(12)	0.3569(7)
C(225)	0.0232(3)	0.5046(12)	0.3109(7)
C(226)	0.0534(3)	0.4772(12)	0.2890(7)

Table 7 (continued)

Atom	*x*	*y*	*z*
C(221)	0.0821(3)	0.5231(12)	0.3132(7)
C(312)	0.0255(3)	0.0187(12)	0.1186(7)
C(313)	0.0225(3)	−0.0715(12)	0.1538(7)
C(314)	0.0502(3)	−0.1315(12)	0.1700(7)
C(315)	0.0808(3)	−0.1014(12)	0.1510(7)
C(316)	0.0838(3)	−0.0112(12)	0.1158(7)
C(311)	0.0561(3)	0.0488(12)	0.0996(7)
C(317)	0.0476(7)	−0.2268(21)	0.2087(12)
C(322)	0.0048(4)	0.2047(12)	−0.0099(7)
C(323)	−0.0270(4)	0.2448(12)	−0.0163(7)
C(324)	−0.0394(4)	0.3085(12)	0.0279(7)
C(325)	−0.0200(4)	0.3321(12)	0.0785(7)
C(326)	0.0118(4)	0.2920(12)	0.0849(7)
C(321)	0.0242(4)	0.2283(12)	0.0407(7)
C(327)	−0.0720(8)	0.3721(31)	0.0134(15)
C(331)	0.0743(3)	0.1128(10)	−0.0144(6)
C(332)	0.0591(3)	0.0216(10)	−0.0372(6)
C(333)	0.0649(3)	−0.0115(10)	−0.0946(6)
C(334)	0.0859(3)	0.0466(10)	−0.1291(6)
C(335)	0.1011(3)	0.1378(10)	−0.1063(6)
C(336)	0.0954(3)	0.1710(10)	−0.0489(6)
C(337)	0.0930(6)	0.0110(21)	−0.1932(11)

Table 8

Non-hydrogen atomic coordinates and equivalent isotropic thermal parameters for $Ru_2(\mu\text{-}I)(\mu\text{-}dppm)(\mu\text{-}C_2Ph)(CO)_4$ (**12**)

Atom	*x*	*y*	*z*	*U*
I	0.00016(3)	−0.04541(4)	0.00011(4)	0.0531(2)
Ru(1)	0.07401(3)	0.13433(4)	0.12190(3)	0.0355(2)
Ru(2)	0.08360(3)	0.12353(4)	−0.01947(3)	0.0346(2)
C(11)	0.1393(4)	0.0170(6)	0.2019(5)	0.052(3)
O(11)	0.1804(3)	−0.0500(5)	0.2496(4)	0.076(3)
C(12)	0.0249(4)	0.1655(7)	0.1763(4)	0.052(3)
O(12)	−0.0069(3)	0.1903(6)	0.2045(4)	0.088(4)
C(21)	0.0698(4)	0.0974(7)	−0.1305(4)	0.052(3)
O(21)	0.0655(3)	0.0759(6)	−0.1936(4)	0.083(3)
C(22)	0.1543(3)	0.0095(6)	0.0420(5)	0.047(3)
O(22)	0.1957(3)	−0.0627(5)	0.0761(4)	0.069(3)
P(1)	0.15293(8)	0.2877(1)	0.1869(1)	0.0346(6)
C(111)	0.2172(3)	0.2678(5)	0.3004(4)	0.037(2)
C(112)	0.1935(4)	0.2414(8)	0.3558(4)	0.061(4)
C(113)	0.2389(4)	0.235(1)	0.4434(5)	0.080(5)
C(114)	0.3072(4)	0.2454(9)	0.4785(5)	0.074(5)
C(115)	0.3318(4)	0.274(1)	0.4258(5)	0.078(5)
C(116)	0.2872(3)	0.2808(9)	0.3370(4)	0.064(4)
C(121)	0.1213(3)	0.4427(5)	0.1888(4)	0.042(3)
C(122)	0.0528(4)	0.4711(6)	0.1379(5)	0.056(3)
C(123)	0.0298(4)	0.5907(7)	0.1365(5)	0.068(4)
C(124)	0.0762(5)	0.6799(7)	0.1879(5)	0.071(4)
C(125)	0.1444(5)	0.6510(7)	0.2402(5)	0.069(4)
C(126)	0.1672(4)	0.5322(6)	0.2419(5)	0.055(3)
C(0)	0.2057(3)	0.3074(6)	0.1385(4)	0.039(3)
P(2)	0.15887(8)	0.2848(1)	0.0202(1)	0.0359(6)
C(211)	0.2281(3)	0.2724(6)	−0.0009(4)	0.045(3)

Table 8 (continued)

Atom	*x*	*y*	*z*	*U*
C(212)	0.2423(3)	0.1618(7)	−0.0275(4)	0.049(3)
C(213)	0.2958(4)	0.1551(8)	−0.0425(5)	0.065(4)
C(214)	0.3339(4)	0.2564(9)	−0.0320(5)	0.072(5)
C(215)	0.3211(5)	0.3669(9)	−0.0053(7)	0.085(6)
C(216)	0.2675(4)	0.3758(7)	0.0078(6)	0.071(5)
C(221)	0.1230(3)	0.4344(6)	−0.0258(4)	0.041(3)
C(222)	0.1296(4)	0.5373(6)	0.0227(4)	0.053(3)
C(223)	0.0983(5)	0.6481(6)	−0.0178(6)	0.066(4)
C(224)	0.0621(5)	0.6580(7)	−0.1044(6)	0.067(4)
C(225)	0.0562(4)	0.5580(7)	−0.1528(5)	0.059(4)
C(226)	0.0860(4)	0.4459(6)	−0.1145(4)	0.051(3)
C(1)	−0.0052(3)	0.2700(6)	−0.0619(4)	0.044(3)
C(2)	0.0214(3)	0.2396(6)	0.0152(4)	0.040(3)
C(101)	−0.0527(3)	0.3363(6)	−0.1394(4)	0.047(3)
C(102)	−0.0693(4)	0.2977(9)	−0.2201(5)	0.070(4)
C(103)	−0.1158(5)	0.365(1)	−0.2914(6)	0.093(6)
C(104)	−0.1446(5)	0.470(1)	−0.2831(7)	0.107(7)
C(105)	−0.1313(5)	0.507(1)	−0.2057(7)	0.096(6)
C(106)	−0.0846(4)	0.4388(9)	−0.1346(6)	0.076(5)
Cl(1)	0.2881(2)	−0.3083(4)	0.2013(4)	0.211(4)
Cl(2)	0.3770(3)	−0.4962(5)	0.2254(5)	0.244(5)
C	0.3645(9)	−0.357(1)	0.259(1)	0.172(9)

tions were performed on a SUN4/280 computer system. The numbering scheme, shown in Fig. 3, was drawn with ORTEP [22] at 15% probability ellipsoids.

Supplementary material (available from the authors) comprises thermal parameters, H atom parameters, all bond distances and angles, and listings of the observed and calculated structure factor amplitudes.

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