

## CLUSTER CHEMISTRY

### LI \*. REACTIONS OF SOME SUBSTITUTED RUTHENIUM AND OSMIUM CLUSTER CARBONYLS WITH DIHYDROGEN. X-RAY CRYSTAL STRUCTURES OF $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPh})(\text{CO})_8(\text{PMePh}_2)$ , $\text{Ru}_4(\mu\text{-H})_4(\mu\text{-dppm})(\text{CO})_{10}$ , $\text{Ru}_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_{10}$ AND $\text{Os}_3(\mu\text{-H})_2(\mu\text{-dppm})(\text{CO})_8$

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### Summary

The reactions of dihydrogen (80°C, 20 bar, 2 h) with a series of tertiary phosphine and phosphite complexes  $\text{Ru}_3(\text{CO})_{12-n}(\text{L})_n$  ( $\text{L} = \text{PMe}_3$ ,  $\text{PPh}_3$ ,  $\text{PPh}(\text{OMe})_2$  or  $\text{P}(\text{OMe})_3$ ;  $n = 1-3$ ), and with complexes containing *dppm*, *dppe*, *dpam* and  $\text{PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2-2)$  have been studied. Complexes containing monodentate ligands gave tetranuclear complexes  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12-n}(\text{L})_n$  ( $n = 0-3$ , but not 4), whereas complexes with bidentate ligands showed varying behaviour. Thus  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$  gave  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_9$ , further hydrogenation of which afforded  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPh})(\text{CO})_8(\text{PMePh}_2)$ .  $\text{Ru}_3(\mu\text{-dppe})(\text{CO})_{10}$  gave a mixture of  $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{CH}_2\text{PPh}_2)(\text{CO})_9$  and  $\text{Ru}_4(\mu\text{-H})_4(\mu\text{-dppe})(\text{CO})_{10}$  as the major products, and  $\text{Ru}_3(\mu\text{-}\eta^2\text{-P-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2)(\text{CO})_{10}$  gave a mixture of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12-n}\{\text{PPh}_2(\text{C}_6\text{H}_4\text{Et}-2)\}_n$  ( $n = 0$  and 1). Pyrolysis of  $\text{Ru}_4(\mu\text{-H})_4(\mu\text{-dppm})(\text{CO})_{10}$  afforded  $\text{Ru}_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu\text{-CO})_2(\text{CO})_8$ . The molecular structures of  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPh})(\text{CO})_8(\text{PMePh}_2)$ ,  $\text{Ru}_4(\mu\text{-H})_4(\mu\text{-dppm})(\text{CO})_{10}$  and  $\text{Ru}_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu\text{-CO})_2(\text{CO})_8$  have been determined: 2286, 4930 and 6393 data ( $I \geq 2.5\sigma(I)$ ) were refined to  $R$  and  $R_w$  values of 0.032 and 0.037, 0.026 and 0.035, and 0.043 and 0.053, respectively. Hydrogenation of  $\text{Os}_3(\mu\text{-dppm})(\text{CO})_{10}$  gave  $\text{Os}_3(\mu\text{-H})_2(\mu\text{-dppm})(\text{CO})_8$ , whose structure was also determined: 3367 data with  $I \geq 2.5\sigma(I)$  were refined to  $R$  0.044,  $R_w$  0.052.

\* For Part L, see ref. 42.

## Introduction

Interest in metal cluster complexes as potential homogeneous catalysts has necessitated examination of their reactions under conditions where they might be expected to display catalytic activity. Under CO, or in the presence of many Lewis bases, the simpler clusters tend to fragment, while in the presence of hydrogen, several types of behaviour have been found. Thus,  $\text{Ru}_3(\text{CO})_{12}$  reacts readily in refluxing octane to give high yields of the tetranuclear derivative,  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  [1]. The osmium analogue forms initially the unsaturated cluster hydride,  $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ ; prolonged treatment with hydrogen is required to generate  $\text{Os}_4(\mu\text{-H})_4(\text{CO})_{12}$  [1].

When the Group 8 cluster carbonyls contain other Lewis bases as ligands, the additional possibility of reaction of the ligand, activated by coordination to the cluster, is recognised. Hydrogenation of  $\text{Ru}_3(\text{CO})_{11}(\text{CNBu}^t)$ , for example, not only gave the series  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12-n}(\text{CNBu}^t)_n$  ( $n = 0-2$ ), but also the formimidoyl complexes  $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-HC=NBu}^t)(\text{CO})_9$  and  $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-HC=NBu}^t)(\text{CO})_8(\text{CNBu}^t)$  [2]. The hydrogenation of benzonitrile in the presence of  $\text{M}_3(\text{CO})_{12}$  ( $\text{M} = \text{Fe}$  or  $\text{Ru}$ ) is instructive in this regard, affording  $\text{Ru}_3(\mu\text{-H})(\mu\text{-N=CHPh})(\text{CO})_{10}$  and  $\text{Ru}_3(\mu\text{-H})(\mu\text{-NHCH}_2\text{Ph})(\text{CO})_{10}$ , together with  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  and benzylamine [3].

The reactivity of Group 15 ligands coordinated to Group 8 cluster carbonyls was early demonstrated in the reaction of  $\text{Os}_3(\text{CO})_{12}$  with  $\text{PPh}_3$ , from which a variety of trinuclear complexes formed by P-C bond cleavage reactions, and in one case, C-C bond formation, were isolated and characterised by X-ray crystallography [4,5]. A predominance of related but binuclear complexes was found in similar reactions of  $\text{Ru}_3(\text{CO})_{12}$  [6]. The subject has been reviewed [7] and consideration of the results reported so far suggests that although the P-C bond cleavage reactions occur readily, elimination of the alkyl or aryl group so formed only occurs in the presence of hydride ligands when intra- or inter-molecular reductive elimination (of alkane or arene) can occur.

In an effort to prevent the breakdown of the metal cluster core, bidentate ligands (L-L) such as  $\text{CH}_2(\text{PPh}_2)_2$  (dppm) or  $\text{CH}_2(\text{AsPh}_2)_2$  (dpam) have been used to bridge one or two of the Ru-Ru bonds in complexes such as  $\text{Ru}_3(\mu\text{-L-L})(\text{CO})_{10}$  or  $\text{Ru}_3(\mu\text{-L-L})_2(\text{CO})_8$ . However, hydrogenation results in modification of the Group 15 ligand by loss of a phenyl group (as benzene) with concomitant capping of one or both sides of the  $\text{Ru}_3$  triangle in the resulting complexes  $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-EPhCH}_2\text{-EPh}_2)(\text{CO})_9$  or  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-EPhCH}_2\text{EPh}_2)_2(\text{CO})_6$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) [8,9]. Similarly, reaction of  $\text{Ru}_3(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_9$  with  $\text{H}_2$  afforded the phosphinidene cluster,  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPh})(\text{CO})_9$ , with loss of benzene [10,11]. Several other workers have noted the reactivity of phosphido-bridged systems under reducing conditions, which may affect their performance as catalysts in these reactions.

The availability of a range of Group 15-ligand substituted derivatives of  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$  from electron transfer-catalysed substitution reactions of the parent carbonyls [12] prompted a study of their reactions with hydrogen. Representative examples of complexes containing monodentate and bidentate ligands were chosen and, after some preliminary studies, were hydrogenated under standard, mild conditions. This paper reports the results of our studies: we show that monodentate tertiary phosphine or phosphite derivatives afford a range of tetra-

nuclear complexes without P–C bond cleavage, whereas bidentate ligands undergo ready cleavage of aryl groups to give phosphido and phosphinidene ligands. In addition, the X-ray structures of four complexes isolated during this work,  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPh})(\text{CO})_8(\text{PMePh}_2)$ ,  $\text{Ru}_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_{10}$ ,  $\text{Ru}_4(\mu\text{-H})_4(\mu\text{-dppm})(\text{CO})_{10}$  and  $\text{Os}_3(\mu\text{-H})_2(\mu\text{-dppm})(\text{CO})_8$ , are described. Some of this work has been reported in a preliminary communication [9] \*; some independent studies by other groups are referenced in this account.

## Results

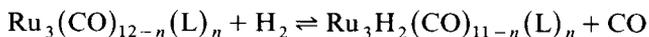
### *Complexes containing monodentate ligands*

Solutions of the complexes  $\text{Ru}_3(\text{CO})_{12-n}(\text{L})_n$  ( $\text{L} = \text{PMe}_3, \text{PPh}_3, \text{PPh}(\text{OMe})_2, \text{P}(\text{OMe})_3$ ;  $n = 1-3$  in each case) in cyclohexane solution were hydrogenated (20 atm,  $80^\circ\text{C}$ , 2 h), and the products were separated by preparative thin layer chromatography (TLC). The yellow complexes so formed were readily identified as the tetranuclear derivatives  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12-n}(\text{L})_n$ , as detailed in Table 1 and in the Experimental section. Where these complexes were new, they were also made and characterised by appropriate reactions between  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  and L.

In all cases, mixtures of complexes were obtained; the percentage yields quoted in Table 1 relate to isolated, pure material. In four cases, amounts of the trinuclear precursors were recovered. However, we had no evidence of the formation of any complexes containing modified ligands, for example, by P–C or P–O bond cleavage, except possibly in the case of the  $\text{P}(\text{OMe})_3$  complexes, where the reaction mixtures were found to contain other complexes in trace amounts only; these were not investigated further.

Interpretation of these results is complicated by the following features:

- (i) disproportionation of mixtures of  $\text{Ru}_3(\text{CO})_{12}$  [13] or  $\text{Ru}_3(\text{CO})_{11}\{\text{P}(\text{OMe})_3\}$  with  $\text{Ru}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_3$  gives  $\text{Ru}_3(\text{CO})_{12-n}\{\text{P}(\text{OMe})_3\}_n$  ( $n = 1-3$ ) on heating;
- (ii) under the same conditions; disproportionation of mixtures of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12-n}(\text{L})_n$  also occurs;
- (iii) exchange of CO between  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Ru}_3(\text{CO})_{12}$ , but not apparently of one metal for another occurs [13], although both  $\text{Fe}_2\text{Ru}(\text{CO})_{11}\{\text{P}(\text{OMe})_3\}$  and  $\text{FeRu}_2(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2$  are formed by heating a mixture of  $\text{Fe}_3(\text{CO})_{12}$  and  $\text{Ru}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_3$ , suggesting that the tertiary phosphite does not migrate from ruthenium to iron [13];
- (iv) disproportionation of mixtures of  $\text{Ru}_3(\text{CO})_{12}$  and  $\text{Os}_3(\text{CO})_{12}$  to give  $\text{Ru}_n\text{Os}_{3-n}(\text{CO})_{12}$  occurs on heating [14];
- (v) direct, reversible substitution of 2H for CO is well-established for several metal cluster complexes, and although we have not observed the reaction



it is reasonable to consider that reactions of this type are among the first to occur under hydrogenation conditions. The extent to which similar substitution of L by  $\text{H}_2$ , and also by CO, might occur under these conditions could not be determined.

\* Unfortunately this communication was processed and published as a full paper.

TABLE 1

PRODUCTS FROM REACTIONS OF  $\text{Ru}_3(\text{CO})_{12-n}(\text{L})_n$  WITH  $\text{H}_2$ 

L	n	$\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12-n}(\text{L})_n$				
		n = 0	1	2	3	4
P(OMe) <sub>3</sub>	1	7.1	57.9	4.0	n.d.	n.d.
	2	0.5	14.9	50.5	2.7	n.d.
	3 <sup>a</sup>	n.d.	n.d.	12.3	11.5	2.7
PMe <sub>3</sub>	1 <sup>b</sup>	2.8	67.6	13.4	n.d.	n.d.
	2 <sup>c</sup>	n.d.	n.d.	55.8	1.7	n.d.
	3 <sup>d</sup>	n.d.	n.d.	49.3	n.d.	n.d.
PPh(OMe) <sub>2</sub>	1	4.4	69.9	5.2	1.2	n.d.
	2	n.d.	34.2	43.9	10.4	n.d.
	3	n.d.	2.2	28.1	21.5	n.d.
PPh <sub>3</sub>	1	4.9	67.0	7.8	n.d.	n.d.
	2	1.7	62.8	10.8	n.d.	n.d.
	3	n.d.	n.d.	64.3	n.d.	n.d.

<sup>a</sup> 17.9%  $\text{Ru}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_3$  recovered. <sup>b</sup> 5.6%  $\text{Ru}_3(\text{CO})_{11}(\text{PMe}_3)$  recovered. <sup>c</sup> 33.3%  $\text{Ru}_3(\text{CO})_{10}(\text{PMe}_3)_2$  recovered. <sup>d</sup> 43.5%  $\text{Ru}_3(\text{CO})_9(\text{PMe}_3)_3$  recovered. n.d. = not detected.

Our results, therefore, show that hydrogenation of  $\text{Ru}_3(\text{CO})_{12-n}(\text{L})_n$  is not a viable synthetic route to complexes  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12-n}(\text{L})_n$ , since we find that mixtures of products are obtained. The route of choice remains the radical-ion initiated stoichiometric substitution of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  or its derivatives [12]. Nor do our results do any more than suggest possible courses of the cluster formation, although we favour initial oxidative addition of  $\text{H}_2$  to the substituted cluster followed by cleavage of one of the Ru–Ru bonds to give mono- or binuclear intermediates which can then reaggregate to the tetranuclear complexes. However, the mononuclear fragments might be expected rapidly to form stable mononuclear dihydrido complexes, which were not detected in the reaction mixtures.

### Complexes containing bidentate ligands

#### (i) Derivatives of *dppm*, *dppe* and *dpam*

As mentioned above, reactions of complexes  $\text{Ru}_3(\text{CO})_{12-n}(\text{L-L})_n$  ( $n = 1$  or  $2$ ) with  $\text{H}_2$  result in loss of arene and formation of derivatives containing  $\mu_3\text{-EPhCH}_2\text{EPh}_2$  ( $\text{E} = \text{P}$  or  $\text{As}$ ) ligands [8,9]. More recently, similar reactions of  $\text{Fe}_2(\text{CO})_9$  with  $\text{PR}_2\text{CH}_2\text{PHR}$  ( $\text{R} = \text{Me}$ ,  $\text{Pr}^i$ ,  $\text{CH}_2\text{Ph}$ ) to give  $\text{Fe}_3$  clusters containing similar  $\mu_3\text{-PRCH}_2\text{PR}_2$  ligands has been described [15]. Pyrolysis of cluster hydrides containing  $\mu_3\text{-SR}$  ligands also results in alkane or arene loss [16].

We have now found that prolonged treatment of  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$  (**1**) or  $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_9$  (**2**) with dihydrogen results in the formation of  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPh})(\text{CO})_8(\text{PMePh}_2)$  (**3**). The complex, which forms yellow crystals, exhibits a six-band  $\nu(\text{CO})$  pattern, while the  $^1\text{H}$  NMR contains the expected doublet at  $\delta$  2.14 for the  $\text{PMePh}_2$  ligand, higher field doublets at  $\delta$  –18.7 and –18.9, and aromatic resonances between  $\delta$  7.3–8.2. The compound was fully characterised by an X-ray structure determination (Fig. 1); further discussion is not

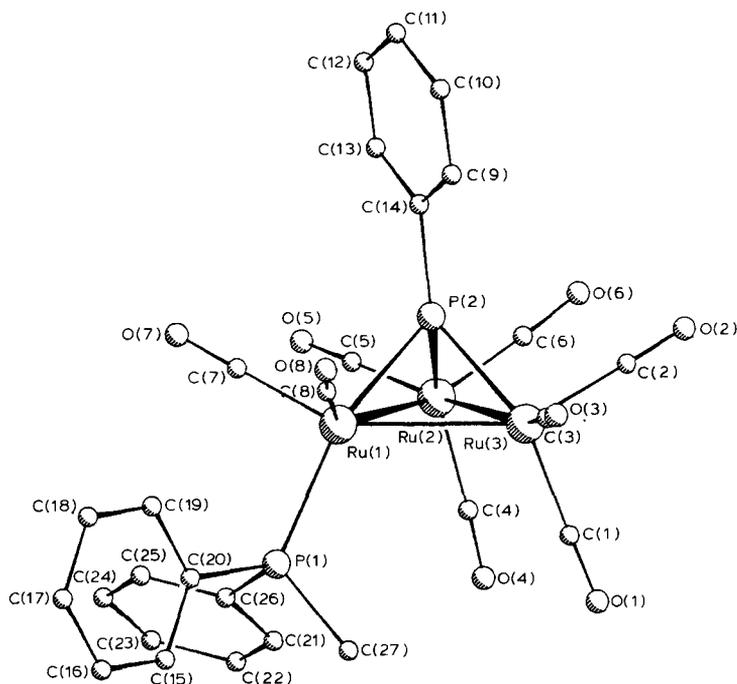


Fig. 1 A molecule of  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPh})(\text{CO})_8(\text{PMePh}_2)$  (**3**), showing atom numbering scheme.

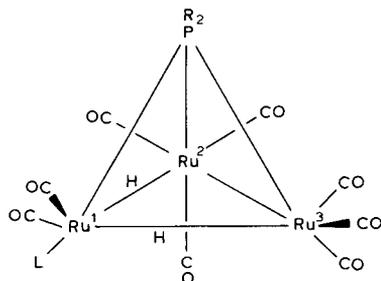
warranted, as there are no significant differences in the major structural parameters of **3** and of previously studied examples (Table 2).

Formation of **3** occurs by addition of 2H to the cluster and to the bridging methylene of the  $\mu_3\text{-PPhCH}_2\text{PPh}_2$  ligand in the precursor **2** to give a  $\text{PMePh}_2$  ligand; the resulting cleavage of the P–C bond generates a phenyl-phosphinidene ligand which caps the  $\text{Ru}_3$  core. Similar complexes have been obtained from  $\text{Ru}_3(\text{CO})_{12}$  and primary phosphines [17,18] and by pyrolysis of  $\text{Fe}_3(\mu\text{-H})(\mu_3\text{-PRCH}_2\text{PR}_2)(\text{CO})_9$  (R = Me, Pr<sup>1</sup>,  $\text{CH}_2\text{Ph}$ ) [15].

Hydrogenation of  $\text{Ru}_3(\text{CO})_{10}(\text{dppe})$  (**4**) afforded two complexes,  $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{CH}_2\text{PPh}_2)(\text{CO})_9$  (**5**) and  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dppe})$  (**6**), in 34 and 23% yields, respectively. The  $\text{Ru}_3$  complex thus shows behaviour common to derivatives containing both mono- and bi-dentate tertiary phosphines, which may be related to the weaker attachment of the ligand containing a four-atom P–C–C–P backbone. It is known that ready isomerisation of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dppe})$  (**6a**) (containing a chelating dppe ligand) to  $\text{Ru}_4(\mu\text{-H})_4(\mu\text{-dppe})(\text{CO})_{10}$  (**6b**) (in which the dppe bridges a metal–metal bond) occurs [19,20]; under hydrogen, presumably  $\text{H}_2$  adds to the vacant coordination site left by dissociation of one arm of the bidentate ligand in the first step towards formation of the tetranuclear complex.

In agreement with this, hydrogenation of  $\{\text{Ru}_3(\text{CO})_{11}\}_2(\mu\text{-dppe})$  (**7**) [21] affords  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  (39%) and  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dppe})$  (37%) as the major products, accompanied by smaller amounts of  $\{\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11}\}_2(\mu\text{-dppe})$  (**8**) and  $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{CH}_2\text{PPh}_2)(\text{CO})_9$  (**5**). The bis-trinuclear complex thus behaves quite similarly to other complexes containing monodentate tertiary phosphines.

TABLE 2

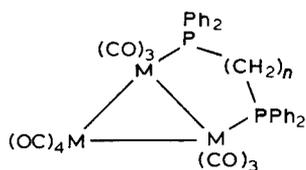
STRUCTURAL PARAMETERS FOR  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPh})(\text{CO})_8(\text{L})$ 

L =	$\text{PMePh}_2^a$	$\text{PPh}_3^b$	$\text{CO}^c$	$\text{CO}^d$	
R =	Ph	Ph	$\text{P}(\text{C}_6\text{H}_4\text{OMe-4})$	Ph	
<i>Bond lengths</i> (Å)					
Ru(1)–Ru(2)	2.934(1)	2.959(1)	2.937(2)	2.932(3)	2.938(3)
Ru(1)–Ru(3)	2.942(1)	2.958(1)	2.928(2)	2.939(3)	2.947(3)
Ru(2)–Ru(3)	2.841(1)	2.842(1)	2.844(2)	2.849(3)	2.842(3)
Ru(1)–P(1)	2.366(2)	2.408(1)	–	–	–
Ru(1)–P(2)	2.310(2)	2.304(1)	2.320(4)	2.329(5)	2.333(5)
Ru(2)–P(2)	2.296(2)	2.282(1)	2.275(4)	2.288(5)	2.296(5)
Ru(3)–P(2)	2.303(2)	2.284(1)	2.273(4)	2.278(5)	2.279(5)
Ru–CO (av)	1.906	1.916	1.94	1.939	1.918
range	1.894–1.937	1.892–1.961	1.89–2.05	1.895–1.985	1.867–1.969
<i>Bond angles</i> (°)					
Ru(2)–Ru(1)–P(1)	112.2(1)	117.1(1)			
Ru(3)–Ru(1)–P(1)	114.7(1)	119.5(1)			
P(2)–Ru(1)–P(1)	160.0(1)	164.8(1)			

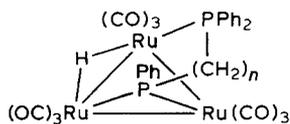
<sup>a</sup> This work. <sup>b</sup> Ref. 41. <sup>c</sup> Ref 17. <sup>d</sup> Ref 18; values for two independent molecules given.

The reaction between  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  and dppm in cyclohexane at 40°C afforded orange  $\text{Os}_3(\text{CO})_{10}(\text{dppm})$  (**9**) in 54% yield. The complex was readily identified by elemental microanalysis and spectroscopic data. The IR  $\nu(\text{CO})$  spectrum closely resembles that of **1**. In a recent report [22] it has been shown that **9** can be obtained in comparable yields to the above by the treatment of a benzene solution of an equimolar mixture of  $\text{Os}_3(\text{CO})_{12}$  and dppm with  $\text{Me}_3\text{NO}\cdot 2\text{H}_2\text{O}$  (2 equiv.) in methanol at 60°C.

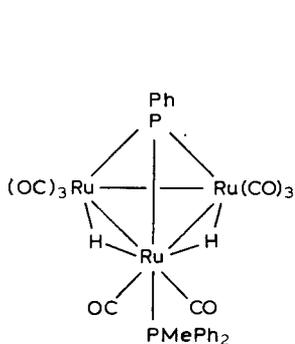
This complex exhibits some interesting reactions. On heating, it forms the cyclometallated complex  $\text{Os}_3(\mu\text{-H})\{\mu_3\text{-PPh}_2\text{CH}_2\text{PPh}(\text{C}_6\text{H}_4)\}(\text{CO})_8$  (**10**) [22]. This reaction differs from that undergone by the ruthenium analogue **1**, which on heating in refluxing cyclohexane, loses benzene to give the cyclometallated dephenylated complex **11** [23,24]. The reaction between **10** and  $\text{H}_2$  in toluene at 80°C produces  $\text{Os}_3(\mu\text{-H})_2(\mu\text{-dppm})(\text{CO})_8$  (**12**) [25], which we obtained directly from  $\text{Os}_3(\mu\text{-dppm})(\text{CO})_{10}$  and dihydrogen under our standard reaction conditions. Solutions of this red complex showed five  $\nu(\text{CO})$  bands between 2080–1955  $\text{cm}^{-1}$ , while in the  $^1\text{H}$  NMR spectrum, the metal-bonded protons resonate at  $\delta$  –10.3, other resonances at  $\delta$  4.15 and 7.3 being assigned to the  $\text{CH}_2$  and Ph protons, respectively. The complex is a further example of a tertiary-phosphine substituted derivative of



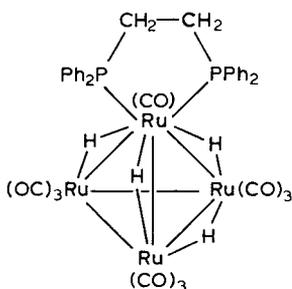
	M	n
1	Ru	1
4	Ru	2
9	Os	1



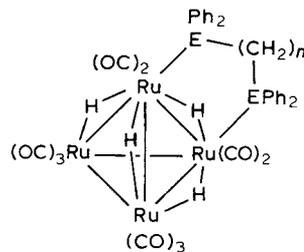
(2, n = 1 ;  
5, n = 2 )



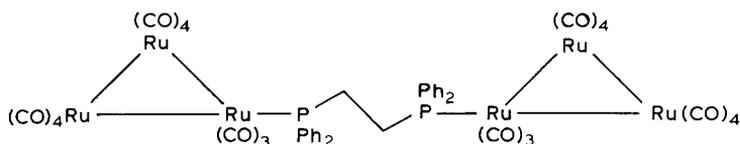
(3)



(6a)



	E	n
6b	P	2
13	P	1
14	As	1

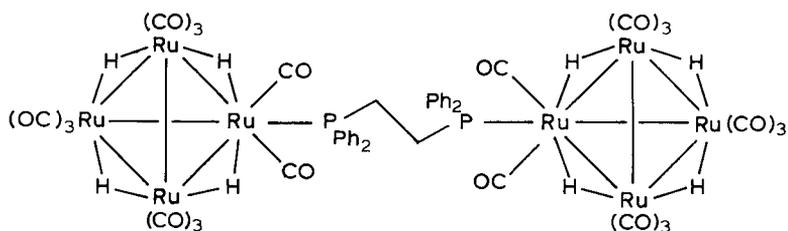


(7)

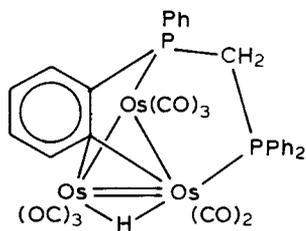
$\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ , of which  $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\text{PPh}_3)$  has been structurally characterised previously [26]. We have determined the molecular structure of **12** (Fig. 2); however, the result is not significantly different from the earlier, independent, determination [25] and merits no further discussion. The shortest Os–Os bond (2.681(1) Å) is bridged by both hydrogens and the dppm ligand.

#### (ii) Tetranuclear ruthenium complexes

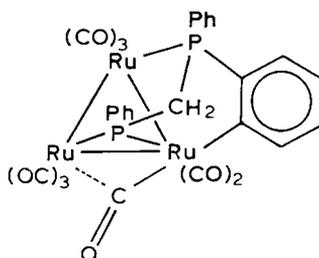
Several tertiary phosphine and phosphite derivatives of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  were prepared independently in the course of identifying these complexes among the products of hydrogenation of complexes  $\text{Ru}_3(\text{CO})_{12-n}(\text{L})_n$ . These complexes ex-



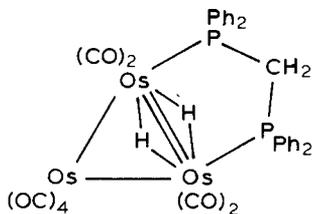
(8)



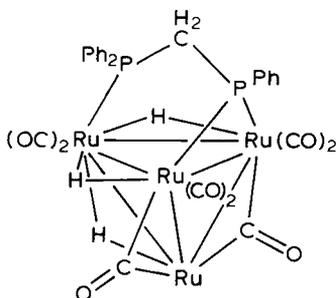
(10)



(11)



(12)



(15)

hibited no special features, and full details of their preparation and characterisation are given in the Experimental section.

We have also examined the synthesis and pyrolytic behaviour of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{L-L})$  ( $\text{L-L} = \text{dppm}, \text{dpam}$ ). The addition of the initiator solution to a stoichiometric mixture of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  and  $\text{L-L}$  ( $\text{L-L} = \text{dppm}, \text{dpam}$ ) afforded the new complexes  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{L-L})$  ( $\text{L-L} = \text{dppm}$  (**13**),  $\text{dpam}$  (**14**)) after crystallisation. These complexes were identified by the usual methods. The  $^1\text{H}$  NMR spectra of **13** and **14** each contained a high-field resonance (of relative intensity 4), at  $\delta -16.72$  and  $\delta -17.00$  respectively, assigned to metal bridging hydrides, and a broad multiplet (of relative intensity 20) at  $\delta 7.20$  and  $\delta 7.31$  respectively assigned to phenyl groups. The methylene ( $\text{CH}_2$ ) protons were shown

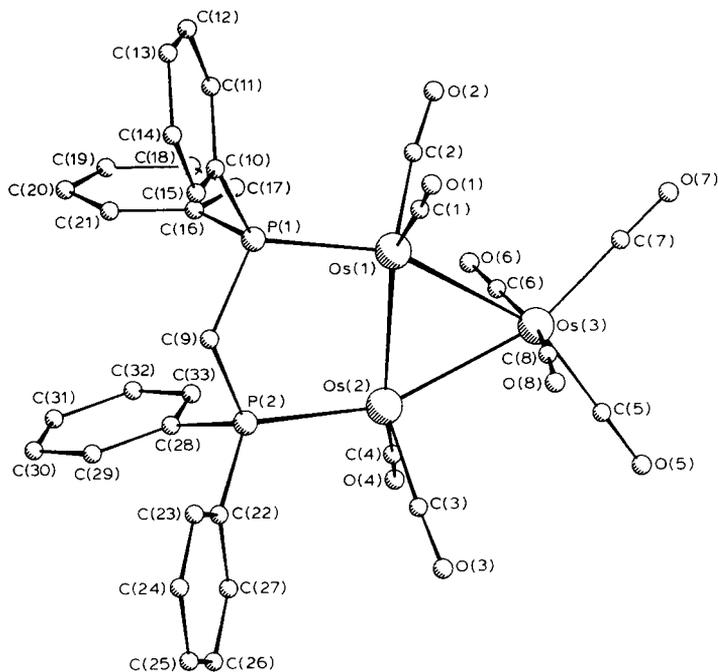


Fig. 2 A molecule of  $\text{Os}_3(\mu\text{-H})_2(\mu\text{-dppm})(\text{CO})_8$  (**12**), showing atom numbering scheme. Significant bond distances: Os(1)–Os(2) 2.681(1), Os(1)–Os(3) 2.815(1), Os(2)–Os(3) 2.823(1), Os(1)–P(1) 2.316(5), Os(2)–P(2) 2.349(5), P(1)–C(9) 1.839(21), P(2)–C(9) 1.829(20) Å. Angles: Os(1)–Os(2)–Os(3) 61.5(1), Os(2)–Os(1)–Os(3) 61.8(1), Os(1)–Os(3)–Os(2) 56.8(1), Os(2)–Os(1)–P(1) 93.5(1), Os(1)–Os(2)–P(2) 95.5(1), Os(1)–P(1)–C(9) 109.1(7), Os(2)–P(2)–C(9) 109.7(7), P(1)–C(9)–P(2) 113.9(9)°

to be magnetically inequivalent; for **13** a complex signal at  $\delta$  3.80 was the AB portion of an  $\text{ABX}_2$  system (where  $\text{X}_2$  are the two phosphorus nuclei) while for **14** an AB quartet at  $\delta$  3.37 ( $J(\text{AB})$  12 Hz) was observed.

It has been shown that there are two isomers of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dppe})$  [19,20]; complex **6a** in which the tertiary phosphine chelates one of the ruthenium atoms, and complex **6b** in which the dppe ligand bridges the Ru(1)–Ru(2) vector. Similar alternatives can be proposed for complexes **13** and **14**, therefore an X-ray diffraction study was performed on complex **13**.

The crystal is composed of discrete molecules with no unusually short intermolecular contacts shorter than Van der Waals separations. The molecular structure of **13**, which is shown in Fig. 3 (see also Table 3), is based upon a distorted tetrahedral  $\text{Ru}_4$  core with the dppm ligand spanning the hydride-bridged Ru(1)–Ru(2) vector (2.987(1) Å) in a similar manner to **6b** [19]. Each of the phosphorus atoms is attached to the cluster via normal 2e-donor bonds (Ru(1)–P(1) 2.360(1), Ru(2)–P(2) 2.337(1) Å). The ten CO ligands are all in terminal positions and are distributed two to each of the dppm-bridged Ru atoms and three each to the other two metal atoms. The Ru–Ru distances fall into two groups, four long hydride-bridged vectors (mean 2.960(1) Å) and two shorter unbridged Ru–Ru bonds (mean 2.777(1) Å). The four hydride ligands, which were located and refined in the X-ray study, are arranged such that the  $\text{Ru}_4(\mu\text{-H})_4$  core has configuration A with idealized  $C_2$  symmetry. This

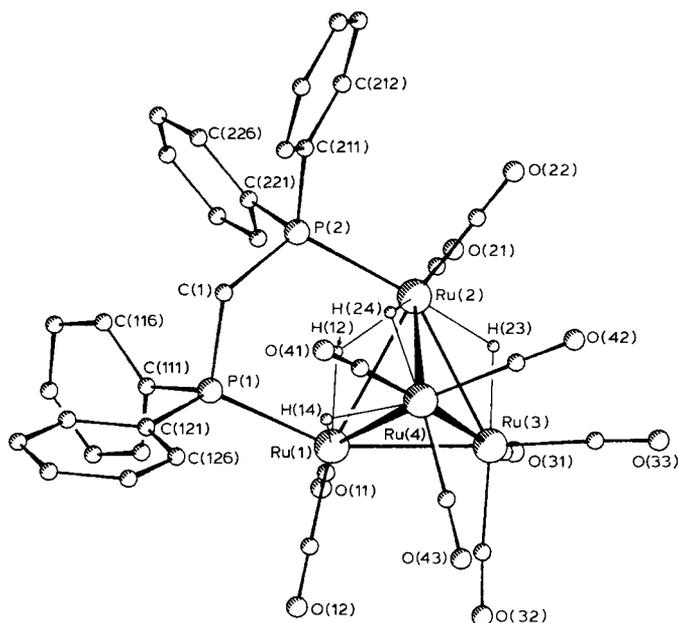


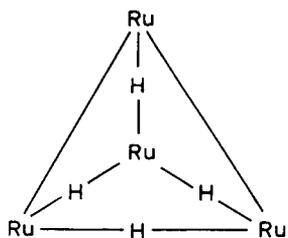
Fig. 3. A molecule of  $\text{Ru}_4(\mu\text{-H})_4(\mu\text{-dppm})(\text{CO})_{10}$  (**13**), showing atom numbering scheme.

arrangement is similar to that observed for complexes **6a** and **6b** but is unlike the  $D_{2d}$  core symmetry **B** observed for  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  [27],  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11}(\text{P}(\text{OMe})_3)$  [28] and  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{PPh}_3)_2$  [27,29].

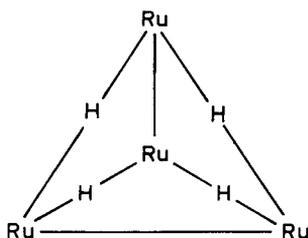
TABLE 3

STRUCTURAL PARAMETERS FOR  $\text{Ru}_4(\mu\text{-H})_4(\mu\text{-dppm})(\text{CO})_{10}$  (**13**)

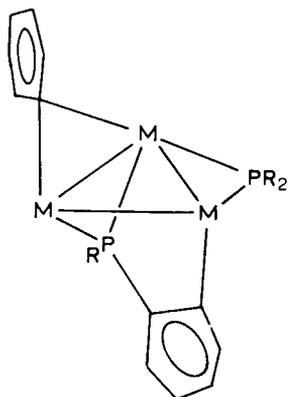
<i>Bond distances (Å)</i>			
Ru(1)–Ru(2)	2.987(1)	Ru(1)–H(12)	1.72(4)
Ru(1)–Ru(3)	2.777(1)	Ru(1)–H(14)	1.79(2)
Ru(1)–Ru(4)	2.935(1)	Ru(2)–H(12)	1.72(5)
Ru(2)–Ru(3)	2.937(1)	Ru(2)–H(23)	1.64(3)
Ru(2)–Ru(4)	2.981(1)	Ru(2)–H(24)	1.81(3)
Ru(3)–Ru(4)	2.776(1)	Ru(3)–H(23)	1.75(2)
Ru(1)–P(1)	2.360(1)	Ru(4)–H(14)	1.79(2)
Ru(2)–P(2)	2.337(1)	Ru(4)–H(24)	1.76(4)
Ru–CO (av.) 1.89 range 1.867(5)–1.937(4)			
<i>Bond angles (°)</i>			
Ru(2)–Ru(1)–Ru(3)	61.1(1)	Ru(2)–Ru(3)–Ru(4)	62.8(1)
Ru(2)–Ru(1)–Ru(4)	60.4(1)	Ru(1)–Ru(4)–Ru(2)	60.7(1)
Ru(3)–Ru(1)–Ru(4)	58.1(1)	Ru(1)–Ru(4)–Ru(3)	58.1(1)
Ru(1)–Ru(2)–Ru(3)	55.9(1)	Ru(2)–Ru(4)–Ru(3)	61.2(1)
Ru(1)–Ru(2)–Ru(4)	58.9(1)	Ru(2)–Ru(1)–P(1)	93.8(1)
Ru(3)–Ru(2)–Ru(4)	55.9(1)	Ru(3)–Ru(1)–P(1)	153.7(1)
Ru(1)–Ru(3)–Ru(2)	63.0(1)	Ru(1)–Ru(2)–P(2)	90.3(1)
Ru(1)–Ru(3)–Ru(4)	63.8(1)	Ru(3)–Ru(2)–P(2)	145.9(1)

 $C_s$ 

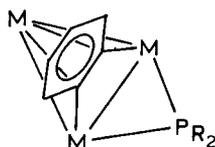
(A)

 $D_{2d}$ 

(B)



(C)



(D)

Consideration of possible mechanisms of elimination of alkane or arene from complexes of the types described above and elsewhere suggests that such processes might proceed more readily if the hydrogen atom(s) were already attached to the cluster core. Following this, hydrido-cluster complexes might be expected to exhibit similar reactions on simple pyrolysis, and indeed this reaction of  $\text{Os}_3(\mu\text{-H})(\mu\text{-SPh})(\text{CO})_{10}$  has been described [30]. However, similar studies have not yet been reported for complexes such as **13**.

Simple heating of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dppm})$  (**13**) in refluxing cyclohexane for 1 h gave a 76% yield of orange  $\text{Ru}_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_{10}$  (**15**). Subsequently we learned that others have prepared this complex by a similar route [31]. The IR  $\nu(\text{CO})$  spectrum contains five medium to strong  $\nu(\text{CO})$  bands between 2075–1980  $\text{cm}^{-1}$ , together with weak bands at 1898 and 1843  $\text{cm}^{-1}$ . The presence of the latter suggested the presence of bridging carbonyl groups. In the  $^1\text{H}$  NMR spectrum, two high-field signals at  $\delta -18.0$  and  $-19.7$ , of relative intensity 1/2 suggested that **15** had a structure such as that illustrated, which was confirmed by the X-ray study.

The unit cell contains two independent molecules which do not differ appreciably. Figure 4 illustrates molecule A and the relevant atom numbering system; an

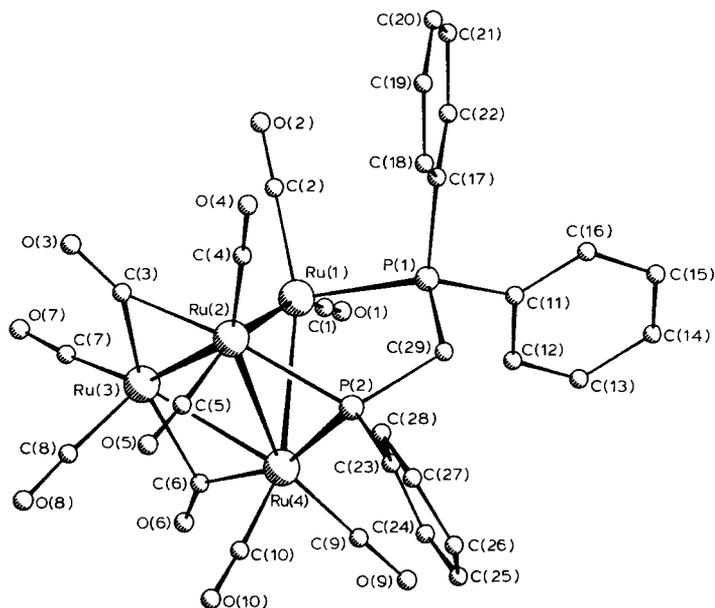


Fig. 4. Molecule A of  $\text{Ru}_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\mu\text{-CO})_2(\text{CO})_8$  (**15**), showing atom numbering scheme.

illustration of molecule B and its numbering system is included in the supplementary material. The following discussion refers to molecule A. In the nearly tetrahedral  $\text{Ru}_4$  core, there are two short ( $\text{Ru}(2)\text{-Ru}(3)$  2.756(1),  $\text{Ru}(3)\text{-Ru}(4)$  2.764(1) Å, one medium ( $\text{Ru}(2)\text{-Ru}(4)$  2.844(1) Å) and three long  $\text{Ru}\text{-Ru}$  separations ( $\text{Ru}(1)\text{-Ru}(2)$  2.988(1),  $\text{Ru}(1)\text{-Ru}(3)$  2.990(1),  $\text{Ru}(1)\text{-Ru}(4)$  2.977(1) Å; see also Table 4). The longer  $\text{Ru}\text{-Ru}$  separations indicate the locations of the three hydride ligands; an approximate mirror plane passes through  $\text{Ru}(1)$ ,  $\text{Ru}(3)$  and the mid-point of  $\text{Ru}(2)\text{-Ru}(4)$ , so that two of the hydride ligands occupy equivalent positions, and the third is in a unique position, which is consistent with the  $^1\text{H}$  NMR spectrum. The dephenylated phosphido-phosphine ligand bestrides the  $\text{Ru}(1)\text{Ru}(2)\text{Ru}(4)$  face, the PPh group bridging the  $\text{Ru}(2)\text{Ru}(4)$  edge ( $\text{Ru}(2)\text{-P}(2)$  2.305(3),  $\text{Ru}(4)\text{-P}(2)$  2.303(2) Å). The other two edges of the  $\text{Ru}(2)\text{Ru}(3)\text{Ru}(4)$  face are bridged by CO groups, the  $\text{Ru}_3\text{C}_2\text{P}$  atom array being approximately planar. The eight terminal CO groups are distributed two to each metal atom. The complex thus contains another example of the dephenylated dppm ligand capping an  $\text{Ru}_3$  face; in this case it has been formed by pyrolysis of the hydrido cluster, combination of a *P*-phenyl group and cluster-bonded hydrogen forming benzene and concomitantly, a  $\mu$ -phosphido group.

(iii) Hydrogenation of  $\text{Ru}_3\{\mu\text{-}\eta^2\text{-P-PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2\text{-}2)\}(\text{CO})_{10}$

The reaction of  $\text{Ru}_3\{\mu\text{-}\eta^2\text{-P-PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2\text{-}2)\}(\text{CO})_{10}$  (**16**) [32] with hydrogen (20 atm, 50°C, 2 h) proceeded readily to give  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  and  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11}\{\text{PPh}_2(\text{C}_6\text{H}_4\text{Et-}2)\}$  (**17**), together with a number of unidentified products. Characterisation of **17** rests on its spectroscopic properties, supported by elemental microanalysis. The IR spectrum of **17** contained the characteristic  $\nu(\text{CO})$

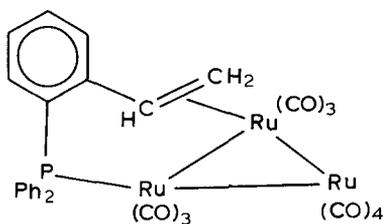
TABLE 4

STRUCTURAL PARAMETERS FOR  $\text{Ru}_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_{10}$  (15)

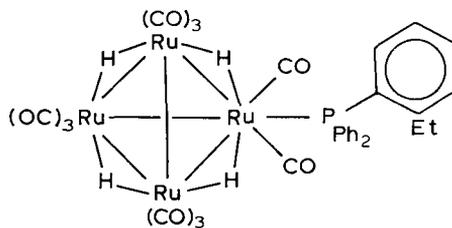
Bond lengths (Å)			
Ru(1)–Ru(2)	2.988(1)	Ru(2)–C(3)	2.13(1)
Ru(1)–Ru(3)	2.990(1)	Ru(3)–C(3)	2.12(1)
Ru(1)–Ru(4)	2.977(1)	Ru(3)–C(6)	2.14(1)
Ru(2)–Ru(3)	2.756(1)	Ru(4)–C(6)	2.10(1)
Ru(2)–Ru(4)	2.844(1)		
Ru(3)–Ru(4)	2.764(1)	Ru–CO(t) (av.) 1.86	
		range 1.825(15)–1.902(11)	
Ru(1)–P(1)	2.349(2)		
Ru(2)–P(2)	2.305(3)		
Ru(4)–P(2)	2.303(2)		
Bond angles (°)			
Ru(2)–Ru(1)–Ru(3)	54.9(1)	Ru(1)–Ru(4)–Ru(2)	61.7(1)
Ru(2)–Ru(1)–Ru(4)	56.9(1)	Ru(1)–Ru(4)–Ru(3)	62.6(1)
Ru(3)–Ru(1)–Ru(4)	55.2(1)	Ru(2)–Ru(4)–Ru(3)	58.9(1)
Ru(1)–Ru(2)–Ru(3)	62.6(1)	Ru(1)–P(1)–C(29)	109.8(3)
Ru(1)–Ru(2)–Ru(4)	61.3(1)	Ru(2)–P(2)–Ru(4)	76.2(1)
Ru(3)–Ru(2)–Ru(4)	59.1(1)	Ru(2)–P(2)–C(29)	117.7(3)
Ru(1)–Ru(3)–Ru(2)	62.5(1)	Ru(4)–P(2)–C(29)	115.8(3)
Ru(1)–Ru(3)–Ru(4)	62.2(1)	P(1)–C(29)–P(2)	112.7(5)
Ru(2)–Ru(3)–Ru(4)	62.0(1)		

bands associated with other  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11}(\text{L})$  complexes, such as  $\text{L} = \text{PPh}_3$  [33],  $\text{P}(\text{OMe})_3$  [34], and others reported herein. In the  $^1\text{H}$  NMR spectrum, the presence of the *ortho*-Et fragment was shown by two resonances, a triplet at  $\delta$  0.98 and a multiplet at  $\delta$  2.51 of relative intensities 3/2. At high-field, a four-proton doublet at  $\delta$  -17.29 ( $J(\text{PH})$  4.5 Hz) was readily assigned to the bridging hydride ligands coupled to phosphorus.

The formation of **17** probably results from initial oxidative addition of hydrogen to the cluster followed by hydrogen transfer to the coordinated vinyl group to give the resultant ethyl fragment. Comparison with the results obtained with trinuclear complexes containing bidentate tertiary phosphines (see above) suggests that the fragmentation, which must precede the formation of the tetranuclear complex, occurs with monodentate ligand complexes only, and therefore that the reduction of the vinyl group to ethyl occurs on the trinuclear complex before this fragmentation.



(16)



(17)

### Conclusion

Hydrogenation of complexes  $\text{Ru}_3(\text{CO})_{12-n}(\text{L})_n$  ( $\text{L} = \text{PMe}_3, \text{PPh}_3, \text{PPh}(\text{OMe})_2, \text{P}(\text{OMe})_3$ ;  $n = 1-3$ ) under mild conditions ( $80^\circ\text{C}$ , 20 bar, 2 h) afforded a mixture of tetranuclear complexes  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12-m}(\text{L})_m$ , where  $m$  is not directly related to  $n$ . Clearly these reactions are complex and the present results do not allow any detailed speculation about mechanism. However, under the conditions used, little or no fragmentation of the coordinated Group 15 ligand occurs.

In contrast, cleavage of P–C or As–C bonds occurs in similar reactions of complexes  $\text{Ru}_3(\text{CO})_{12-2n}(\text{L-L})_n$  ( $\text{L-L} = \text{dppm}, \text{dppe}$  or  $\text{dpam}$ ;  $n = 1$  or  $2$ ), with formation of  $\mu_3$ -phosphido-phosphine ligands and elimination of benzene. Further reaction of dihydrogen with a complex containing the  $\mu_3$ - $\text{PPhCH}_2\text{PPh}_2$  ligand resulted in fragmentation to give  $\mu_3$ - $\text{PPh}$  and  $\text{PMePh}_2$  ligands. In both cases, hydrogen also adds to the metal core. Pyrolysis of a tetranuclear hydrido-cluster containing a bidentate tertiary phosphine resulted in arene elimination and formation of the same phosphido-phosphine ligand capping an  $\text{Ru}_3$  face.

How does P–C bond cleavage occur? After addition of hydrogen across a metal–metal bond to form a hydrido-cluster, intramolecular combination of a *P*-phenyl group and cluster-bonded H occurs to give arene and a P–metal bond. Our results do not require initial oxidative addition of the *P*-aryl group across a metal–metal bond, although the intermediacy of reactions of this type is suggested by the variety of products obtained by simply heating trinuclear tertiary phosphine-containing osmium clusters, in which moieties such as **C** and **D** feature [4]. However, in cases where edge-bridging phenyl groups are formed, cleavage of the P–C bond must still take place on hydrogenation (by  $\text{H}_2$  or by cluster-bound H atoms), and others have already noted an instance where hydrogenation of such a complex **10** merely reforms the tertiary phosphine [25].

Comparisons of the cluster chemistry of ruthenium and osmium show that the latter are generally the more stable, and that their disproportionation does not occur so readily. The formation of  $\text{Os}_3(\mu\text{-H})_2(\mu\text{-dppm})(\text{CO})_8$  (**11**) by hydrogenation of **9** is paralleled by the conversion of  $\text{Os}_3(\text{CO})_{12}$  to  $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ ; however, activation of the chelating bis-tertiary-phosphine in  $\text{Ru}_3(\mu\text{-dppm})(\text{CO})_{10}$  appears to be greater than in **9**, since loss of arene and preservation of the  $\text{Ru}_3$  cluster is found on hydrogenation, in contrast to the reaction of  $\text{Ru}_3(\text{CO})_{12}$  which affords the tetranuclear  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  [1].

These results bear out the conclusions of several other groups concerning the role of tertiary phosphines in modifying cluster complexes as potential cluster precursors. The Group 15 ligands are not inert under mild hydrogenation conditions, so that active species may contain  $\mu$ -phosphido or  $\mu_3$ -phosphinidene ligands, which in turn may facilitate some or all of the steps in catalytic reactions by bridge-opening and creation of vacant coordination sites [7].

### Experimental

*Instrumentation.* Perkin–Elmer 683 double-beam, NaCl optics (IR); Bruker WP80 ( $^1\text{H}$  NMR at 80 MHz); GEC-Kratos MS 3074 (mass, at 70 eV ionising energy, 8 kV accelerating potential).

*General conditions.* All reactions were run routinely under nitrogen or hydrogen, but no special precautions to exclude air were taken during workup. Pressure

reactions were carried out in a laboratory autoclave (internal volume 100 ml, containing a glass liner) (Carl R oth, Karlsruhe).

*Sources.*  $\text{Ru}_3(\text{CO})_{12}$  [35],  $\text{Os}_3(\text{CO})_{12}$  [36],  $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$  [37],  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  [1] and Group 5 ligand-substituted derivatives [12] were prepared by the cited literature methods; hydrogen was High Purity grade from CIG, Sydney; Group 5 ligands were commercial products, used as received from BDH, England ( $\text{PPh}_3$ ) or Strem Chemicals, Newburyport (others).

*Reactions of substituted ruthenium cluster carbonyls with hydrogen. Complexes containing monodentate tertiary phosphines or phosphites*

Standard reaction conditions were as follows. The cluster was dissolved in cyclohexane in a glass liner. The glass liner was placed in a small laboratory autoclave and after flushing with hydrogen, the apparatus was pressurized with hydrogen to 20 atm. The reaction was left at 80°C for 2 h. After cooling, solvent was removed (rotary evaporator), and the residue was dissolved in the minimum amount of  $\text{CH}_2\text{Cl}_2$ . Separation was achieved by preparative TLC (Kieselgel GF<sub>254</sub> (type 60)) on glass plates (20 cm × 20 cm), developing with 1/9 acetone/petroleum ether. The products were identified by comparison with authentic samples (IR  $\nu(\text{CO})$  and TLC behaviour) and are summarised in Table 1.

*Characterisation of tetranuclear complexes*

(a)  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11}\{\text{PPh}(\text{OMe})_2\}$ . m.p. 140°C (dec.). Found: C, 25.88; H, 1.66; P, 3.10;  $\text{C}_{19}\text{H}_{15}\text{O}_{13}\text{PRu}_4$  calcd.: C, 25.74; H, 1.71; P, 3.49%. IR (cyclohexane):  $\nu(\text{CO})$  2097m, 2092w(sh), 2070vs, 2060vs, 2034vs, 2018s(sh), 2010s, 1998m, 1981m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  ( $\text{CDCl}_3$ ) 7.5 (m, 5H, PPh), 3.6 (m, 6H, OMe), -17.6 (m, 4H, RuH). Mass spectrum:  $M^+$  at  $m/z$  888 with ions formed by competitive loss of 11 CO and 2 OMe groups.

(b)  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}\{\text{PPh}(\text{OMe})_2\}_2$ . m.p. 113°C. Found: C, 30.30; H, 2.56;  $\text{C}_{26}\text{H}_{26}\text{O}_{14}\text{P}_2\text{Ru}_4$  calcd.: C, 30.36; H, 2.55%. IR (cyclohexane):  $\nu(\text{CO})$  2080s, 2059vs, 2044ms, 2025vs, 2014(sh), 2001vs, 1997(sh), 1987(sh), 1976m, 1972m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  ( $\text{CDCl}_3$ ) 7.5 (m, 10H, PPh), 3.5 (m, 12H, OMe), -17.4 (m, 4H, RuH). Mass spectrum:  $M^+$  at  $m/z$  1032 with ions formed by competitive loss of 10 CO and 4 OMe groups.

(c)  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_9\{\text{PPh}(\text{OMe})_2\}_3$ . m.p. 115°C. Found: C, 33.71; H, 3.09;  $\text{C}_{33}\text{H}_{37}\text{O}_{15}\text{P}_3\text{Ru}_4$  calcd.: C, 33.85; H, 3.19%. IR (cyclohexane):  $\nu(\text{CO})$  2066vs, 2036vs, 2016s, 1999s, 1985m, 1978m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  ( $\text{CDCl}_3$ ) 7.4 (m, 15H, PPh), 3.5 (m, 18H, OMe), -17.3 (m, 4H, RuH). Mass spectrum:  $M^+$  at  $m/z$  1167 with ions formed by competitive loss of 9 CO and 6 OMe groups.

*Reaction between  $\text{Ru}_3(\text{CO})_{11}\{\text{P}(\text{OMe})_3\}$  and  $\text{Ru}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_3$*

An equimolar mixture of the two complexes (0.084 mmol) was heated in refluxing cyclohexane (25 ml) for 2.5 h, when IR spectra showed the presence of all three complexes  $\text{Ru}_3(\text{CO})_{12-n}\{\text{P}(\text{OMe})_3\}_n$  ( $n = 1, 2$  and 3). After a further 18 h heating, evaporation of solvent and preparative TLC (developer, 1/9 acetone/petroleum ether) enabled isolation of  $\text{Ru}_3(\text{CO})_{11}\{\text{P}(\text{OMe})_3\}$  (12.5 mg, 20.2%),  $\text{Ru}_3(\text{CO})_{10}\{\text{P}(\text{OMe})_3\}_2$  (43.7 mg, 31.3%) and  $\text{Ru}_3(\text{CO})_9\{\text{P}(\text{OMe})_3\}_3$  (28 mg, 35.9%), all of which were identified from their  $\nu(\text{CO})$  spectra. Several other complexes were present in trace amounts and not further investigated.

### Hydrogenation of $Ru_3(\mu\text{-dppm})(CO)_{10}$ (1)

(a) *Under mild conditions.* The reaction between  $Ru_3(\mu\text{-dppm})(CO)_{10}$  (in cyclohexane) and  $H_2$  (80°C, 20 atm, 2 h) was carried out as previously described [9] to give  $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(CO)_9$  in 67% yield, together with  $Ru_4(\mu\text{-H})_4(\mu\text{-dppm})(CO)_{10}$  (12.6%) and recovered  $Ru_3(\mu\text{-dppm})(CO)_{10}$  (10%).

(b) *Under more vigorous conditions.*  $Ru_3(CO)_{10}(\text{dppm})$  (300 mg, 0.31 mmol) was dissolved in cyclohexane (70 ml) and the solution placed in the glass liner of a small autoclave. Hydrogen (high purity) was charged into the autoclave (20 atm) and mixture was heated at 80°C for 40 h. After cooling, solvent was removed (rotary evaporator), and the solid residue was dissolved in the minimum amount of  $CH_2Cl_2$ . Preparative TLC (3/17 acetone/petroleum ether) gave three bands: Band 1 ( $R_f = 0.89$ ) contained the major product, yellow  $Ru_3(\mu\text{-H})_2(\mu_3\text{-PPh})(CO)_8(\text{PMePh}_2)$  (3) (102 mg, 45.4%), m.p. 124°C, which was recrystallised from  $CH_2Cl_2/\text{MeOH}$ . Found: C, 38.65; H, 2.44;  $C_{27}H_{20}Ru_3O_8P_3$  calcd.: C, 38.72; H, 2.41%. IR (cyclohexane):  $\nu(\text{CO})$  at 2077s, 2044vs, 2008vs, 1999(sh), 1996vs, 1980m  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$ :  $\delta$  ( $\text{CDCl}_3$ ) 7.27–8.18 (m, 15H, Ph), 2.14 (d,  $J(\text{PH})$  7.7 Hz, 3H, Me), –18.71 (d,  $J(\text{HP})$  12.9 Hz, 1H, RuH), –18.91 (d,  $J(\text{HP})$  12.0 Hz, 1H, RuH). Band 2 ( $R_f = 0.83$ ) contained  $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(CO)_9$  (40 mg, 13.3%). Band 3 ( $R_f = 0.72$ ) contained  $Ru_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(CO)_{10}$  (30 mg, 12.9%).

### Hydrogenation of $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(CO)_9$ (2)

Complex 2 was hydrogenated (20 atm, 70°C, 90 h) as described for  $Ru_3(\mu\text{-dppm})(CO)_{10}$ . Preparative TLC afforded  $Ru_3(\mu\text{-H})_2(\mu_3\text{-PPh})(CO)_8(\text{PMePh}_2)$  (3) (56.2%),  $Ru_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(CO)_{10}$  (25.2%) and recovered  $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{PPh}_2)(CO)_9$  (20%) as the major products; six other unidentified complexes were present in trace amounts only.

### Complexes containing chelating tertiary phosphines

(a)  $Ru_3(CO)_{10}(\text{dppe})$ . A solution of  $Ru_3(CO)_{10}(\text{dppe})$  (200 mg, 0.204 mmol) in cyclohexane (40 ml) was hydrogenated in an autoclave (80°C, 20 atm, 5 h). The resulting yellow solution was taken to dryness and chromatographed by preparative TLC (90/10 light petroleum/acetone) to give 4 bands. Band 1, ( $R_f = 0.36$ ) yellow, recrystallised from  $CH_2Cl_2/\text{MeOH}$  to give an orange powder of  $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{CH}_2\text{PPh}_2)(CO)_9$  (5) (60 mg, 34%), m.p. 110–115°C. Found: C, 39.83; H, 2.30,  $M$  (mass spectrum) 879;  $C_{29}H_{20}O_9P_2Ru_3$  calcd.: C, 39.69; H, 2.30%,  $M$  879. IR (cyclohexane):  $\nu(\text{CO})$  2087m, 2043s, 2016vs, 2007w, 1995w, 1990w, 1979m, 1968w  $\text{cm}^{-1}$ .  $^1\text{H NMR}$ :  $\delta$  ( $\text{CDCl}_3$ ) 7.45 (m, 15H, Ph), 4.46 (s(br), 4H,  $\text{CH}_2$ ), –16.36 (s(br), 1H, RuH). Band 4 ( $R_f = 0.13$ ), yellow, recrystallised from  $CH_2Cl_2/\text{MeOH}$  to give orange crystals of  $Ru_4(\mu\text{-H})_4(CO)_{10}(\text{dppe})$  (6) (52 mg, 23%) identified by comparison of infrared and  $^1\text{H NMR}$  data with literature values [19]. Bands 2 and 3 were obtained in trace amounts and were not identified.

(b)  $\{Ru_3(CO)_{11}\}_2(\mu\text{-dppe})$ . A solution of  $\{Ru_3(CO)_{11}\}_2(\mu\text{-dppe})$  (250 mg, 0.154 mmol) in cyclohexane (40 ml) was hydrogenated in an autoclave (80°C, 20 atm, 10 h). The resulting yellow solution was taken to dryness and chromatographed by preparative TLC (90/10 light petroleum/acetone) to give ten bands. Band 1 ( $R_f = 0.80$ ) yellow,  $Ru_4(\mu\text{-H})_4(CO)_{12}$  (45 mg, 39%). Band 2 ( $R_f = 0.37$ ) yellow, recrystallised from  $CH_2Cl_2/\text{MeOH}$  to give an orange powder of  $Ru_3(\mu\text{-H})(\mu_3\text{-PPhCH}_2\text{CH}_2\text{PPh}_2)(CO)_9$  (5) (11 mg, 8%). Band 3 ( $R_f = 0.32$ ) orange, recrystallised

from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  to give red crystals of  $\{\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11}\}_2(\mu\text{-dppe})$  (**8**) (27 mg, 10%), m.p. 190–195°C (dec.). Found: C, 31.85; H, 1.77;  $\text{C}_{48}\text{H}_{32}\text{O}_{22}\text{P}_2\text{Ru}_8$  calcd.: C, 31.48; H, 1.76%. IR (cyclohexane):  $\nu(\text{CO})$  2098m, 2072vs, 2062vs, 2029vs, 2014s, 1996w, 1978w, 1966m  $\text{cm}^{-1}$ . Band 8 ( $R_f = 0.13$ ) orange, recrystallised from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  to give red crystals of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dppe})$  (**6**) (62 mg, 37%). Bands 1, 2 and 8 were identified by comparison of their infrared  $\nu(\text{CO})$  spectra with those of authentic samples. Band 4–7, 9 and 10 were obtained in trace amounts and were not identified.

#### Preparation of $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dppm})$ (**13**)

A mixture of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  (200 mg, 0.269 mmol) and dppm (110 mg, 0.286 mmol) in thf (40 ml) was warmed to ca. 40°C to dissolve all of the cluster. A solution of  $\text{Na}[\text{Ph}_2\text{CO}]$  in thf (ca. 0.025 mol  $\text{l}^{-1}$ ) was added dropwise from a syringe until the solution darkened and the 2084  $\text{cm}^{-1}$  band of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  was absent (0.5 ml). Evaporation and recrystallisation from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  gave red crystals of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dppm})$  (**13**) (249 mg, 86%), m.p. 150–153°C. Found: C, 39.01; H, 2.30;  $\text{C}_{35}\text{H}_{26}\text{O}_{10}\text{P}_2\text{Ru}_4$  calcd.: C, 39.19; H, 2.44%. IR (cyclohexane):  $\nu(\text{CO})$  2088w, 2076m, 2054s, 2037vs, 2026w, 2015s, 1999w, 1985w, 1976m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  ( $\text{CDCl}_3$ ) –16.72 (s, 4H, RuH), 3.80 (m, 2H,  $\text{CH}_2$ ), 7.20 (m, 20H, Ph).

#### Preparation of $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dpam})$ (**14**)

This complex, m.p. >150°C (dec.), was obtained in 58% yield by the  $\text{Na}[\text{Ph}_2\text{CO}]$ -catalysed reaction between  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  and dpam, carried out as described above for the dppm complex. Found: C, 36.47; H, 2.42;  $\text{C}_{35}\text{H}_{26}\text{As}_2\text{O}_{10}\text{Ru}_4$  calcd.: C, 36.22; H, 2.26%. IR (cyclohexane):  $\nu(\text{CO})$  2077m, 2054s, 2038vs, 1998w, 1987w, 1977m, 1975w  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  ( $\text{CDCl}_3$ ) –17.00 (s, 4H, RuH), 3.37 (AB quartet,  $J(\text{AB})$  12 Hz, 2H,  $\text{CH}_2$ ), 7.31 (m, 20H, Ph).

#### Thermolysis of $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dppm})$ (**13**)

A solution of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{10}(\text{dppm})$  (**13**) (100 mg, 0.093 mmol) was heated in refluxing cyclohexane (10 ml) for 1 h, after which time the reaction was adjudged complete (the disappearance of the  $\nu(\text{CO})$  band at 2015  $\text{cm}^{-1}$  was monitored). Filtration, addition of n-heptane (5 ml), reduction in volume to ca. 5 ml (rotary evaporator) and cooling gave fine orange crystals of  $\text{Ru}_4(\mu\text{-H})_3(\mu_3\text{-PPhCH}_2\text{PPh}_2)(\text{CO})_{10}$  (**15**) (70 mg, 76%), m.p. 180–185°C (dec.). Found: C, 35.00; H, 2.00,  $M$  (mass spectrum) 996;  $\text{C}_{29}\text{H}_{20}\text{O}_{10}\text{P}_2\text{Ru}_4$  calcd.: C, 35.12; H, 2.03%,  $M$  996. IR (cyclohexane):  $\nu(\text{CO})$  2075m, 2056s, 2024vs, 1996m, 1981m, 1898w, 1843m  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  ( $\text{CDCl}_3$ ) –17.95 (s(br), 1H, RuH), –19.74 (s(br), 2H, RuH), 3.22 (t,  $J(\text{PH})$  10.5 Hz, 2H,  $\text{CH}_2$ ), 7.55 (m, 15H, Ph).

#### Preparation of $\text{Os}_3(\text{CO})_{10}(\text{dppm})$ (**9**)

A mixture of  $\text{Os}_3(\text{CO})_{10}(\text{CNMe})_2$  (317 mg, 0.34 mmol), MeCN (20 ml) and dppm (130 mg, 0.34 mmol) in cyclohexane (100 ml) was stirred at 40°C for 4 h. Evaporation and preparative TLC (90/10 light petroleum/acetone) afforded one major band ( $R_f = 0.30$ ), yellow, recrystallised from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  to give large yellow-orange crystals of  $\text{Os}_3(\text{CO})_{10}(\text{dppm})$  (**9**) (225 mg, 54%), m.p. >165°C (dec.). Found: C, 34.12; H, 1.65;  $\text{C}_{35}\text{H}_{22}\text{O}_{10}\text{Os}_3\text{P}_2$  calcd.: C, 34.04; H, 1.78%. IR (cyclohexane):  $\nu(\text{CO})$  2098m, 2033m, 2019s, 2010vs, 1986m, 1968m, 1958s, 1947w,

1922vw  $\text{cm}^{-1}$ .  $^1\text{H NMR}$ :  $\delta$  ( $\text{CDCl}_3$ ) 5.05 (t,  $J(\text{PH})$  10.5 Hz, 2H,  $\text{CH}_2$ ), 7.38 (m, 20H, Ph).

*Hydrogenation of  $\text{Os}_3(\text{CO})_{10}(\text{dppm})$  (9)*

A solution of  $\text{Os}_3(\text{CO})_{10}(\text{dppm})$  (9) (90 mg, 0.073 mmol) in toluene (30 ml) was hydrogenated in an autoclave (85°C, 25 atm, 12 h). The resulting red solution was taken to dryness and the residue recrystallised from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  to give red plate-like crystals of  $\text{Os}_3(\mu\text{-H})_2(\mu\text{-dppm})(\text{CO})_8$  (12) (58 mg, 67%), m.p. 235–238°C. Found: C, 33.44; H, 1.84,  $M$  (mass spectrum) 1181;  $\text{C}_{33}\text{H}_{24}\text{O}_8\text{Os}_3\text{P}_2$  calcd.: C, 33.55; H, 2.05%,  $M$  1181. IR (cyclohexane):  $\nu(\text{CO})$  2076m, 2013s, 1995vs, 1974m, 1959m  $\text{cm}^{-1}$ .  $^1\text{H NMR}$ :  $\delta$  ( $\text{CDCl}_3$ ) -10.31 (t,  $J(\text{PH})$  10.5 Hz, 2H, OsH), 4.15 (t,  $J(\text{PH})$  10.5 Hz, 2H,  $\text{CH}_2$ ), 7.30 (m, 20H, Ph).

*Hydrogenation of  $\text{Ru}_3\{\mu\text{-PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2)\}(\text{CO})_{10}$*

A solution of  $\text{Ru}_3\{\mu\text{-PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2)\}(\text{CO})_{10}$  (140 mg, 0.160 mmol) in cyclohexane (40 ml) was hydrogenated in an autoclave (20 atm, 50°C, 2 h). The resulting red solution was evaporated to dryness and separated by preparative TLC (80/20 light petroleum/acetone) to give eight bands. Band 1 ( $R_f = 0.87$ ), yellow,  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{12}$  (7 mg, 6%), identified by comparison of its IR  $\nu(\text{CO})$  spectrum

TABLE 5  
CRYSTAL DATA FOR 3, 12, 13 AND 15

	3	12	13	15
Formula	$\text{C}_{27}\text{H}_{20}\text{O}_8\text{P}_2\text{Ru}_3$	$\text{C}_{33}\text{H}_{24}\text{O}_8\text{P}_2\text{Os}_3$	$\text{C}_{35}\text{H}_{26}\text{O}_{11}\text{P}_2\text{Ru}_4$	$\text{C}_{29}\text{H}_{20}\text{O}_{10}\text{P}_2\text{Ru}_4$
Formula weight	837.6	1181.1	1072.8	994.7
Crystal system	monoclinic	orthorhombic	triclinic	triclinic
Space group	$P2_1$ ( $C_2^2$ , No. 4)	$Pbca$ ( $D_{2h}^{15}$ , No. 61)	$P\bar{1}$ ( $C_1^1$ , No. 2)	$P\bar{1}$ ( $C_1^1$ , No. 2)
$a$ (Å)	9.952(1)	16.419(5)	10.206(2)	16.364(2)
$b$ (Å)	14.337(2)	16.929(3)	11.412(3)	17.888(3)
$c$ (Å)	11.164(1)	25.403(6)	18.860(3)	12.083(2)
$\alpha$ (°)	90	90	70.99(2)	90.83(1)
$\beta$ (°)	104.44(1)	90	73.98(1)	106.05(1)
$\gamma$ (°)	90	90	72.27(2)	94.48(1)
$U$ (Å <sup>3</sup> )	1542.6	7061.0	1939.7	3386.3
$D_m$	1.80	2.22	1.82	1.90
$Z$	2	8	2	4
$D_x$ (g $\text{cm}^{-3}$ )	1.803	2.222	1.84	1.951
$\mu(\text{Mo-K}\alpha)$ ( $\text{cm}^{-1}$ )	15.7	108.9	16.01	18.3
$F(000)$	816	4351	1044	1920
$\theta$ -range (°)	1.4–25.0	1.0–25.0	1.2–23.0	1.0–22.5
Reflections measured	2387	6992	5290	9834
Unique reflections	2387	5998	5290	8842
Reflections with $I \geq 2.5\sigma(I)$	2286	3367	4930	6393
$R$	0.032	0.044	0.026	0.043
$k$	3.33	1.00	1.00	0.67
$g$	0.0004	0.0150	0.0007	0.0035
$R_w$	0.037	0.052	0.035	0.053
max. $\rho$ ( $\text{e}\text{\AA}^{-3}$ )	0.90	1.07	0.60	0.96

TABLE 6

ATOMIC COORDINATES (Ru  $\times 10^5$ , other atoms  $\times 10^4$ ) FOR NON-HYDROGEN ATOMS IN  $\text{Ru}_3(\mu\text{-H})_2(\mu_3\text{-PPh})(\text{CO})_8(\text{PMePh}_2)$  (3) <sup>a</sup>

Atom	x	y	z
Ru(1)	-79703(5)	-25000	-13786(4)
Ru(2)	-82605(6)	-24394(7)	-40577(4)
Ru(3)	-106967(5)	-25156(6)	-31694(5)
P(1)	-7202(2)	-3973(1)	-523(1)
P(2)	-8998(2)	-1386(1)	-2810(1)
O(1)	-11583(10)	-4486(6)	-4062(8)
O(2)	-12553(10)	-1580(7)	-5408(9)
O(3)	-12525(9)	-2149(6)	-1378(9)
O(4)	-8598(9)	-4468(5)	-4959(6)
O(5)	-5329(11)	-1966(10)	-4178(10)
O(6)	-9598(15)	-1441(7)	-6465(7)
O(7)	-5170(7)	-1563(6)	-572(6)
O(8)	-9098(8)	-1631(6)	654(6)
C(1)	-11218(10)	-3751(7)	-3704(9)
C(2)	-11893(11)	-1914(8)	-4581(10)
C(3)	-11884(9)	-2275(8)	-2067(10)
C(4)	-8470(10)	-3698(7)	-4673(7)
C(5)	-6422(14)	-2140(9)	-4131(10)
C(6)	-9061(15)	-1845(8)	-5549(8)
C(7)	-6204(9)	-1908(6)	-853(6)
C(8)	-8619(8)	-1961(6)	-79(6)
C(9)	-9952(4)	278(3)	-2092(4)
C(10)	-9888(4)	1232(3)	-1839(4)
C(11)	-8813(4)	1768(3)	-2077(4)
C(12)	-7802(4)	1349(3)	-2567(4)
C(13)	-7866(4)	395(3)	-2819(4)
C(14)	-8942(4)	-141(3)	-2582(4)
C(15)	-6434(6)	-4849(3)	1801(4)
C(16)	-5968(6)	-4864(3)	3087(4)
C(17)	-5618(6)	-4032(3)	3740(4)
C(18)	-5734(6)	-3186(3)	3106(4)
C(19)	-6200(6)	-3171(3)	1819(4)
C(20)	-6550(6)	-4002(3)	1167(4)
C(21)	-6050(4)	-5023(4)	-2126(4)
C(22)	-4959(4)	-5359(4)	-2583(4)
C(23)	-3593(4)	-5132(4)	-1988(4)
C(24)	-3317(4)	-4570(4)	-934(4)
C(25)	-4407(4)	-4234(4)	-477(4)
C(26)	-5773(4)	-4461(4)	-1073(4)
C(27)	-8504(9)	-4890(7)	-844(8)
Ru(1')	-822(2)	-251(3)	-233(2)
Ru(2')	-854(3)	-246(4)	-498(2)
Ru(3')	-1100(3)	-261(3)	-415(3)
Ru(1'')	-766(2)	-255(3)	-50(2)
Ru(2'')	-809(3)	-246(4)	-318(3)
Ru(3'')	-1042(3)	-259(4)	-223(3)

<sup>a</sup> The occupancy of each of the primed Ru-atoms (coordinates  $\times 10^3$ ) is 2% (see text).

with that of an authentic sample. Band 2 ( $R_f = 0.57$ ) red, recrystallised from  $\text{CH}_2\text{Cl}_2/\text{MeOH}$  to give red crystals of  $\text{Ru}_4(\mu\text{-H})_4(\text{CO})_{11}\{\text{PPh}_2(\text{C}_6\text{H}_4\text{Et-2})\}$  (**17**) (33 mg, 20%). Found: C, 38.01; H, 2.42;  $\text{C}_{33}\text{H}_{25}\text{O}_{11}\text{PRu}_4$  calcd.: C, 38.38; H,

(Continued on p. 209)

TABLE 7

ATOMIC COORDINATES ( $\text{Os} \times 10^5$ , other atoms  $\times 10^4$ ) FOR NON-HYDROGEN ATOMS IN  $\text{Os}_3(\mu\text{-H})_2(\mu\text{-dppm})(\text{CO})_8$  (**12**)

Atom	x	y	z
Os(1)	38922(4)	42523(4)	14050(3)
Os(2)	30163(4)	30734(4)	9851(3)
Os(3)	22145(4)	41871(4)	16298(3)
P(1)	5123(3)	3726(3)	1130(2)
P(2)	4107(3)	2503(3)	523(2)
C(1)	4087(14)	5294(15)	1140(11)
O(1)	4230(13)	5890(9)	977(10)
C(2)	4193(13)	4519(17)	2087(12)
O(2)	4316(12)	4726(13)	2526(10)
C(3)	2250(13)	3001(12)	440(8)
O(3)	1762(12)	3017(12)	89(8)
C(4)	2505(13)	2159(14)	1294(9)
O(4)	2238(12)	1602(10)	1500(8)
C(5)	1133(12)	3786(12)	1589(11)
O(5)	466(12)	3518(14)	1586(10)
C(6)	2568(12)	3494(13)	2189(8)
O(6)	2837(11)	3098(12)	2522(6)
C(7)	2032(16)	5120(21)	2092(9)
O(7)	1916(13)	5628(12)	2356(7)
C(8)	2149(13)	4824(11)	1029(8)
O(8)	2038(11)	5138(12)	629(7)
C(9)	4967(12)	3190(13)	509(8)
C(11)	6416(8)	4686(8)	1416(4)
C(12)	7025(8)	5250(8)	1345(4)
C(13)	7178(8)	5556(8)	845(4)
C(14)	6722(8)	5296(8)	415(4)
C(15)	6113(8)	4732(8)	486(4)
C(10)	1560(8)	4426(8)	986(4)
C(17)	5292(6)	2843(7)	2051(5)
C(18)	5653(6)	2277(7)	2374(5)
C(19)	6341(6)	1869(7)	2202(5)
C(20)	6668(6)	2026(7)	1707(5)
C(21)	6307(6)	2592(7)	1383(5)
C(16)	5619(6)	3001(7)	1555(5)
C(23)	4253(7)	2716(7)	-594(5)
C(24)	4037(7)	2530(7)	-1111(5)
C(25)	3483(7)	1923(7)	-1209(5)
C(26)	3145(7)	1502(7)	-790(5)
C(27)	3361(7)	1688(7)	-274(5)
C(22)	3916(7)	2295(7)	-176(5)
C(29)	5074(8)	1151(7)	421(4)
C(30)	5466(8)	477(7)	610(4)
C(31)	5348(8)	238(7)	1130(4)
C(32)	4839(8)	672(7)	1460(4)
C(33)	4446(8)	1346(7)	1271(4)
C(28)	4564(8)	1585(7)	751(4)

TABLE 8

ATOMIC COORDINATES ( $\text{Ru} \times 10^5$ , other atoms  $\times 10^4$ ) FOR NON-HYDROGEN ATOMS IN  $\text{Ru}_4(\mu\text{-H})_4(\mu\text{-dppm})(\text{CO})_{10}$  (**13**)

Atom	x	y	z
Ru(1)	81736(3)	46107(3)	20451(2)
Ru(2)	51231(3)	51936(3)	27467(2)
Ru(3)	69462(3)	69542(3)	23720(2)
Ru(4)	73025(3)	48485(3)	36205(2)
P(1)	82810(9)	24562(9)	21788(5)
P(2)	50198(9)	31308(9)	28371(5)
O(11)	8245(4)	5723(4)	350(2)
O(12)	11249(3)	4484(4)	1825(2)
O(21)	3402(4)	6629(4)	1519(2)
O(22)	2620(3)	5696(3)	4022(2)
O(31)	6162(6)	8447(4)	831(2)
O(32)	9859(4)	7425(4)	1931(2)
O(33)	5769(5)	9094(4)	3164(2)
O(41)	7787(4)	2316(3)	4855(2)
O(42)	5357(4)	6518(4)	4635(2)
O(43)	9785(4)	5767(4)	3636(2)
C(11)	8218(4)	5313(4)	998(3)
C(12)	10088(4)	4525(4)	1909(2)
C(21)	4050(4)	6060(4)	1972(3)
C(22)	3541(4)	5517(4)	3543(3)
C(31)	6503(6)	7883(4)	1400(3)
C(32)	8783(6)	7204(4)	2094(3)
C(33)	6184(5)	8279(4)	2880(2)
C(41)	7592(4)	3248(4)	4402(2)
C(42)	6083(5)	5895(5)	4250(3)
C(43)	8834(5)	5433(4)	3627(3)
C(1)	6741(3)	2006(3)	2895(2)
C(112)	9292(3)	2512(3)	669(2)
C(113)	9439(3)	2217(3)	-15(2)
C(114)	8658(3)	1433(3)	-50(2)
C(115)	7729(3)	943(3)	598(2)
C(116)	7581(3)	1238(3)	1283(2)
C(111)	8363(3)	2022(3)	1318(2)
C(122)	10121(3)	21(2)	2397(2)
C(123)	11094(3)	-988(2)	2760(2)
C(124)	11614(3)	-853(2)	3332(2)
C(125)	11161(3)	292(2)	3542(2)
C(126)	10188(3)	1302(2)	3180(2)
C(121)	9668(3)	1167(2)	2607(2)
C(212)	2408(2)	2964(3)	3733(1)
C(213)	1462(2)	2636(3)	4415(1)
C(214)	1956(2)	1846(3)	5073(1)
C(215)	3396(2)	1384(3)	5049(1)
C(216)	4341(2)	1713(3)	4368(1)
C(211)	3847(2)	2502(3)	3710(1)
C(222)	4780(3)	3597(2)	1323(1)
C(223)	4465(3)	3319(2)	730(1)
C(224)	3871(3)	2289(2)	885(1)
C(225)	3593(3)	1537(2)	1633(1)
C(226)	3908(3)	1815(2)	2226(1)
C(221)	4502(3)	2845(2)	2071(1)

TABLE 9

ATOMIC COORDINATES (Ru $\times 10^5$ , other atoms  $\times 10^4$ ) FOR NON-HYDROGEN ATOMS IN Ru<sub>4</sub>( $\mu$ -H)<sub>3</sub>( $\mu_3$ -PPhCH<sub>2</sub>PPh<sub>2</sub>)( $\mu$ -CO)<sub>2</sub>(CO)<sub>8</sub> (15)

Atom	x	y	z
Ru(1)	34738(4)	34427(4)	37226(6)
Ru(2)	17265(5)	28365(4)	37533(7)
Ru(3)	29147(5)	31696(5)	58482(7)
Ru(4)	22800(5)	43501(4)	45183(6)
Ru(5)	33911(4)	-16090(4)	38328(6)
Ru(6)	22911(5)	-5674(4)	23393(6)
Ru(7)	28730(5)	-16940(5)	12590(7)
Ru(8)	16393(5)	-20863(4)	23606(7)
P(1)	2971(2)	3764(1)	1788(2)
P(2)	1426(1)	3911(1)	2741(2)
P(3)	2846(2)	-1438(1)	5422(2)
P(4)	1374(1)	-1059(1)	3343(2)
C(29)	1883(6)	4068(5)	1511(8)
C(59)	1794(6)	-1063(6)	4921(9)
C(1)	4528(6)	4018(6)	4099(9)
O(1)	5181(5)	4364(5)	4322(7)
C(2)	4037(6)	2598(6)	3449(9)
O(2)	4398(5)	2112(5)	3292(7)
C(3)	2379(6)	2120(6)	5035(9)
O(3)	2420(5)	1486(5)	5242(7)
C(4)	1250(7)	2039(6)	2694(10)
O(4)	954(5)	1541(5)	2041(8)
C(5)	775(8)	2802(7)	4305(10)
O(5)	180(6)	2743(6)	4654(9)
C(6)	3177(7)	4357(6)	6137(10)
O(6)	3628(5)	4768(5)	6889(8)
C(7)	3804(7)	2818(6)	6974(10)
O(7)	4362(6)	2566(5)	7638(9)
C(8)	2248(8)	3142(1)	6836(11)
O(8)	1803(7)	3136(6)	7452(10)
C(9)	2475(6)	5379(6)	4319(9)
O(9)	2574(6)	6010(5)	4157(8)
C(10)	1382(8)	4511(7)	5138(11)
O(10)	803(7)	4564(6)	5518(9)
C(30)	4468(6)	-1094(6)	4514(9)
O(30)	5121(6)	-809(5)	4973(8)
C(31)	3867(7)	-2522(6)	4164(9)
O(31)	4204(5)	-3070(5)	4309(7)
C(32)	3204(7)	-535(6)	1368(9)
O(32)	3657(5)	-94(5)	1089(8)
C(33)	2618(7)	435(6)	2811(9)
O(33)	2847(6)	1061(5)	3045(8)
C(34)	2321(7)	-2781(6)	1575(9)
O(34)	2415(5)	-3408(5)	1420(7)
C(35)	3709(7)	-2017(6)	645(9)
O(35)	4229(6)	-2193(5)	209(8)
C(36)	2179(8)	-1656(7)	-203(11)
O(36)	1718(6)	-1662(5)	-1177(9)
C(37)	697(8)	-2035(6)	1101(11)
O(37)	96(6)	-2023(6)	319(9)
C(38)	1440(7)	-313(6)	1067(10)

TABLE 9 (continued)

Atom	x	y	z
O(38)	925(7)	-135(6)	273(10)
C(39)	1085(7)	-2880(6)	2941(10)
O(39)	713(6)	-3350(6)	3283(9)
C(12)	3844(4)	5163(3)	1978(4)
C(13)	4211(4)	5796(3)	1577(4)
C(14)	4251(4)	5804(3)	439(4)
C(15)	3923(4)	5179(3)	-300(4)
C(16)	3556(4)	4546(3)	101(4)
C(11)	3517(4)	4538(3)	1239(4)
C(18)	2131(3)	2503(4)	402(6)
C(19)	2122(3)	1829(4)	-196(6)
C(20)	2876(3)	1606(4)	-375(6)
C(21)	3637(3)	2059(4)	43(6)
C(22)	3645(3)	2734(4)	642(6)
C(17)	2892(3)	2956(4)	821(6)
C(24)	188(5)	4931(4)	2135(7)
C(25)	-631(5)	5140(4)	1618(7)
C(26)	-1283(5)	4597(4)	1074(7)
C(27)	-1116(5)	3845(4)	1046(7)
C(28)	-298(5)	3636(4)	1563(7)
C(23)	354(5)	4179(4)	2107(7)
C(41)	1917(3)	-2654(4)	6095(6)
C(42)	1854(3)	-3347(4)	6592(6)
C(43)	2591(3)	-3692(4)	7124(6)
C(44)	3391(3)	-3343(4)	7160(6)
C(45)	3454(3)	-2649(4)	6664(6)
C(40)	2718(3)	-2305(4)	6131(6)
C(47)	3587(5)	-24(4)	6268(5)
C(48)	3978(5)	526(4)	7120(5)
C(49)	4194(5)	344(4)	8278(5)
C(50)	4018(5)	-388(4)	8584(5)
C(51)	3627(5)	-938(4)	7732(5)
C(46)	3411(5)	-756(4)	6574(5)
C(53)	369(5)	-1281(3)	3175(7)
C(54)	-1183(5)	-1043(3)	3030(7)
C(55)	-1315(5)	-285(3)	2893(7)
C(56)	-633(5)	236(3)	2900(7)
C(57)	181(5)	-1(3)	3044(7)
C(52)	313(5)	-760(3)	3182(7)

2.44%. IR (cyclohexane):  $\nu(\text{CO})$  2099m, 2071m, 2061s, 2052s, 2030s, 2020vs, 2001(sh), 1994w, 1971w, 1964w  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR:  $\delta$  ( $\text{CDCl}_3$ ) -17.29 (d,  $J(\text{PH})$  4.5 Hz, 4H, RuH), 0.98 (t,  $J$  7.3 Hz, 3H,  $\text{CH}_3$ ), 2.51 (m, 2H,  $\text{CH}_2$ ), 7.45 (m, 14H, Ph and  $\text{C}_6\text{H}_4$ ). Bands 3–8 were obtained in trace amounts and were not identified.

### Crystallography

**Data collection.** Intensity data for compounds **3**, **12**, **13** and **15** were measured at room-temperature on an Enraf–Nonius CAD4-F diffractometer fitted with  $\text{Mo-K}\alpha$  (graphite monochromator) radiation,  $\lambda$  0.7107 Å. The  $\omega$ -2/3 $\theta$  scan technique was employed for **3** and **13** and the  $\omega$ -2 $\theta$  technique was used for the data collections of **12** and **15**. The net intensity values of three standard reflections were monitored

after every 3600 seconds X-ray exposure time for each crystal. These measurements indicated that no significant decomposition of the samples had occurred during their respective data collections. Corrections were routinely applied for Lorentz and polarization effects and for absorption with the use of the SUSCAD and ABSORB programs for **3** and **13** and the PREABS, PROCES, and SHELX programs for **12** and **15** [38]. Relevant crystal data for each compound are summarized in Table 5.

*Solution and refinement.* The heavy atom positions for each of the structures were determined with the use of the direct-methods routine in SHELX [38]. Subsequent difference map calculations enabled the location of all non-hydrogen atoms for each compound. The structures of **3**, **13** and **15** were refined by a block-matrix least-squares procedure and that of **12** by a full-matrix least-squares procedure. The phenyl rings in each compound were refined as hexagonal rigid groups and hydrogen atoms were included in each model at their calculated positions. A weighting scheme,  $w = k/[\sigma^2(F) + g|F|^2]$ , was included in all refinements; final refinement details are listed in Table 5. Neutral Ru and Os atom scattering factors (corrected for  $\Delta f'$  and  $\Delta f''$ ) were from International Tables for X-ray Crystallography [39] while those for the remaining atoms were those incorporated in SHELX [38].

In the course of the refinement of **3** it became evident that there was disorder associated with the Ru<sub>3</sub> triangle. In contrast to the previously reported disorder associated with the Ru<sub>3</sub> clusters, which has been described as a 'Star-of-David' arrangement of partially occupied metal atom sites [40], the disorder in **3** is best described as two Ru<sub>3</sub> triangles translated one to each side of the parent Ru<sub>3</sub> triangle. In the final refinement cycle of **3** the site occupation factors of each of the two 'translated' Ru<sub>3</sub> triangles were set to 2% and that of the parent Ru<sub>3</sub> triangle at 96% (see Figure S1 (Supplementary material)).

The molecular structures and atom numbering schemes are given in Figures 1–4; atomic coordinates of the non-hydrogen atoms are listed in Tables 6–9. Tables of thermal parameters, atomic coordinates and thermal parameters for hydrogen atoms, complete bond distance and bond angle tables, and observed and calculated structure factors are available from the authors.

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