

Reactions of  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$  with functional phosphines. X-ray structures of  
 $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{dppm})(\text{CO})_{12} \cdot \text{CHCl}_3$   
 $\text{Ru}_5(\mu_5\text{-C}_2\text{H})(\mu\text{-PPh}_2)_2(\mu\text{-P}, N\text{-PPh}_2\text{C}_6\text{H}_4\text{NH-2})(\mu\text{-CO})(\text{CO})_{10}$ ,  
 $\text{Ru}_4\{\mu_4\text{-C}_2\text{PPh}_2[\text{Ru}(\mu\text{-OH})(C, P\text{-2-CHMeC}_6\text{H}_4\text{PPh}_2\text{-2})(\text{CO})_2]\}\text{-}$   
 $(\mu\text{-PPh}_2)(\text{CO})_{10} \cdot \text{CHCl}_3$  and  
 $\text{Ru}_5(\mu\text{-H})_2\{\mu_5\text{-PPh}_2\text{C}_2\text{CHC}(\text{C}_6\text{H}_4\text{PPh}_2\text{-2})\}(\mu\text{-PPh}_2)(\text{CO})_{11}$

Chris J. Adams<sup>a</sup>, Michael I. Bruce<sup>a,\*</sup>, Brian W. Skelton<sup>b</sup>, Allan H. White<sup>b</sup>

<sup>a</sup> Jordan Laboratories, Department of Chemistry, University of Adelaide, Adelaide, S.A. 5005, Australia

<sup>b</sup> Department of Chemistry, University of Western Australia, Nedlands, W.A. 6907, Australia

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## Abstract

When  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$  (**1**) is treated with dppm,  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{dppm})(\text{CO})_{12}$  (**3**) is formed, in which the dppm ligand chelates one Ru atom; the resulting  $\text{Ru}_5$  cluster is a spiked butterfly. Reaction between **1** and  $\text{PPh}_2(\text{C}_6\text{H}_4\text{NH}_2\text{-2})$  yields  $\text{Ru}_5(\mu_5\text{-C}_2\text{H})(\mu\text{-PPh}_2)_2(\mu\text{-PPh}_2\text{C}_6\text{H}_4\text{NH-2})(\mu\text{-CO})(\text{CO})_{10}$  (**4**) as the major product, in which the deprotonated anilino-phosphine ligand is attached to a triangulated square  $\text{Ru}_5$  core with an open envelope conformation. In a similar reaction with  $\text{PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2\text{-2})$  the major product further reacts to give a number of complexes, including  $\text{Ru}_4\{\mu_4\text{-C}_2\text{PPh}_2[\text{Ru}(\mu\text{-OH})(C, P\text{-2-CHMeC}_6\text{H}_4\text{PPh}_2)(\text{CO})_2]\}\text{-}$   $(\mu\text{-PPh}_2)(\text{CO})_{10}$  (**6**), formed by incorporation of  $\text{H}_2\text{O}$  into the cluster; in this case, one Ru atom interacts with an  $\text{Ru}_4$  butterfly by means of a  $\mu\text{-OH}$  ligand and coordination to the  $\text{PPh}_2$  group of the  $\text{C}_2\text{PPh}_2$  ligand. A minor product is  $\text{Ru}_5(\mu\text{-H})_2\{\mu_5\text{-PPh}_2\text{C}_2\text{CH}=\text{C}(\text{C}_6\text{H}_4\text{PPh}_2\text{-2})\}(\mu\text{-PPh}_2)(\text{CO})_{11}$  (**7**), in which the diphosphine ligand has been formed by linkage of the  $\text{C}_2\text{PPh}_2$  ligand with the olefinic portion of the  $\text{PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2)$  ligand with concomitant migration of two H atoms to the cluster. The resulting  $\mu_5\text{-PPh}_2\text{C}_2\text{CHCC}_6\text{H}_4\text{PPh}_2$  fragment is attached to a ‘‘bow-tie’’  $\text{Ru}_5$  cluster by the two P atoms and all four carbon atoms of the  $\text{PC}_4$  chain.

**Keywords:** Ruthenium; Carbonyl; Phosphine; Cluster; Crystal structure; Amine; Hydroxy; Olefin–acetylide coupling

## 1. Introduction

Some time ago, we described a study of some substitution reactions of the open  $\text{Ru}_5$  cluster  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$  (**1**; Scheme 1) with  $\text{P}(\text{OEt})_3$  [**1**]. Substitution occurs preferentially at the basal [Ru(2)] or wing-tip [Ru(1)] atoms in thermal or  $\text{Me}_3\text{NO}$ -induced reactions respectively. Also formed was a disubstituted complex which contained both phosphite ligands on wing-tip Ru atoms [Ru(1) and Ru(5)], the latter also being coordinated to the P atom of the cluster-spanning

$\text{C}_2\text{PPh}_2$  ligand. A similar complex containing two  $\text{PMe}_2\text{Ph}$  ligands was obtained, but with triarylphosphines, the monosubstituted complex [probably residing on Ru(2)] was transformed via a reaction with the  $\text{C}_2\text{PPh}_2$  ligand on the cluster to give  $\text{PPh}$ ,  $\text{PAr}_2$  and  $\text{PhC}_2\text{Ar}$  ligands in **2** [2]. This paper describes reactions, summarised in Scheme 2, between **1** and dppm to give a complex in which Ru(2) is chelated by the dppm ligand, with concomitant cleavage of an Ru–Ru bond from this atom, and with the functional phosphines  $\text{PPh}_2(\text{C}_6\text{H}_4\text{R-2})$  ( $\text{R} = \text{NH}_2$  and  $\text{CH}=\text{CH}_2$ ). In the latter reactions, more extensive degradations of the cluster and associated non-carbonyl ligands occur.

\* Corresponding author.

## 2. Results

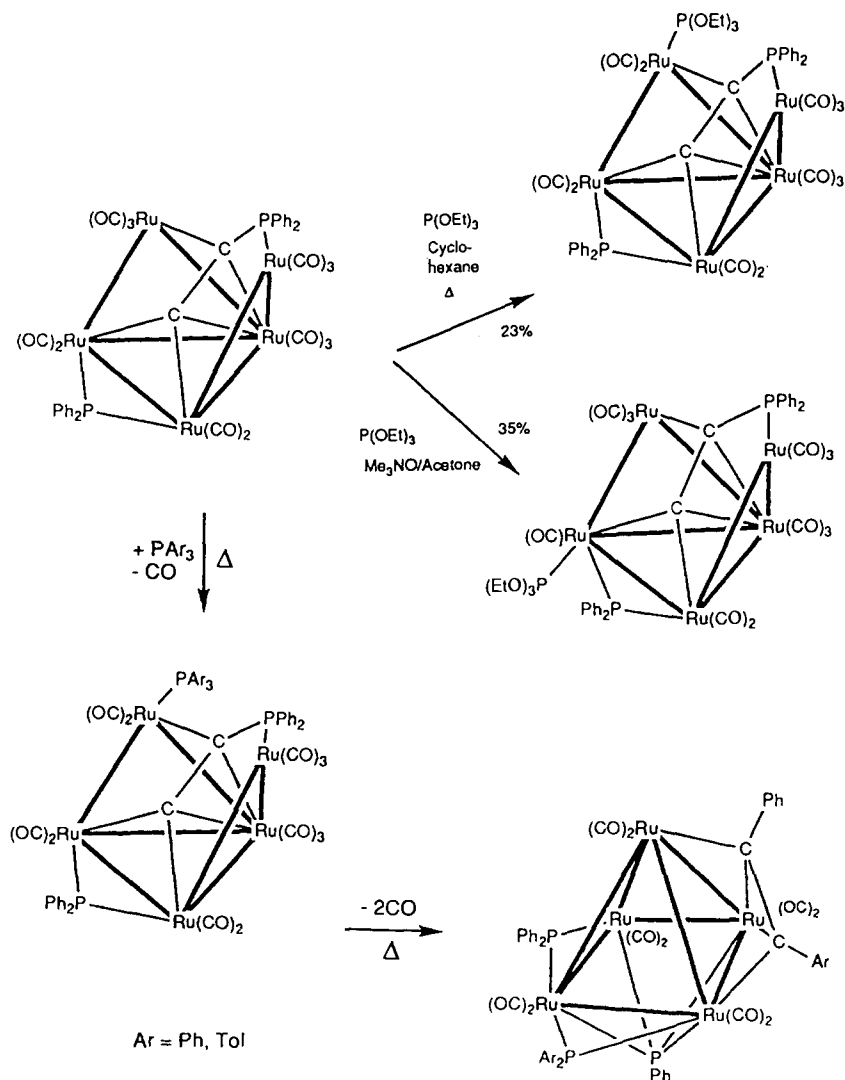
### 2.1. Reaction with *dppm*

The reaction between **1** and *dppm* was induced by addition of  $\text{Me}_3\text{NO}$  to a solution of the reactants in tetrahydrofuran. The major product (67%) was purified by thin-layer chromatography (TLC) to give black crystals which were characterised by a single crystal X-ray structure determination as the cluster **3**. The spectroscopic properties of **3** were in accord with its solid-state structure: the IR  $\nu(\text{CO})$  spectrum contained six bands in the terminal region. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were not informative, although specific assignments of the resonances have been made and are detailed in the Experimental section. The FAB mass spectrum contained a molecular ion which fragmented by loss of up to 12 CO groups. A change in the reaction solvent to  $\text{CH}_2\text{Cl}_2$  resulted in a significant increase in the yield of a second black product (from 6 to 37%), which ap-

peared to have only 11 CO groups; however, we were not able to obtain crystals suitable for an X-ray study.

### 2.2. Molecular structure of $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{12}(\text{dppm})$ (**3**)

Fig. 1(a) depicts a molecule of **3** and significant bond parameters are collected in Table 1. As can be seen, the complex is formed by addition of the *dppm* ligand to **1** with the loss of only one CO group. The diphosphine chelates Ru(5), the same atom to which P(1) of the  $\text{C}_2\text{PPh}_2$  ligand is attached; this results in cleavage of the Ru(2)–Ru(5) bond. The  $\text{C}(1)\text{--}\text{C}(2)$  fragment of the  $\text{C}_2\text{PPh}_2$  ligand behaves like an alkyne [ $\text{C}(1)\text{--}\text{C}(2)$  1.35(1) Å] and is bonded to Ru(1)–Ru(2)–Ru(4) in the familiar  $2\eta^1, \eta^2$  alkyne mode [Ru(4)–C(1,2) 2.286, 2.121(8); Ru(1)–C(1) 2.093(8), Ru(2)–C(2) 2.048(9) Å], Ru(3) being the second alkyne “substituent” on C(2) [2.095(8) Å]. As in **1**, P(2) bridges Ru(2)–Ru(3) somewhat unsymmetrically [Ru(2,3)–P(2) 2.274,



Scheme 1.

Table 1  
Selected bond lengths (Å) and angles (°) for  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_2(\text{dppm})$  (3)

<i>Bond lengths</i>			
Ru(1)–Ru(2)	2.848(2)	Ru(1)–C(1)	2.093(8)
Ru(1)–Ru(4)	2.758(2)	Ru(1)–C(2)	2.453(8)
Ru(2)–Ru(3)	2.773(2)	Ru(2)–C(2)	2.048(9)
Ru(2)–Ru(4)	2.831(2)	Ru(3)–C(2)	2.095(8)
Ru(3)–Ru(4)	2.954(2)	Ru(4)–C(1)	2.286(8)
Ru(3)–Ru(5)	2.997(3)	Ru(4)–C(2)	2.121(8)
Ru(5)–P(1)	2.381(3)		
Ru(2)–P(2)	2.274(3)	C(1)–C(2)	1.35(1)
Ru(3)–P(2)	2.314(3)	C(1)–P(1)	1.808(8)
Ru(5)–P(3)	2.399(3)	P(3)–C(0)	1.835(9)
Ru(5)–P(4)	2.362(3)	P(4)–C(0)	1.838(9)
Ru–CO	range 1.83–1.92(1), av. 1.88 Å		
C–O	range 1.13–1.17(1), av. 1.15 Å		
P–C(Ph)	range 1.812–1.851(9), av. 1.830 Å		
<i>Bond angles</i>			
Ru(2)–Ru(1)–Ru(4)	60.64(4)	Ru(4)–Ru(3)–Ru(5)	97.36(5)
Ru(1)–Ru(2)–Ru(4)	58.10(3)	Ru(1)–Ru(4)–Ru(2)	61.26(5)
Ru(3)–Ru(2)–Ru(4)	63.61(4)	Ru(2)–Ru(4)–Ru(3)	57.23(3)
Ru(2)–Ru(3)–Ru(4)	59.16(4)		
Ru(2)–Ru(3)–Ru(5)	124.24(4)	P(3)–C(0)–P(4)	94.6(4)
Dihedral	Ru(1)–Ru(2)–Ru(4)/Ru(2)–Ru(3)–Ru(4) 129.79(4)°		

2.314(3) Å]. At 76 cluster valence electrons, the electron count corresponds to an electron-precise  $\text{Ru}_5$  cluster with six Ru–Ru bonds. Compared with **1**, the change

in conformation of the  $\text{Ru}_5$  cluster to accommodate the steric and electronic requirements of the bridging ligand has resulted in changes in coordination of the  $\text{C}_2$  moi-

Table 2  
Selected bond lengths and angles for  $\text{Ru}_5(\mu_5\text{-C}_2\text{H})(\mu\text{-PPh}_2)_2(\mu\text{-P,N-PPh}_2\text{C}_6\text{H}_4\text{NH}_2)(\mu\text{-CO})(\text{CO})_{10}$  (4) and  $\text{Ru}_5(\mu_5\text{-C}_2\text{H})(\mu\text{-SPh})(\mu\text{-PPh}_2)_2(\mu\text{-CO})(\text{CO})_{11}$  (5) [4]

<i>Bond lengths (Å)</i>					
	<b>4</b>	<b>5</b>		<b>4</b>	<b>5</b>
Ru(1)–Ru(2)	2.839(5)	2.826(2)	Ru(1)–C(1)	2.01(3)	2.079(7)
Ru(1)–Ru(4)	2.677(5)	2.657(2)	Ru(2)–C(2)	2.44(3)	2.260(9)
Ru(2)–Ru(3)	2.881(4)	2.843(2)	Ru(3)–C(2)	2.06(4)	2.13(1)
Ru(2)–Ru(4)	2.971(6)	2.989(2)	Ru(4)–C(1)	2.20(3)	2.178(9)
Ru(3)–Ru(5)	2.762(5)	2.796(2)	Ru(4)–C(2)	2.20(3)	2.155(8)
Ru(4)–Ru(5)	2.861(4)	2.848(2)	Ru(5)–C(2)	2.06(3)	2.233(7)
Ru(1)–P(1)	2.27(1)	2.275(3)	Ru(1)–C(42)	2.22(5)	2.706(4)
Ru(2)–P(1)	2.46(1)	2.457(3)	Ru(4)–C(42)	1.86(4)	1.907(5)
Ru(2)–P(2)	2.31(1)	2.323(3)	Ru(3)–E(312)	2.15(3)	2.423(3)
Ru(3)–P(2)	2.29(1)	2.290(3)	Ru(5)–E(312)	2.05(3)	2.393(3)
Ru(5)–P(3)	2.33(1)	—			
C(1)–C(2)	1.64(5)	1.41(1)	P(3)–C(311)	1.77(4)	—
C(312)–N(312)	1.46(4)	—			
Ru–CO	range 1.73(3)–2.07(5), av. 1.85 Å				
C–O	range 1.04(6)–1.26(5), av. 1.18 Å				
P–C(Ph)	range 1.75(4)–1.84(5), av. 1.81 Å				
<i>Bond angles (°) for 4</i>					
Ru(1)–Ru(2)–Ru(4)	54.8(1)		Ru(2)–Ru(4)–Ru(5)	88.8(2)	
Ru(1)–Ru(4)–Ru(2)	60.1(1)		Ru(3)–Ru(2)–Ru(4)	86.4(1)	
Ru(2)–Ru(1)–Ru(4)	65.1(2)		Ru(3)–Ru(5)–Ru(4)	90.9(1)	
Ru(2)–Ru(3)–Ru(5)	92.6(2)				
Dihedral	Ru(2)–Ru(3)–Ru(4)–Ru(5)/Ru(1)–Ru(2)–Ru(4) 124.9(1)°				

ety to the more regular  $\mu_3$ -alkyne mode if, as mentioned above, P(1) and Ru(4) are considered to be the alkyne substituents.

A second complex was isolated from the reaction in tetrahydrofuran as black crystals. Crystals suitable for an X-ray study have not been obtained, but its colour and formulation as containing one CO group fewer than **3** (by analysis and FAB mass spectrometry) suggests that it retains the Ru<sub>5</sub> skeleton found in **1**. We cannot say whether the dppm ligand bridges one of the Ru–Ru vectors or chelates a single metal atom as found in **3**.

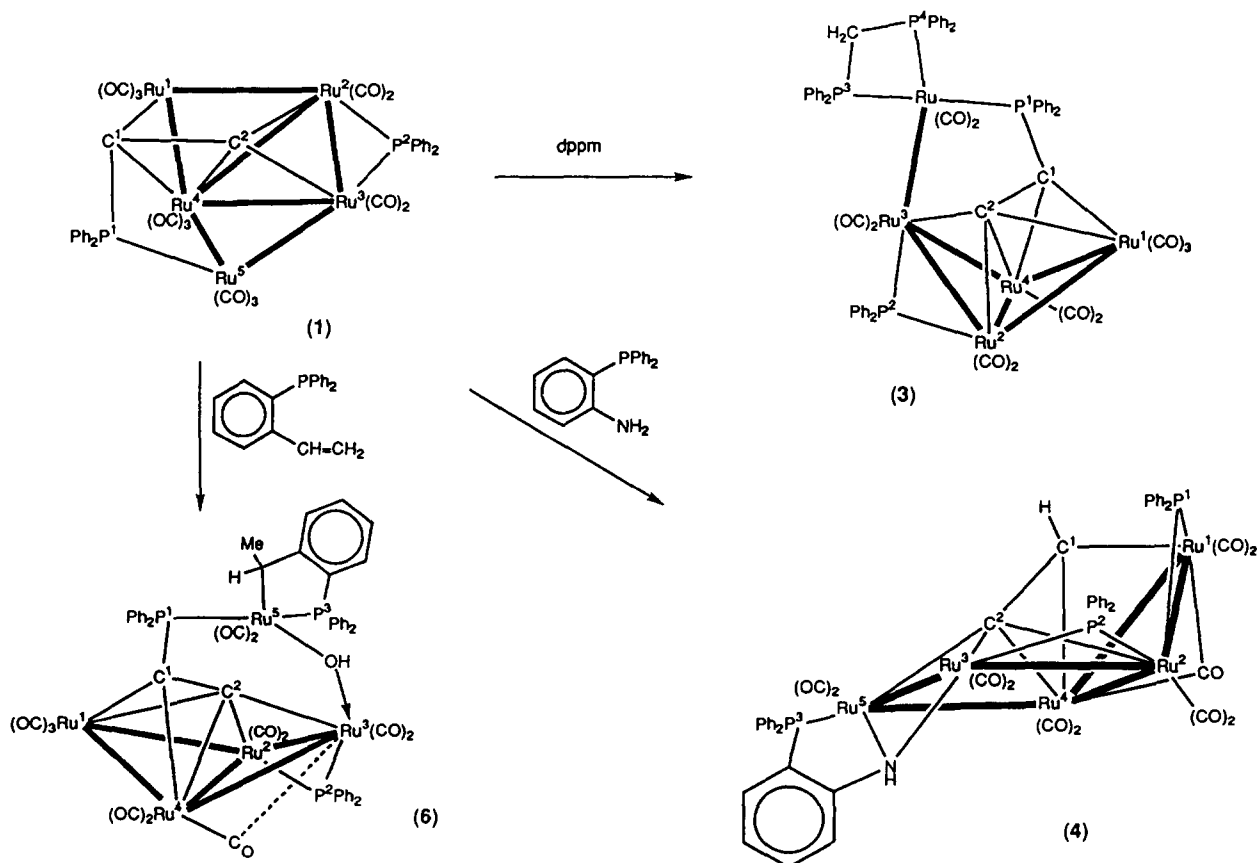
### 2.3. Reaction with PPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-2)

The only tractable product obtained from the reaction between **1** and PPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-2) was a dark red crystalline solid, isolated in 25% yield, which was crystallographically characterised, fairly definitively if imprecisely, as Ru<sub>5</sub>( $\mu_5$ -C<sub>2</sub>H)( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>( $\mu$ -PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-2)( $\mu$ -CO)(CO)<sub>10</sub> (**4**). The <sup>1</sup>H NMR spectrum contains peaks at  $\delta$  0.33 (broad) and 9.96, assigned to the NH and C<sub>2</sub>H protons respectively, and an unusually high-field signal at  $\delta$  4.70, which was assigned to one of the aromatic protons with the help of a COSY spectrum. The IR  $\nu$ (CO) spectrum contains nine bands in the terminal region, together with one at 1855 cm<sup>-1</sup> as-

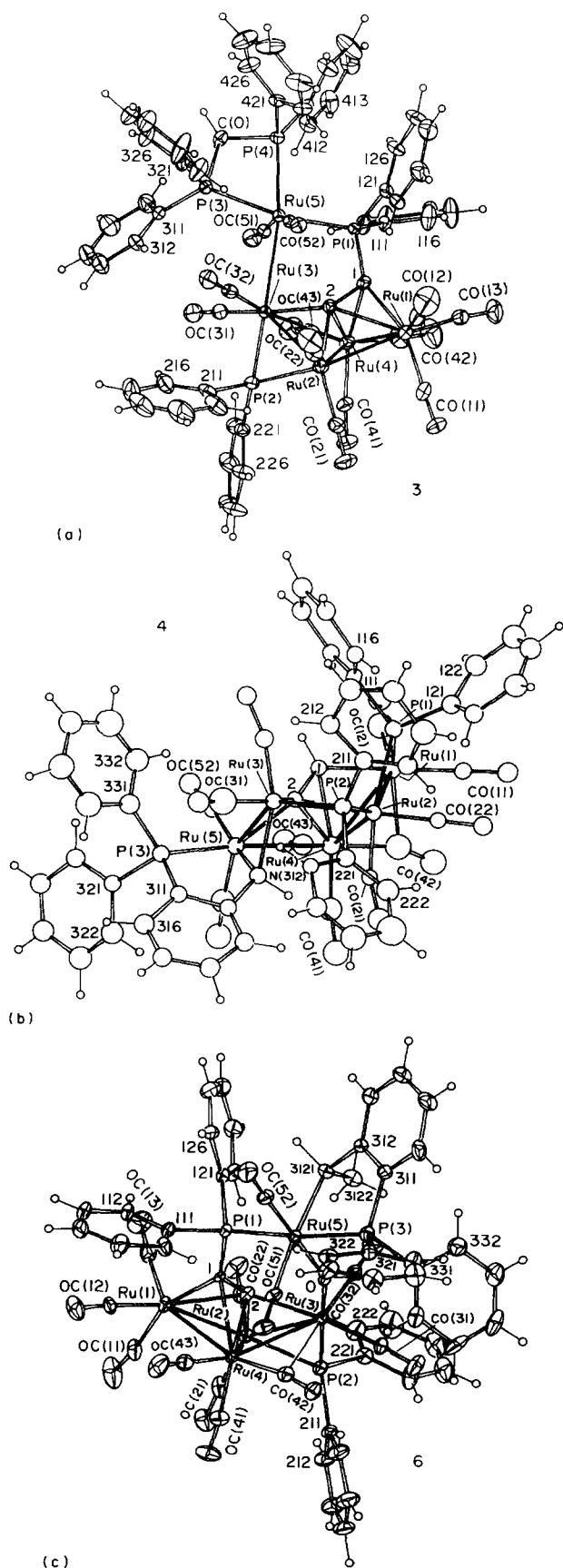
signed to the CO group bridging Ru(4)–Ru(5) (see below). The FAB mass spectrum contained a molecular ion which fragmented by the usual loss of CO groups.

### 2.4. Molecular structure of Ru<sub>5</sub>( $\mu_5$ -C<sub>2</sub>H)( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>( $\mu$ -PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-2)( $\mu$ -CO)(CO)<sub>10</sub> (**4**)

A molecule of **4** is depicted in Fig. 1(b) and selected bond distances and angles are given in Table 2. The Ru<sub>5</sub> core adopts an open envelope conformation, with a C<sub>2</sub>H group sitting between the flap and the body of the envelope. Various edges are bridged by CO [Ru(1,4)–C(42) 2.22, 1.86(4) Å], PPh<sub>2</sub> [Ru(2,3)–P(2) 2.31, 2.29(1); Ru(1,2)–P(1) 2.27, 2.46(1) Å] or PPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-2) groups [Ru(3,5)–N(312) 2.15, 2.05(3) Å], the latter being formed by deprotonation of the amino group in the anilino-phosphine. The C<sub>2</sub>H ligand interacts with all five metal atoms, spanning the Ru(1)–Ru(2)–Ru(4) face in the  $2\eta^1, \eta^2$ -mode found above in **3** [Ru(4)–C(1,2) both 2.20(3); Ru(1)–C(1) 2.01(3), Ru(2)–C(2) 2.44(3); C(1)–C(2) 1.64(5) Å], but on this occasion it is the Ru(3)–Ru(5) atoms which form the second alkyne “substituent”. The molecular structure bears a close resemblance to that of the complex Ru<sub>5</sub>( $\mu_5$ -C<sub>2</sub>H)( $\mu$ -SPh)( $\mu$ -PPh<sub>2</sub>)( $\mu$ -CO)(CO)<sub>11</sub> (**5**), which is one of the products formed in reactions between **1** and PhSH [3];



Scheme 2.



some relevant structural parameters of **5** are also listed in Table 2.

Although TLC resulted in the separation of several other bands, none were obtained in a crystalline form suitable for X-ray studies, so that they could not be characterised further.

### 2.5. Reaction with $PPh_2(C_6H_4CH=CH_2-2)$

The  $Me_3NO$ -induced reaction between **1** and  $PPh_2(C_6H_4CH=CH_2-2)$  afforded several products; a brown fraction, with a complex IR  $\nu(CO)$  spectrum, gave crystals from dichloromethane–methanol, which were shown by an X-ray structure determination to have a structure based on an  $Ru_4$  butterfly, namely  $Ru_4\{\mu_4-C_2PPh_2[Ru(\mu-OH)(C,P-2-CHMeC_6H_4PPh_2)(CO)_2]\}(\mu-PPh_2)(CO)_{10}$  (**6**). Further separation gave several fractions, one of which afforded crystals suitable for an X-ray study. By this means, the complex was characterised as being formed by formal linking of the olefinic moiety of the functional phosphine with the  $C_2$  unit of **1** to give  $Ru_5(\mu-H)_2\{\mu_5-PPh_2C_2CH=C(C_6H_4PPh_2-2)\}(\mu-PPh_2)(CO)_{11}$  (**7**).

### 2.6. Molecular structure of $Ru_4\{\mu_4-C_2PPh_2[Ru(\mu-OH)(C,P-2-CHMeC_6H_4PPh_2)(CO)_2]\}(\mu-PPh_2)(CO)_{10} \cdot CHCl_3$ (**6**)

A molecule of **6** is depicted in Fig. 1(c) and significant bond parameters are listed in Table 3. In this complex, loss of a metal atom from the  $Ru_5$  core, although not from the complex, has occurred to give a flattened  $Ru_4$  butterfly [Ru–Ru separations 2.744(2)–2.911(2); hinge 2.843(2) Å; dihedral 130.51(4)°] spanned by the  $C_2$  moiety of the original  $C_2PPh_2$  ligand from **1**. The ligand is attached as an asymmetric  $\eta^1,2\eta^2$ -mode [Ru(4)–C(1,2) 2.291(8), 2.124(8); Ru(1)–C(1,2) 2.14(1), 2.34(1); C(1)–C(2) 1.35(2) Å], with an additional interaction between C(2) and Ru(3) [2.18(1) Å]. The Ru(2)–Ru(3) vector is bridged by the  $PPh_2$  group [Ru(2,3)–P(2) 2.253(3), 2.302(4) Å], and ten CO groups are distributed among the four metal atoms. The fifth Ru atom remains attached to P(1) from the  $C_2PPh_2$  ligand [Ru(5)–P(1) 2.367(3) Å] and to two CO groups. In addition, a  $PPh_2(C_6H_4CHMe-2)$  ligand, derived from the styrylphosphine, chelates Ru(5) via the P(3) and C(3121) atoms [Ru(5)–C(3121) 2.184(8), Ru(5)–P(3)

Fig. 1. Plots of molecules of (a)  $Ru_5(\mu_5-C_2PPh_2)(\mu-PPh_2)(CO)_{12}(dppm)$  (**3**), (b)  $Ru_5(\mu_5-C_2H)(\mu-PPh_2)_2(\mu-P,N-PPh_2C_6H_4NH-2)(\mu-CO)(CO)_{10}$  (**4**), and (c)  $Ru_4\{\mu_4-C_2PPh_2[Ru(\mu-OH)(C,P-2-CHMeC_6H_4PPh_2-2)(CO)_2]\}(\mu-PPh_2)(CO)_{10} \cdot CHCl_3$  (**6**). Views consistent with the structural formulas given in Scheme 2. The atom numbering schemes are shown. In this and subsequent figures, non-hydrogen atoms are shown with 20% thermal envelopes; hydrogen atoms have arbitrary radii of 0.1 Å.

2.341(4) Å], and a hydroxyl group bridges the non-bonded Ru(3) ··· Ru(5) vector [Ru(3,5)–O(1) 2.215(9), 2.132(8) Å]. The Ru<sub>4</sub> cluster is a 60-electron system.

2.7. Molecular structure of Ru<sub>5</sub>(μ-H){μ<sub>5</sub>-PPh<sub>2</sub>C<sub>2</sub>CH=C(C<sub>6</sub>H<sub>4</sub>)PPh<sub>2</sub>}(μ-PPh<sub>2</sub>)(CO)<sub>11</sub> (7)

Fig. 2 shows a plot of a molecule of 7 and Table 4 lists important bond distances and angles. The metal core consists of two Ru<sub>3</sub> triangles linked through a common apex [Ru(5)], with Ru–Ru distances between 2.738(1) and 3.035(1) Å; the dihedral Ru(1,2,5)/Ru(3,4,5) is 12.81(4)°. The longest, Ru(3)–Ru(4) [3.035(1) Å], is associated with one of the two bridging H atoms located in the X-ray study. The second core-bonded H atom is found bridging Ru(3)–Ru(5) [2.850(1) Å], also spanned by C(1). Although the Ru(1)–Ru(5) separation is longer [at 2.976(2) Å], other factors determining bond length variations within the Ru<sub>5</sub> core include the degree of interaction with the PC<sub>4</sub> string. In this context, we note that the formal electron counts of Ru(1), Ru(2) and Ru(5) are 9, 11 and 10, respectively, so that the H atom would not be expected to reside in this portion of the butterfly core. Unusually, the PPh<sub>2</sub> group bridges the non-bonded Ru(2) ··· Ru(3) vector [Ru(2)–Ru(3) 3.675(2), Ru(2,3)–P(2) 2.369(2), 2.351(2) Å; Ru(2)–P(2)–Ru(3) 102.26(5)°]. 11 CO ligands are attached to the cluster, two to each Ru atom except for Ru(4), which has three.

The PPh<sub>2</sub>C<sub>2</sub>CH=CC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub> ligand spans all five metal atoms, being attached to Ru(1) and Ru(4) by P(3) and P(1) respectively [Ru(1)–P(3) 2.279(1), Ru(4)–P(1) 2.369(2) Å]. Atoms C(1), C(2) and C(4) bridge the Ru(3)–Ru(5), Ru(2)–Ru(5) and Ru(1)–Ru(2) vectors respectively. Atoms C(1,2) thus form an η<sup>2</sup>-attachment to Ru(5), while atoms C(2,3,4) form an η<sup>3</sup>-attachment to Ru(2); the former resembles the usual 2σ,π(∥) bonding found in alkyne–M<sub>3</sub> clusters. The C(1)–C(2)–C(3)–C(4) separations [1.371(5), 1.392(5), 1.422(5) Å respectively] indicate some electron delocalisation along the C<sub>4</sub> chain. The ligand thus donates 11 electrons to the cluster, which, with 27 from (2H + 11CO + PR<sub>2</sub>), has a total of 78 cluster valence electrons, as predicted for a “bow-tie” M<sub>5</sub> cluster.

### 3. Discussion

In the reactions of 1 which have been described above, we find an extension of the simple substitution

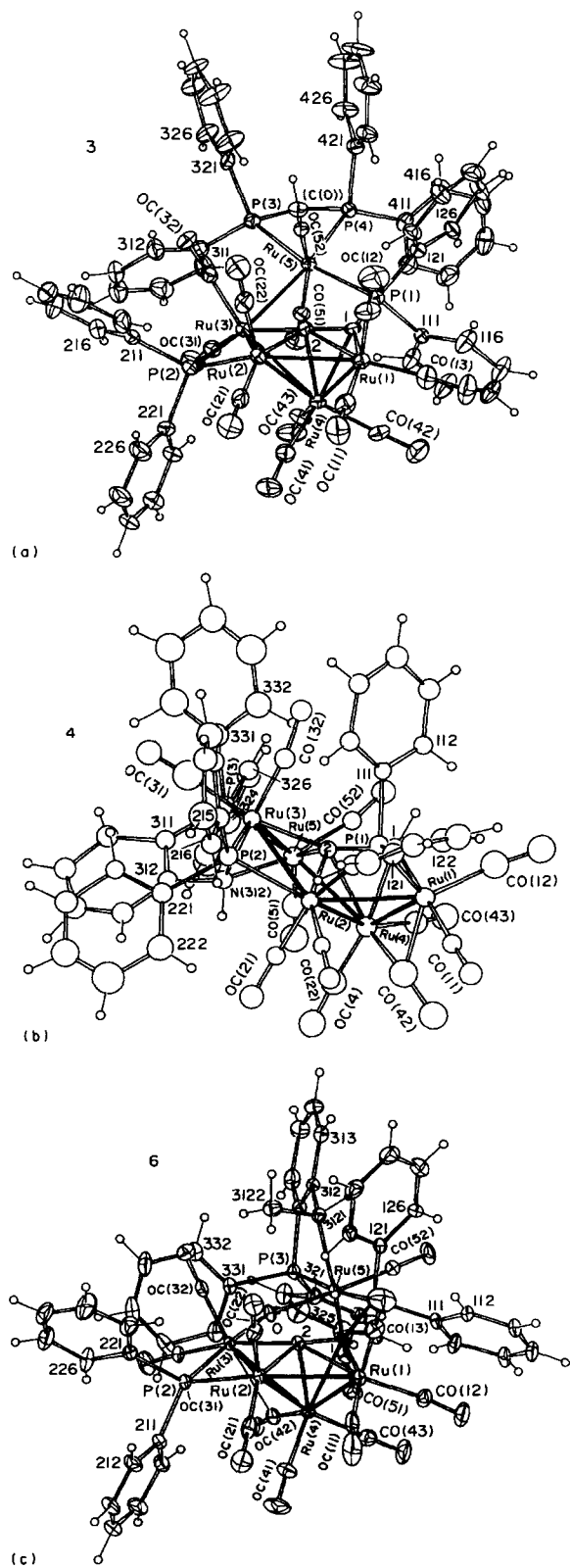


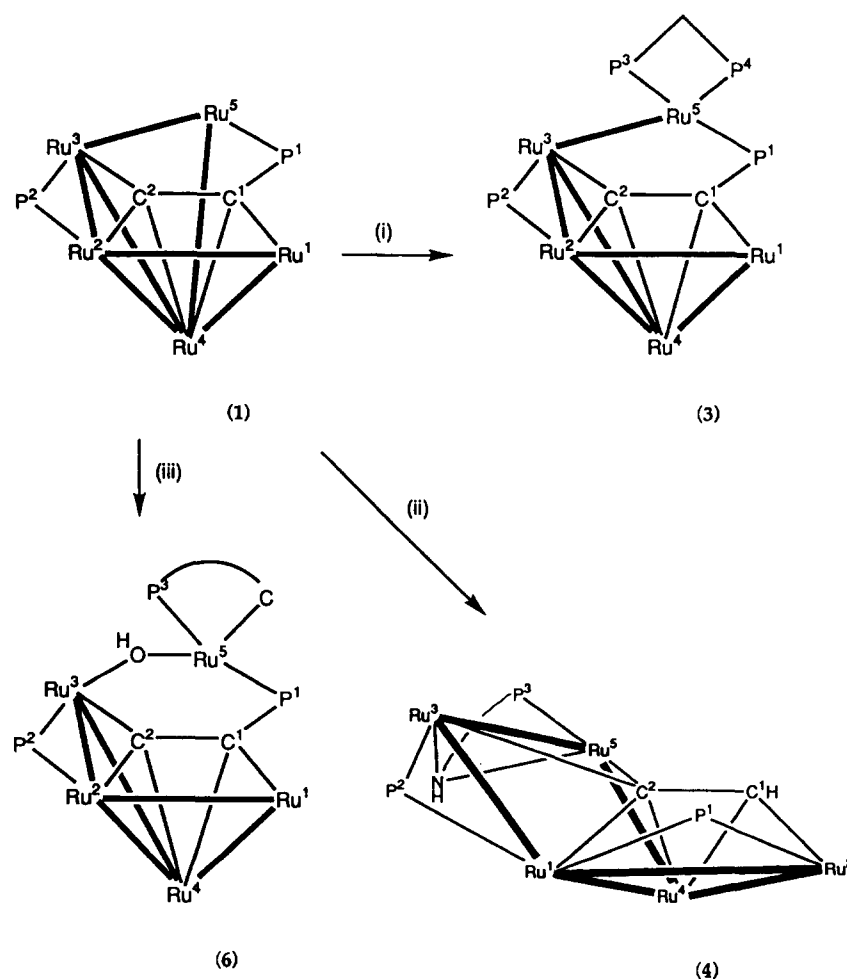
Fig. 2. Alternative plots of molecules of (a) Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)(CO)<sub>12</sub>(dppm) (3), (b) Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>H)(μ-PPh<sub>2</sub>)<sub>2</sub>(μ-P,N-PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH-2)(μ-CO)(CO)<sub>10</sub> (4), and (c) Ru<sub>4</sub>(μ<sub>4</sub>-C<sub>2</sub>PPh<sub>2</sub>[Ru(μ-OH)(C,P-2-CHMeC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>-2)(CO)<sub>2</sub>])(μ-PPh<sub>2</sub>)(CO)<sub>10</sub> · CHCl<sub>2</sub> (6). Views consistent with the core depictions given in Scheme 3.

of CO by  $\text{P}(\text{OEt})_3$  that we examined previously [2]. All the above reactions were initiated by TMNO; in agreement with our earlier findings, substitution occurs at Ru(5), which also bears P(2) of the  $\text{C}_2\text{PPh}_2$  ligand. The other functional groups in the ligands have resulted in further alterations of the cluster cores (Scheme 3). Thus, in the case of dppm, chelation of the diphosphine to Ru(5) does not result in loss of two CO ligands, but only of one, the preferred reaction being cleavage of one of the Ru–Ru bonds involving Ru(5) to give the core structure found in **3**. The isolation of a second product (of as yet undetermined structure) with a composition corresponding to the replacement of two CO groups in **1** by a dppm ligand may indicate that both reaction paths can be followed, however. We have no evidence for the interconvertibility of these two complexes. It is likely that chelation of the dppm results in steric hindrance around Ru(5) which is better relieved by Ru–Ru bond breaking than by loss of CO.

Several groups have looked at the reactions of or-

ganic molecules containing functional groups such as amines, aldehydes and imines with ruthenium and osmium cluster carbonyls [4–7]. Other studies of tertiary phosphines containing similar functional groups with ruthenium and osmium cluster carbonyls have been carried out. Characteristic reactions include cleavage of element–hydrogen bonds to give hydrido-clusters, as found in products obtained from reactions with  $\text{PPh}_2(\text{C}_6\text{H}_4\text{X}-2)$  ( $\text{X} = \text{NH}_2$ ,  $\text{N} = \text{CHPh}$  or  $\text{CHO}$ ) ligands [8], while ligands such as  $\text{PPh}_2\text{R}$  ( $\text{R} = \text{CH}_2\text{COPh}$  [9],  $\text{C}_5\text{H}_4\text{N}$  [10]) have been found to undergo P–C bond breaking.

The reaction between **1** and  $\text{PPh}_2(\text{C}_6\text{H}_4\text{NH}_2-2)$  which afforded **4** has resulted in cleavage of the  $\text{C}_2$ – $\text{PPh}_2$  bond, the resulting  $\text{PPh}_2$  ligand bridging the Ru(1)–Ru(2) bond. [Scheme 2 attempts to depict the clusters with a common (crystallographic) numbering system. However, to avoid “migration” of a  $\text{PPh}_2$  group from Ru(1) to Ru(5), required by the crystallographic numbering, we suggest that, in this case, the



Scheme 3. Core transformations of **1** in reactions with tertiary phosphines, drawn to emphasise relationships between geometries; no mechanistic implications are intended. Reagents: (i) dppm; (ii)  $\text{PPh}_2(\text{C}_6\text{H}_4\text{NH}_2-2)$ ; (iii)  $\text{PPh}_2(\text{C}_6\text{H}_4\text{CH}=\text{CH}_2-2)$ .

Table 3

Selected bond lengths (Å) and angles (°) for Ru<sub>4</sub>{μ<sub>4</sub>-C<sub>2</sub>PPh<sub>2</sub>[Ru(μ-OH)(C,P-2-CHMeC<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>)(CO)<sub>2</sub>]}(μ-PPh<sub>2</sub>)(CO)<sub>10</sub> · CHCl<sub>3</sub> (6)

<i>Bond lengths</i>			
Ru(1)–Ru(2)	2.793(2)	Ru(3)–O	2.215(9)
Ru(1)–Ru(4)	2.744(2)	Ru(5)–O	2.132(8)
Ru(2)–Ru(4)	2.843(2)	Ru(5)–P(1)	2.367(3)
Ru(2)–Ru(3)	2.799(2)	Ru(2)–P(2)	2.253(3)
Ru(3)–Ru(4)	2.911(2)	Ru(3)–P(2)	2.302(4)
Ru(1)–C(1)	2.14(1)	Ru(5)–P(3)	2.341(4)
Ru(4)–C(1)	2.291(8)	C(1)–C(2)	1.35(2)
Ru(2)–C(2)	2.04(1)	C(1)–P(1)	1.78(1)
Ru(3)–C(2)	2.18(1)	C(3121)–C(3122)	1.55(2)
Ru(4)–C(2)	2.124(8)	C(3121)–C(312)	1.55(2)
Ru(5)–C(3121)	2.184(8)	P(3)–C(311)	1.809(9)
Ru–CO range 1.83–1.94(1), av. 1.88 Å			
C–O range 1.11–1.17(4), av. 1.14 Å			
P–C(Ph) range 1.80(1)–1.834(9), av. 1.82 Å			
<i>Bond angles</i>			
Ru(2)–Ru(1)–Ru(4)	61.79(4)	Ru(1)–Ru(4)–Ru(2)	59.95(4)
Ru(1)–Ru(2)–Ru(4)	58.27(4)	Ru(2)–Ru(4)–Ru(3)	58.18(4)
Ru(3)–Ru(2)–Ru(4)	62.13(5)		
Ru(2)–Ru(3)–Ru(4)	59.69(5)	Ru(3)–O–Ru(5)	152.3(4)
Dihedral Ru(1)–Ru(2)–Ru(4)/Ru(2)–Ru(3)–Ru(4) 130.51(4)°			

phosphino-amine has added to the other wing-tip atom, Ru(1)]. Deprotonation of the amino group and addition of the hydrogen atom to the C<sub>2</sub> unit has formed an ethynyl group, while the amido group bridges the Ru(3)–Ru(5) bond. In the Ru<sub>5</sub> core, it is the Ru(3)–Ru(4) bond which is cleaved to give the C(2)-capped Ru<sub>4</sub> part of the cluster, presumably because bridging of Ru(3)–Ru(5) by the N atom serves to preserve this bond (in contrast to the situation found with **3**). The structure

is entirely analogous to that of **5**, one of three products isolated from reactions between **1** and PhSH [3]. As described for the latter, the C<sub>2</sub>H ligand may best be considered as an alkyne, being bonded in the common 2η<sup>1</sup>,η<sup>2</sup>-fashion to the Ru<sub>3</sub> part of the cluster, with a C(1)–C(2) separation, imprecisely determined, of 1.65(6) Å. The second substituent of the alkyne is the Ru(2)–Ru(3) moiety. However, an alternative view, consistent with many of the other reactions of **1**, is that

Table 4

Selected bond lengths (Å) and angles (°) for Ru<sub>5</sub>(μ-H){μ<sub>5</sub>-PPh<sub>2</sub>C<sub>2</sub>CHC(C<sub>6</sub>H<sub>4</sub>PPh<sub>2</sub>-2)}(μ-PPh<sub>2</sub>)(CO)<sub>11</sub> (7)

<i>Bond lengths</i>			
Ru(1)–Ru(2)	2.738(1)	Ru(1)–C(4)	2.096(3)
Ru(1)–Ru(5)	2.976(2)	Ru(2)–C(2)	2.162(4)
Ru(2)–Ru(5)	2.8463(8)	Ru(2)–C(3)	2.274(4)
Ru(3)–Ru(4)	3.035(1)	Ru(2)–C(4)	2.268(4)
Ru(3)–Ru(5)	2.850(1)	Ru(3)–C(1)	2.133(4)
Ru(4)–Ru(5)	2.879(1)	Ru(5)–C(1)	2.218(3)
Ru(1)–P(3)	2.279(1)	Ru(5)–C(2)	2.128(3)
Ru(2)–P(2)	2.369(2)	P(1)–C(1)	1.786(4)
Ru(3)–P(2)	2.351(1)	C(1)–C(2)	1.371(5)
Ru(4)–P(1)	2.369(2)	C(2)–C(3)	1.392(5)
		C(3)–C(4)	1.422(5)
		C(4)–C(312)	1.496(5)
<i>Bond angles</i>			
Ru(1)–Ru(5)–Ru(4)	158.36(2)	P(1)–C(1)–C(2)	131.3(3)
Ru(2)–Ru(5)–Ru(3)	80.36(3)	C(1)–C(2)–C(3)	150.4(4)
Ru(2)–P(2)–Ru(3)	102.26(5)	C(2)–C(3)–C(4)	118.8(3)
		C(3)–C(4)–C(312)	116.2(3)
Dihedral Ru(1)Ru(2)Ru(5)/Ru(3)Ru(4)Ru(5) 12.81(4)°			



C(1) is pulled into a close, strongly-bonded association with the approximately square  $Ru_4$  portion of the cluster.

In complex **6**, the  $Ru_5$  cluster in **1** has fragmented to give a butterfly bridged by the  $C_2$  moiety of the  $C_2PPh_2$  originally present in **1**. Similar extrusion of one of the Ru atoms, which remains incorporated into the complex, was found in the reaction of **1** with allyl chloride [11]. However, coordination of the tertiary phosphine, followed by addition of water (presumably from adventitious water present in a solvent or on the adsorbent during work-up) has resulted in cleavage of one of the Ru atoms from the  $Ru_5$  cluster, although it remains in the complex by virtue of its being coordinated to the  $PPh_2$  group of the  $C_2PPh_2$  ligand and the OH group which bridges it and Ru(4) of the butterfly. The lone Ru is also coordinated by the  $P,C$ - $PPh_2(C_6H_4CHMe-2)$  ligand and by two CO groups. It is possible that addition of water across the Ru–Ru bond and attack on a coordinated vinyl group, for example, could lead to the observed structure. Similar reactions of alkyne com-

plexes with water on surfaces have been reported [12,13] and under homogeneous conditions, for example the reactions of  $C_2Et_2$  with  $Fe_3(CO)_{12}$  [14] or  $Co_2(CO)_8$  [15], or of  $Ru_3((CO)_{11}(PPh_2(C_2^iPr))$  in aqueous THF [16]. The carboxylato complexes  $Fe_2(\mu-CR=CR'C(O)O)(CO)_6$  have been obtained from reactions of  $Fe_3(\mu_3-RC_2R')(CO)_9$  with water during TLC purification [17].

The structure of **7** is perhaps the most interesting, although the small amounts available have precluded anything other than an X-ray determination of its structure. The origins of this complex are obscure and the numbering scheme in Fig. 3 carries no mechanistic implications vis-à-vis **1**. Formally, however, the organo-diphosphine ligand has been formed by combination of the  $PPh_2$  ligand present in **1** with the olefinic side-chain of  $PPh_2(C_6H_4CH=CH_2-2)$ , with concomitant migration of two hydrogen atoms from the vinyl group to the cluster. We are not able to say anything about how this interesting process occurred, but we recall the ready dehydrogenation of  $Ru_3(\mu-P,\eta^2-PPh_2C_6H_4CH=CH_2)(CO)_{10}$  which occurs on heating to give  $Ru_3(\mu-H)_2(\mu_3-P,\eta^2-PPh_2C_6H_4C\equiv CH)$  [18]. Carbon–carbon bond forming reactions on polynuclear clusters have been described on many occasions [19], perhaps the most relevant to the present case being those involving alkynes and diynes on an  $Ru_4P$  cluster found by Carty's group [20]. Similar reactions of an intermediate phosphine-substituted derivative of **1**, followed by coupling of the two acetylenic groups on the  $Ru_5$  cluster, would not be unexpected.

The core transformations undergone in the conversions of **1** to three of the complexes described herein are shown in Scheme 3 in a form which emphasises the relationships between precursor and products. However, these diagrams assume that no ligand migration from one metal to another has occurred, and consequently they have no mechanistic implications.

## 4. Experimental

### 4.1. General conditions

All reactions were carried out under dry, high purity nitrogen using standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were by the Canadian Microanalytical Service, Delta, B.C. V4G 1G7, Canada. TLC was carried out on glass plates ( $20 \times 20 \text{ cm}^2$ ) coated with silica gel (Merck 60 GF<sub>254</sub>, 0.5 mm thick).

#### 4.1.1. Reagents

Complex **1** was prepared by the literature method [21].  $Me_3NO \cdot 2H_2O$  (Aldrich) was dehydrated by

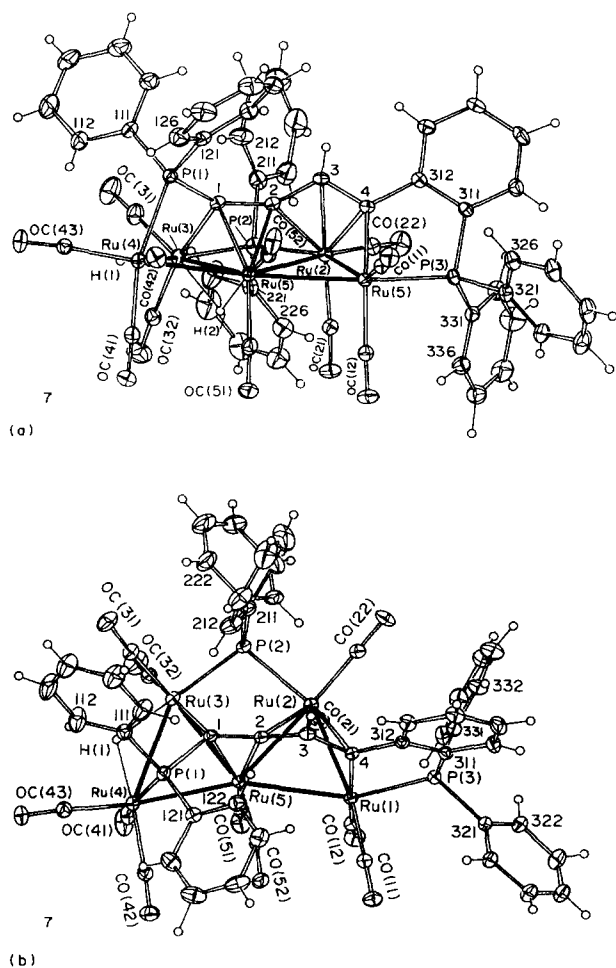


Fig. 3. Two views of a molecule of  $Ru_5(\mu-H)_2\{\mu_5-PPh_2C_2CHC-(C_6H_4PPh_2-2)(\mu-PPh_2)(CO)_{11}\}$  (**7**) showing the atom numbering scheme.

sublimation (100°C, 0.1 mm<sup>-1</sup>). The ligands PPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>X-2) (X = NH<sub>2</sub> and CH=CH<sub>2</sub>) were gifts from Dr. P.A. Duckworth and Professor M.A. Bennett respectively; dppm was obtained from Aldrich.

#### 4.1.2. Instrumentation

IR: Perkin-Elmer 1700X FT IR; 683 double beam, NaCl optics; NMR: Bruker CXP300 or ACP300 (<sup>1</sup>H NMR at 300.13 MHz, <sup>13</sup>C NMR at 75.47 MHz). 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).

#### 4.2. Reactions of 1 with dppm

##### 4.2.1. In THF

TMNO (ca. 20 mg, 0.27 mmol) was added to a solution of **1** (100 mg, 0.079 mmol) and dppm (31 mg, 0.08 mmol) in tetrahydrofuran (30 cm<sup>3</sup>) until no starting material remained. The solvent was removed and the residue was purified by preparative TLC (light petroleum/acetone 5:4) to yield two major bands. A brown band (*R<sub>f</sub>* 0.5) was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to yield black crystals of Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)(CO)<sub>11</sub>(dppm) (**8**) (8 mg, 6%), m.p. 223–226°C (decomp.). Anal. Found: C, 46.38; H, 2.66%; M, 1593 (mass spectrometry). C<sub>62</sub>H<sub>42</sub>O<sub>11</sub>P<sub>4</sub>Ru<sub>5</sub>. Calc.: C, 46.77; H, 2.66%; M, 1593. IR: ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>) 2056s, 2011s, 1999vs, 1982(sh), 1962m, 1920m, 1799w cm<sup>-1</sup>. <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>) 4.11 (1H, q, *J* = 12.5 Hz, CH<sub>2</sub>), 5.85 (1H, q, *J* = 11.9 Hz, CH<sub>2</sub>), 6.66–7.65 (40H, m, Ph). FAB MS (*m/z*): 1593, M<sup>+</sup>, 1537, 1509, 1453–1341, [M-*n*CO]<sup>+</sup> (*n* = 2, 3, 5–9). A black band (*R<sub>f</sub>* 0.4) was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to yield Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)(CO)<sub>12</sub>(dppm) (**3**) (86 mg, 67%), m.p. 235–237°C (decomp.). Anal. Found: C, 42.33; H, 2.77%; M, 1621 (mass spectrometry). C<sub>63</sub>H<sub>42</sub>O<sub>12</sub>P<sub>4</sub>Ru<sub>5</sub> · CHCl<sub>3</sub>. Calc. C, 44.19; H, 2.49%; M, 1621. IR: ν(CO) (CH<sub>2</sub>Cl<sub>2</sub>) 2049s, 2017vs, 2002s, 1990vs, 1981s, 1969(sh), 1959(sh), 1943(sh) cm<sup>-1</sup>. <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>) 4.0–4.7 (two broad multiplets, CH<sub>2</sub>), 7.22–7.67 (40H, m, Ph). FAB MS (*m/z*): 1621, M<sup>+</sup>; 1593–1285, [M-*n*CO]<sup>+</sup> (*n* = 1–12).

##### 4.2.2. In CH<sub>2</sub>Cl<sub>2</sub>

TMNO (ca. 20 mg, 0.27 mmol) was added to a solution of **1** (100 mg, 0.079 mmol) and dppm (31 mg, 0.08 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (30 cm<sup>3</sup>) until no starting material remained. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 5:4) to yield two major bands. A brown band (*R<sub>f</sub>* 0.5) was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to yield black crystals of Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)(dppm)(CO)<sub>11</sub> (**4**) (46 mg, 37%). A black band (*R<sub>f</sub>* 0.4) was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to yield **3** (39 mg, 30%).

#### 4.3. Reaction of 1 with PPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-2)

TMNO was added to a solution of **1** (125 mg, 0.099 mmol) and PPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>-2) (28 mg, 0.099 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (20 ml) until no starting material remained. The solution was filtered through a short plug of silica and left for a further 2 h. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 2:1) to yield at least six bands. The major red band (*R<sub>f</sub>* 0.4) was recrystallised from CH<sub>2</sub>Cl<sub>2</sub>/MeOH to yield Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>H)(μ-PPh<sub>2</sub>)<sub>2</sub>(μ-*P,N*-PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>NH<sub>2</sub>)(μ-CO)(CO)<sub>10</sub> (**4**) (38 mg, 25%). Anal. Found: C, 43.75; H, 2.49; N, 0.93%; M, 1486 (mass spectrometry). C<sub>55</sub>H<sub>36</sub>NO<sub>11</sub>P<sub>3</sub>Ru<sub>5</sub>. Calc.: C, 44.48; H, 2.44; N, 0.94%; M, 1486. IR: ν(CO) (cyclohexane) 2051vs, 2029vs, 2012s, 2004m, 1998m, 1984m, 1964m, 1958m, 1931m(br), 1855m(br) cm<sup>-1</sup>. <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>) 0.33 [1H, s(br), NH], 4.70 [1H, dd, *J* = 7.9, 4.3 Hz, Ph (confirmed by 2D COSY NMR)], 6.68 (1H, t, *J* = 7.6 Hz, Ph), 6.92 (1H, t, *J* = 7.5 Hz, Ph), 7.07–7.54 (28H, m, Ph), 7.70 (1H, t, *J* = 7.8 Hz, Ph), 8.16 (2H, dd, *J* = 12.5, 6.6 Hz, Ph), 9.96 (1H, s, CCH). <sup>13</sup>C NMR: δ (CDCl<sub>3</sub>) 119.13 [d, *J*<sub>CP</sub> = 11.5 Hz, C(313)], 122.69 [d, *J*<sub>CP</sub> = 50.7 Hz, C(311)], 122.91 [d, *J*<sub>CP</sub> = 6.5 Hz, C(315)], 127.30–135.58 (m, Ph), 135.85 [d, *J*<sub>CP</sub> = 52.7 Hz, *ipso* C (PPh)], 138.43 [d, *J*<sub>CP</sub> = 54.9 Hz, *ipso* C (PPh)], 140.69 [d, *J*<sub>CP</sub> = 18.4 Hz, *ipso* C (PPh)], 141.83 [d, *J*<sub>CP</sub> = 25.4 Hz, *ipso* C (PPh)], 144.27 [d, *J*<sub>CP</sub> = 29.4 Hz, *ipso* C (PPh)], 145.70 [d, *J*<sub>CP</sub> = 24.0 Hz, *ipso* C (PPh)], 168.96 [d, *J*<sub>CP</sub> = 52.7 Hz, C(312)], 181.99 [s(br), CCH], 189.27 (s, CO), 196.45 (s, CO), 198.45 (m, CO), 198.56 (d,

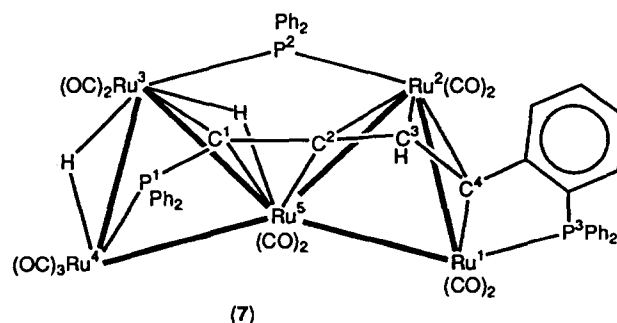
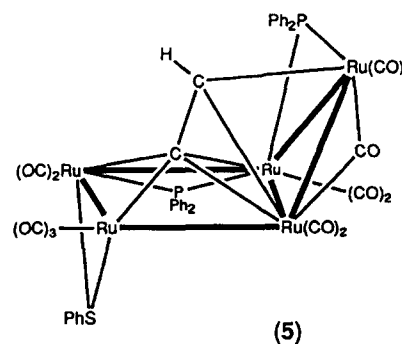


Table 5

Non-hydrogen atomic coordinates and isotropic thermal parameters for  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_2(\text{dppm})$  (3)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{eq}} \text{ \AA}^2$
Ru(1)	0.95190(6)	0.17248(4)	0.40058(3)	0.0493(3)
Ru(2)	1.09922(5)	0.15758(4)	0.32359(3)	0.0474(3)
Ru(3)	1.04195(5)	0.21603(4)	0.21735(3)	0.0420(3)
Ru(4)	1.00525(5)	0.27901(4)	0.33303(3)	0.0465(3)
Ru(5)	0.85243(5)	0.21255(4)	0.16963(3)	0.0363(2)
C(11)	1.0442(8)	0.1675(6)	0.4617(4)	0.088(5)
O(11)	1.0961(5)	0.1645(6)	0.4990(3)	0.135(5)
C(12)	0.9253(8)	0.0843(6)	0.4086(4)	0.087(5)
O(12)	0.9033(7)	0.0294(4)	0.4127(4)	0.138(5)
C(13)	0.8663(7)	0.2024(6)	0.4533(4)	0.079(5)
O(13)	0.8183(5)	0.2204(5)	0.4895(3)	0.120(4)
C(21)	1.1922(6)	0.1525(6)	0.3821(4)	0.070(5)
O(21)	1.2498(5)	0.1514(5)	0.4167(3)	0.116(4)
C(22)	1.0968(7)	0.0675(5)	0.3105(5)	0.070(5)
O(22)	1.0894(5)	0.0115(3)	0.3014(4)	0.110(4)
C(31)	1.0714(6)	0.2811(5)	0.1599(4)	0.061(4)
O(31)	1.0915(5)	0.3216(4)	0.1271(3)	0.087(3)
C(32)	1.0510(6)	0.1466(5)	0.1648(4)	0.054(4)
O(32)	1.0595(5)	0.1013(3)	0.1341(3)	0.080(3)
C(41)	1.1178(6)	0.2957(6)	0.3708(4)	0.075(5)
O(41)	1.1807(5)	0.3123(4)	0.3968(3)	0.100(4)
C(42)	0.9379(8)	0.3246(6)	0.3892(5)	0.094(6)
O(42)	0.8927(6)	0.3533(5)	0.4222(4)	0.140(5)
C(43)	1.0059(7)	0.3496(5)	0.2767(5)	0.070(5)
O(43)	1.0109(6)	0.3981(3)	0.2498(3)	0.098(4)
C(51)	0.8772(6)	0.3041(5)	0.1576(4)	0.050(4)
O(51)	0.8907(4)	0.3584(3)	0.1446(3)	0.072(3)
C(52)	0.8701(6)	0.1214(5)	0.1919(4)	0.045(4)
O(52)	0.8794(4)	0.0673(3)	0.2078(3)	0.056(3)
C(1)	0.8956(6)	0.2011(4)	0.3181(3)	0.039(3)
C(2)	0.9743(6)	0.1860(4)	0.2934(3)	0.041(3)
P(1)	0.8015(2)	0.2218(1)	0.2690(1)	0.0381(8)
C(111)	0.7479(5)	0.2969(4)	0.2962(4)	0.040(3)
C(112)	0.7588(7)	0.3562(5)	0.2696(4)	0.066(4)
C(113)	0.7155(8)	0.4131(5)	0.2884(5)	0.081(5)
C(114)	0.6630(8)	0.4115(5)	0.3362(5)	0.074(5)
C(115)	0.6546(9)	0.3525(6)	0.3646(5)	0.105(6)
C(116)	0.6964(8)	0.2958(5)	0.3442(5)	0.084(5)
C(121)	0.7139(6)	0.1596(5)	0.2844(4)	0.048(4)
C(122)	0.7355(6)	0.0981(5)	0.3078(4)	0.059(4)
C(123)	0.6682(8)	0.0514(6)	0.3160(5)	0.085(5)
C(124)	0.5833(8)	0.0643(6)	0.2982(5)	0.094(6)
C(125)	0.5604(7)	0.1236(6)	0.2746(6)	0.092(6)
C(126)	0.6250(6)	0.1737(5)	0.2678(5)	0.066(4)
P(2)	1.1878(2)	0.1962(1)	0.2504(1)	0.051(1)
C(211)	1.2561(6)	0.1409(5)	0.2057(5)	0.060(4)
C(212)	1.2858(7)	0.0808(6)	0.2283(6)	0.099(6)
C(213)	1.3404(9)	0.0401(7)	0.1945(7)	0.137(8)
C(214)	1.3609(8)	0.0581(7)	0.1404(7)	0.132(7)
C(215)	1.3342(9)	0.1169(8)	0.1151(6)	0.132(7)
C(216)	1.2809(7)	0.1585(6)	0.1494(5)	0.089(5)
C(221)	1.2694(6)	0.2618(5)	0.2665(4)	0.058(4)
C(222)	1.2564(7)	0.3261(5)	0.2523(5)	0.070(4)
C(223)	1.3200(7)	0.3736(6)	0.2661(5)	0.089(5)
C(224)	1.3978(7)	0.3571(6)	0.2942(5)	0.098(6)
C(225)	1.4143(7)	0.2919(6)	0.3080(6)	0.099(6)
C(226)	1.3489(7)	0.2452(6)	0.2958(5)	0.084(5)
P(3)	0.8737(2)	0.2023(1)	0.0644(1)	0.0433(9)
C(311)	0.9575(6)	0.2479(5)	0.0232(4)	0.049(4)
C(312)	1.0395(6)	0.2186(6)	0.0165(4)	0.070(4)
C(313)	1.1065(7)	0.2533(6)	−0.0130(5)	0.085(5)
C(314)	1.0907(8)	0.3126(6)	−0.0374(5)	0.095(6)
C(315)	1.0080(8)	0.3415(6)	−0.0324(5)	0.094(6)

Table 5 (continued)

Atom	x	y	z	$U_{eq}$ Å <sup>2</sup>
C(316)	0.9398(7)	0.3092(5)	-0.0014(5)	0.075(5)
C(321)	0.8692(6)	0.1233(5)	0.0247(4)	0.052(4)
C(322)	0.8773(9)	0.0637(5)	0.0519(4)	0.092(6)
C(323)	0.867(1)	0.0054(6)	0.0198(5)	0.126(7)
C(324)	0.8510(8)	0.0056(6)	-0.0387(5)	0.090(6)
C(325)	0.8442(8)	0.0654(6)	-0.0662(5)	0.088(5)
C(326)	0.8555(7)	0.1248(5)	-0.0366(4)	0.069(5)
C(0)	0.7646(6)	0.2410(5)	0.0477(3)	0.048(4)
P(4)	0.7134(2)	0.2122(1)	0.1167(1)	0.0424(9)
C(411)	0.6179(6)	0.2679(5)	0.1297(4)	0.048(4)
C(412)	0.6344(7)	0.3334(5)	0.1387(5)	0.068(4)
C(413)	0.5652(8)	0.3778(6)	0.1476(5)	0.087(5)
C(414)	0.4788(8)	0.3534(6)	0.1471(5)	0.096(6)
C(415)	0.4633(7)	0.2896(6)	0.1397(7)	0.119(7)
C(416)	0.5313(7)	0.2457(6)	0.1297(6)	0.089(6)
C(421)	0.6619(6)	0.1336(5)	0.0967(4)	0.052(4)
C(422)	0.6619(6)	0.0807(5)	0.1355(4)	0.061(4)
C(423)	0.6288(8)	0.0213(5)	0.1162(6)	0.099(6)
C(424)	0.5941(8)	0.0124(6)	0.0599(6)	0.118(7)
C(425)	0.5962(9)	0.0640(6)	0.0216(6)	0.119(7)
C(426)	0.6254(8)	0.1254(6)	0.0396(5)	0.087(5)
Cl(1)	1.1638(5)	0.5003(3)	-0.0067(3)	0.253(4)
Cl(2)	1.1279(6)	0.4949(4)	0.1136(3)	0.336(6)
Cl(3)	1.2784(5)	0.4446(5)	0.0731(4)	0.383(7)
C	1.170(2)	0.454(1)	0.0573(6)	0.24(1)

Table 6

Non-hydrogen atomic coordinates and isotropic thermal parameters for  $Ru_5(\mu_5-C_2H)(\mu-PPh_2)_2(\mu-P,N-PPh_2C_6H_4NH-2)(\mu-CO(CO))_{10}(4)$ 

Atom	x	y	z	$U_{eq}$ Å <sup>2</sup>
Ru(1)	0.1966(2)	0.4636(3)	0.4387(2)	0.055(2)
Ru(2)	0.1693(1)	0.4742(3)	0.5658(2)	0.048(2)
Ru(3)	0.2648(1)	0.3998(3)	0.6959(2)	0.045(1)
Ru(4)	0.2630(2)	0.5926(3)	0.5411(2)	0.058(2)
Ru(5)	0.3465(2)	0.5334(3)	0.6836(2)	0.052(2)
C(11)	0.122(2)	0.491(3)	0.362(2)	0.05(1)
O(11)	0.075(1)	0.509(2)	0.311(1)	0.075(9)
C(12)	0.238(2)	0.418(3)	0.379(2)	0.11(2)
O(12)	0.256(1)	0.391(2)	0.334(1)	0.11(1)
C(21)	0.173(1)	0.596(3)	0.601(2)	0.05(1)
O(21)	0.158(1)	0.674(2)	0.619(1)	0.09(1)
C(22)	0.097(1)	0.503(2)	0.507(2)	0.04(1)
O(22)	0.045(1)	0.524(2)	0.466(1)	0.066(8)
C(31)	0.295(2)	0.349(4)	0.794(3)	0.12(2)
O(31)	0.306(1)	0.320(2)	0.850(1)	0.09(1)
C(32)	0.277(2)	0.279(3)	0.670(2)	0.06(1)
O(32)	0.298(1)	0.195(2)	0.666(1)	0.064(8)
C(41)	0.263(2)	0.713(3)	0.575(2)	0.09(2)
O(41)	0.256(1)	0.797(2)	0.593(2)	0.11(1)
C(42)	0.198(2)	0.626(4)	0.455(2)	0.12(2)
O(42)	0.173(1)	0.684(2)	0.402(2)	0.12(1)
C(43)	0.327(2)	0.628(3)	0.515(2)	0.08(2)
O(43)	0.365(1)	0.642(2)	0.501(1)	0.10(1)
C(51)	0.377(2)	0.661(3)	0.692(2)	0.10(2)
O(51)	0.393(1)	0.740(2)	0.697(2)	0.11(1)
C(52)	0.398(1)	0.493(2)	0.643(2)	0.05(1)
O(52)	0.438(1)	0.460(2)	0.628(1)	0.082(9)
C(1)	0.275(1)	0.435(2)	0.523(2)	0.04(1)
C(2)	0.277(1)	0.455(3)	0.606(2)	0.05(1)
P(1)	0.1595(5)	0.3353(8)	0.4817(5)	0.050(5)
C(111)	0.199(1)	0.217(3)	0.506(2)	0.05(1)
C(112)	0.245(2)	0.195(3)	0.484(2)	0.05(1)
C(113)	0.275(2)	0.105(3)	0.499(2)	0.06(1)

Table 6 (continued)

Atom	x	y	z	$U_{eq} \text{ \AA}^2$
C(114)	0.251(2)	0.028(3)	0.530(2)	0.07(1)
C(115)	0.206(2)	0.051(3)	0.550(2)	0.06(1)
C(116)	0.174(2)	0.143(3)	0.538(2)	0.05(1)
C(121)	0.088(2)	0.291(3)	0.426(2)	0.07(1)
C(122)	0.074(2)	0.241(3)	0.360(2)	0.08(2)
C(123)	0.024(2)	0.190(3)	0.317(2)	0.10(2)
C(124)	-0.017(2)	0.182(3)	0.348(2)	0.08(2)
C(125)	-0.014(2)	0.229(3)	0.402(2)	0.10(2)
C(126)	0.040(2)	0.283(3)	0.448(2)	0.06(1)
P(2)	0.1634(5)	0.3954(8)	0.6667(5)	0.054(5)
C(211)	0.120(2)	0.283(3)	0.660(2)	0.06(1)
C(212)	0.151(2)	0.195(3)	0.690(2)	0.06(1)
C(213)	0.113(2)	0.112(3)	0.679(2)	0.09(2)
C(214)	0.056(2)	0.114(3)	0.651(2)	0.09(2)
C(215)	0.028(2)	0.206(3)	0.631(2)	0.11(2)
C(216)	0.061(2)	0.288(3)	0.636(2)	0.06(1)
C(221)	0.137(2)	0.463(3)	0.729(2)	0.06(1)
C(222)	0.091(2)	0.537(3)	0.700(2)	0.09(2)
C(223)	0.069(2)	0.590(4)	0.748(3)	0.15(2)
C(224)	0.097(2)	0.572(3)	0.818(2)	0.11(2)
C(225)	0.137(2)	0.501(3)	0.845(2)	0.07(1)
C(226)	0.160(1)	0.444(2)	0.800(2)	0.05(1)
P(3)	0.4079(5)	0.4964(8)	0.8050(6)	0.053(3)
C(311)	0.364(2)	0.544(3)	0.850(2)	0.05(1)
C(312)	0.304(2)	0.577(3)	0.811(2)	0.05(1)
N(312)	0.288(1)	0.548(2)	0.735(1)	0.050(9)
C(313)	0.268(2)	0.622(3)	0.843(2)	0.07(1)
C(314)	0.294(2)	0.642(3)	0.914(2)	0.07(1)
C(315)	0.348(2)	0.610(3)	0.960(2)	0.06(1)
C(316)	0.384(2)	0.566(3)	0.932(2)	0.07(1)
C(321)	0.478(2)	0.564(3)	0.840(2)	0.05(1)
C(322)	0.481(2)	0.662(3)	0.860(2)	0.08(2)
C(323)	0.528(2)	0.719(3)	0.883(2)	0.10(2)
C(324)	0.579(2)	0.672(3)	0.889(2)	0.08(2)
C(325)	0.582(2)	0.580(3)	0.870(2)	0.07(1)
C(326)	0.531(2)	0.524(3)	0.844(2)	0.06(1)
C(331)	0.431(2)	0.375(3)	0.835(2)	0.07(1)
C(332)	0.433(2)	0.306(3)	0.789(2)	0.10(2)
C(333)	0.454(2)	0.215(4)	0.815(3)	0.13(2)
C(334)	0.483(2)	0.184(3)	0.880(2)	0.10(2)
C(335)	0.483(2)	0.252(4)	0.929(3)	0.12(2)
C(336)	0.460(2)	0.343(3)	0.906(2)	0.11(2)

$J_{CP} = 5.1$  Hz, CO), 198.87 (d,  $J_{CP} = 11.8$  Hz, CO), 199.13 (d,  $J_{CP} = 16.9$  Hz, CO), 199.64 (d,  $J_{CP} = 5.2$  Hz, CO), 199.97 (d,  $J_{CP} = 8.5$  Hz, CO), 203.67 (m, CO), 233.88 [d,  $J_{CP} = 30.2$  Hz, CO-(bridging)], 329.46 (m, CCH). FAB MS ( $m/z$ ): 1486,  $M^+$ . The remaining minor bands were not identified.

#### 4.4. Reaction of **1** with $PPh_2(C_6H_4CH=CH_2-2)$

TMNO was added to a solution of **1** (104 mg, 0.082 mmol) and  $PPh_2(C_6H_4CH=CH_2-2)$  (24 mg, 0.082 mmol) in  $CH_2Cl_2$  (20 ml) until no starting material remained. The solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 5:2) to yield four bands. In attempting to crystallise ( $CH_2Cl_2$ /MeOH) the major brown band ( $R_f$  0.60; 65 mg) [IR:  $\nu(CO)$  (cyclohexane) 2060s, 2034(sh), 2029vs,

2008s, 1998s, 1989m, 1971m, 1961m, 1950m, 1925w  $cm^{-1}$ ], an alteration product shown to be  $Ru_4\{\mu_4-C_2PPh_2[Ru(\mu-OH)(C,P-2-CHMeC_6H_4PPh_2-2)-(CO)_2]\}(\mu-PPh_2)(CO)_{10} \cdot CHCl_3$  (**6**) was obtained (4 mg, 3%). A red band ( $R_f$  0.40; 5 mg) afforded a few crystals identified by an X-ray structure determination as  $Ru_5(\mu-H)_2\{\mu_5-PPh_2C_2CH=C(C_6H_4PPh_2-2)\}(\mu-PPh_2)(CO)_{11}$  (**7**).

## 5. Crystallography

Unique data sets were measured at ca. 295 K within the specified  $2\theta_{max}$  limits using an Enraf-Nonius CAD4 diffractometer ( $2\theta/\theta$  scan mode; monochromatic Mo K  $\alpha$  radiation,  $\lambda$  0.71073  $\text{\AA}$ );  $N$  independent reflections were obtained,  $N_o$  with  $I > 3\sigma(I)$  being considered

Table 7

Non-hydrogen atomic coordinates and isotropic thermal parameters for  $\text{Ru}_4\{\mu_4\text{-C}_2\text{PPh}_2[\text{Ru}(\mu\text{-OH})(C,P\text{-}2\text{-CHMeC}_6\text{H}_4\text{PPh}_2\text{-}2\text{X}(\text{CO})_2)](\mu\text{-PPh}_2\text{X}(\text{CO})_{10})\cdot\text{CHCl}_3$  (6)

Atom	x	y	z	$U_{\text{eq}} \text{ \AA}^2$
Ru(1)	0.33729(7)	0.24900(6)	0.45260(7)	0.0356(4)
Ru(2)	0.39477(6)	0.12657(6)	0.57438(6)	0.0325(4)
Ru(3)	0.31205(6)	0.12775(6)	0.72067(6)	0.0279(3)
Ru(4)	0.20785(6)	0.11798(6)	0.51094(6)	0.0303(3)
Ru(5)	0.18173(6)	0.32808(6)	0.73633(6)	0.0283(3)
C(11)	0.361(1)	0.173(1)	0.3563(9)	0.076(9)
O(11)	0.377(1)	0.1378(9)	0.2968(8)	0.14(1)
C(12)	0.2671(9)	0.2930(9)	0.3462(8)	0.052(6)
O(12)	0.2251(8)	0.3122(8)	0.2771(6)	0.098(7)
C(13)	0.4504(9)	0.3500(9)	0.4827(9)	0.058(6)
O(13)	0.5218(8)	0.4098(8)	0.5052(9)	0.113(7)
C(21)	0.3996(9)	0.039(1)	0.4789(9)	0.059(7)
O(21)	0.3994(7)	-0.0194(7)	0.4196(7)	0.082(6)
C(22)	0.5215(8)	0.1985(9)	0.6175(8)	0.050(6)
O(22)	0.5978(6)	0.2456(7)	0.6431(8)	0.081(5)
C(31)	0.2570(8)	0.0406(8)	0.7936(8)	0.041(5)
O(31)	0.2240(7)	-0.0160(6)	0.8351(7)	0.074(5)
C(32)	0.4166(8)	0.1855(7)	0.8319(8)	0.045(5)
O(32)	0.4853(6)	0.2233(6)	0.8992(6)	0.071(5)
C(41)	0.1902(9)	0.0033(8)	0.4270(9)	0.057(6)
O(41)	0.1765(7)	-0.0627(6)	0.3724(7)	0.086(5)
C(42)	0.1311(8)	0.0579(8)	0.5836(8)	0.044(5)
O(42)	0.0731(5)	0.0158(6)	0.6121(6)	0.055(4)
C(43)	0.1159(8)	0.1479(9)	0.4116(9)	0.056(6)
O(43)	0.0601(7)	0.1654(7)	0.3549(7)	0.095(5)
C(51)	0.0736(7)	0.2344(7)	0.6313(8)	0.035(5)
O(51)	0.0060(5)	0.1843(5)	0.5763(6)	0.057(4)
C(52)	0.1433(8)	0.4309(7)	0.7178(8)	0.043(5)
O(52)	0.1225(7)	0.4960(6)	0.7069(7)	0.068(5)
O	0.2373(5)	0.2171(5)	0.7589(5)	0.036(3)
C(1)	0.2926(7)	0.2787(6)	0.5744(7)	0.027(4)
C(2)	0.3365(7)	0.2197(7)	0.6117(7)	0.032(4)
P(1)	0.2654(2)	0.3725(2)	0.6259(2)	0.029(1)
C(111)	0.2091(7)	0.4164(7)	0.5168(7)	0.034(5)
C(112)	0.2613(8)	0.4728(8)	0.4663(8)	0.043(5)
C(113)	0.2212(9)	0.5075(8)	0.3845(9)	0.054(6)
C(114)	0.126(1)	0.4859(9)	0.3517(9)	0.068(7)
C(115)	0.075(1)	0.4359(9)	0.402(1)	0.065(7)
C(116)	0.1138(9)	0.3970(9)	0.4846(8)	0.057(7)
C(121)	0.3773(7)	0.4715(7)	0.6826(7)	0.034(5)
C(122)	0.4618(8)	0.4593(8)	0.7138(9)	0.047(5)
C(123)	0.5432(8)	0.5375(9)	0.7629(9)	0.060(6)
C(124)	0.542(1)	0.629(1)	0.781(1)	0.076(7)
C(125)	0.458(1)	0.6419(9)	0.750(1)	0.069(7)
C(126)	0.3781(8)	0.5665(7)	0.7024(8)	0.043(5)
P(2)	0.3735(2)	0.0194(2)	0.6767(2)	0.034(1)
C(211)	0.2978(8)	-0.1070(7)	0.6227(8)	0.042(5)
C(212)	0.3414(9)	-0.1679(8)	0.5948(9)	0.058(6)
C(213)	0.293(1)	-0.2633(9)	0.558(1)	0.082(9)
C(214)	0.200(1)	-0.3030(9)	0.549(1)	0.077(7)
C(215)	0.1587(9)	-0.2438(9)	0.577(1)	0.072(7)
C(216)	0.2074(8)	-0.1453(8)	0.6120(9)	0.058(6)
C(221)	0.4654(8)	0.0034(8)	0.7764(8)	0.041(5)
C(222)	0.5556(9)	0.050(1)	0.794(1)	0.071(7)
C(223)	0.622(1)	0.030(1)	0.869(1)	0.10(1)
C(224)	0.597(1)	-0.034(1)	0.926(1)	0.088(9)
C(225)	0.510(1)	-0.079(1)	0.908(1)	0.088(9)
C(226)	0.441(1)	-0.066(1)	0.834(1)	0.069(7)
P(3)	0.1178(2)	0.2961(2)	0.8630(2)	0.036(1)
C(311)	0.1837(8)	0.4029(7)	0.9603(8)	0.042(5)
C(312)	0.2648(7)	0.4600(7)	0.9498(7)	0.036(5)
C(3121)	0.2966(7)	0.4267(7)	0.8661(7)	0.035(5)

Table 7 (continued)

Atom	x	y	z	$U_{eq}$ Å <sup>2</sup>
C(3122)	0.3723(8)	0.3857(9)	0.9141(9)	0.053(6)
C(313)	0.3193(9)	0.5478(8)	1.0175(9)	0.054(6)
C(314)	0.293(1)	0.5761(9)	1.0942(9)	0.065(7)
C(315)	0.212(1)	0.517(1)	1.1045(9)	0.072(8)
C(316)	0.156(1)	0.4301(9)	1.0387(9)	0.063(7)
C(321)	−0.0045(8)	0.2743(8)	0.8363(8)	0.041(5)
C(322)	−0.0576(8)	0.2983(8)	0.7543(9)	0.047(5)
C(323)	−0.1505(9)	0.2813(9)	0.734(1)	0.059(7)
C(324)	−0.1924(9)	0.240(1)	0.799(1)	0.068(7)
C(325)	−0.1405(9)	0.217(1)	0.884(1)	0.075(8)
C(326)	−0.0478(9)	0.234(1)	0.902(1)	0.061(7)
C(331)	0.1285(8)	0.1950(7)	0.9204(8)	0.041(5)
C(332)	0.1856(9)	0.2044(9)	1.0169(9)	0.064(7)
C(333)	0.191(1)	0.125(1)	1.060(1)	0.10(1)
C(334)	0.132(1)	0.035(1)	1.006(1)	0.09(1)
C(335)	0.075(1)	0.0200(9)	0.908(1)	0.083(9)
C(336)	0.0753(9)	0.104(1)	0.867(1)	0.063(7)
Cl(1)	0.0848(4)	0.5952(4)	0.8990(4)	0.124(3)
Cl(2)	0.0689(6)	0.7616(4)	0.8256(5)	0.183(5)
Cl(3)	0.2463(5)	0.7495(6)	0.9061(6)	0.203(6)
C(0)	0.131(1)	0.693(1)	0.843(1)	0.10(1)

Table 8

Non-hydrogen atomic coordinates and isotropic thermal parameters for  $Ru_5(\mu-H)_2(\mu_5-PPH_2C_2CHC(C_6H_4PPH_2-2))(\mu-PPH_2)CO)_{11}$  (7)

Atom	x	y	z	$U_{eq}$ Å <sup>2</sup>
Ru(1)	0.19688(2)	0.49994(2)	0.17934(3)	0.02526(9)
Ru(2)	0.30896(2)	0.63602(2)	0.29462(3)	0.02674(9)
Ru(3)	0.24461(2)	0.85130(2)	0.24271(3)	0.0319(1)
Ru(4)	0.06586(2)	0.82679(2)	0.14192(3)	0.0328(1)
Ru(5)	0.15993(2)	0.68255(2)	0.16370(3)	0.02747(9)
C(11)	0.1035(2)	0.4295(2)	0.1698(4)	0.033(1)
O(11)	0.0454(2)	0.3877(2)	0.1636(3)	0.051(1)
C(12)	0.1870(2)	0.4731(2)	−0.0072(4)	0.035(1)
O(12)	0.1840(2)	0.4540(2)	−0.1157(3)	0.054(1)
C(21)	0.3183(2)	0.6093(2)	0.1197(4)	0.037(1)
O(21)	0.3301(2)	0.6022(2)	0.0168(3)	0.052(1)
C(22)	0.4112(2)	0.6096(3)	0.3703(4)	0.042(1)
O(22)	0.4747(2)	0.5957(2)	0.4128(3)	0.073(1)
C(31)	0.2780(3)	0.9545(3)	0.3617(4)	0.050(2)
O(31)	0.3026(2)	1.0173(2)	0.4296(4)	0.087(2)
C(32)	0.2897(2)	0.8994(3)	0.1145(4)	0.044(1)
O(32)	0.3164(2)	0.9266(2)	0.0357(3)	0.078(2)
C(41)	0.0741(3)	0.8192(3)	−0.0394(4)	0.050(2)
O(41)	0.0781(2)	0.8162(2)	−0.1445(3)	0.080(2)
C(42)	−0.0321(2)	0.7530(3)	0.0987(4)	0.041(1)
O(42)	−0.0925(2)	0.7138(2)	0.0724(3)	0.058(1)
C(43)	0.0142(2)	0.9304(3)	0.1444(4)	0.042(1)
O(43)	−0.0189(2)	0.9906(2)	0.1385(3)	0.064(1)
C(51)	0.1456(2)	0.6520(3)	−0.0218(4)	0.040(1)
O(51)	0.1424(2)	0.6384(2)	−0.1314(3)	0.062(1)
C(52)	0.0695(2)	0.6082(2)	0.1722(4)	0.039(1)
O(52)	0.0097(2)	0.5728(2)	0.1735(4)	0.062(1)
C(1)	0.1874(2)	0.7705(2)	0.3526(3)	0.031(1)
C(3)	0.2334(2)	0.6251(2)	0.4444(3)	0.032(1)
C(2)	0.2135(2)	0.6905(2)	0.3672(3)	0.030(1)
C(4)	0.2372(2)	0.5401(2)	0.3816(3)	0.029(1)
P(1)	0.09631(6)	0.81156(6)	0.3682(1)	0.0333(3)
C(111)	0.1206(2)	0.9083(3)	0.4917(4)	0.041(1)
C(112)	0.1172(4)	0.9898(3)	0.4576(5)	0.077(2)
C(113)	0.1401(4)	1.0632(3)	0.5505(6)	0.094(3)
C(114)	0.1647(4)	1.0548(3)	0.6782(5)	0.079(2)
C(115)	0.1687(4)	0.9742(4)	0.7150(5)	0.079(2)

Table 8 (continued)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	$U_{eq}$ Å <sup>2</sup>
C(116)	0.1457(3)	0.9009(3)	0.6228(4)	0.062(2)
C(121)	0.0343(2)	0.7368(3)	0.4340(4)	0.038(1)
C(122)	0.0647(2)	0.6816(3)	0.5194(4)	0.047(2)
C(123)	0.0157(3)	0.6218(3)	0.5612(5)	0.056(2)
C(124)	−0.0652(3)	0.6185(4)	0.5164(5)	0.068(2)
C(125)	−0.0968(3)	0.6744(4)	0.4349(5)	0.068(2)
C(126)	−0.0475(3)	0.7338(3)	0.3930(4)	0.055(2)
P(2)	0.35723(6)	0.78556(6)	0.3344(1)	0.0341(3)
C(211)	0.3933(3)	0.8146(3)	0.5146(4)	0.050(2)
C(212)	0.3427(3)	0.8314(3)	0.5955(4)	0.065(2)
C(213)	0.3681(4)	0.8424(4)	0.7298(5)	0.089(3)
C(214)	0.4452(5)	0.8379(4)	0.7873(5)	0.115(3)
C(215)	0.4964(4)	0.8224(5)	0.7109(6)	0.118(3)
C(216)	0.4717(3)	0.8091(4)	0.5726(5)	0.078(2)
C(221)	0.4444(2)	0.8228(3)	0.2764(4)	0.043(1)
C(222)	0.4779(3)	0.9080(3)	0.3175(6)	0.078(2)
C(223)	0.5428(3)	0.9394(4)	0.2768(7)	0.096(3)
C(224)	0.5748(3)	0.8882(4)	0.1919(6)	0.085(3)
C(225)	0.5429(3)	0.8055(4)	0.1502(6)	0.071(2)
C(226)	0.4783(2)	0.7716(3)	0.1934(5)	0.054(2)
P(3)	0.27220(5)	0.38999(6)	0.23187(9)	0.0296(3)
C(311)	0.2905(2)	0.3982(2)	0.4085(3)	0.032(1)
C(312)	0.2713(2)	0.4766(2)	0.4689(3)	0.031(1)
C(313)	0.2825(2)	0.4873(3)	0.6049(4)	0.042(1)
C(314)	0.3122(3)	0.4233(3)	0.6769(4)	0.050(2)
C(315)	0.3307(3)	0.3473(3)	0.6166(4)	0.051(2)
C(316)	0.3196(2)	0.3346(3)	0.4828(4)	0.044(1)
C(321)	0.2341(2)	0.2758(2)	0.1797(4)	0.036(1)
C(322)	0.2665(3)	0.2205(3)	0.0969(4)	0.051(2)
C(323)	0.2369(3)	0.1340(3)	0.0642(5)	0.068(2)
C(324)	0.1751(3)	0.1018(3)	0.1127(5)	0.070(2)
C(325)	0.1428(3)	0.1552(3)	0.1932(5)	0.061(2)
C(326)	0.1712(2)	0.2421(3)	0.2275(4)	0.047(2)
C(331)	0.3687(2)	0.3966(2)	0.1903(4)	0.035(1)
C(332)	0.4376(2)	0.3952(3)	0.2853(4)	0.052(2)
C(333)	0.5102(3)	0.3993(4)	0.2515(5)	0.071(2)
C(334)	0.5153(3)	0.4037(3)	0.1252(5)	0.067(2)
C(335)	0.4479(3)	0.4062(3)	0.0314(5)	0.061(2)
C(336)	0.3746(3)	0.4030(3)	0.0635(4)	0.049(2)

“observed” and used in the full-matrix least-squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (*x*, *y*, *z*,  $U_{iso}$ ) 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 2.4 program system [22] implemented by S.R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in the figures and tables. Tables of thermal and hydrogen parameters, full molecular non-hydrogen geometries and structure factor amplitudes have been deposited at the Cambridge Crystallographic Data Centre.

### 5.1. Abnormal features / variations in procedure

(3) Although solvent thermal motion is high, site occupancies when refined did not differ significantly from unity and were constrained at this value.

(4) Weak and limited data would support isotropic thermal parameters from refinement only for N, O, C.

(6) A difference map artefact was modelled as OH, the hydrogen of this moiety [and of the CH(PPh<sub>2</sub>) entity] also being locatable; although solvent thermal motion was high, site occupancy when refined did not differ significantly from unity and was constrained at this value.

(7) All ligand hydrogen atoms were clearly evident in difference maps and refined satisfyingly in (*x*, *y*, *z*,  $U_{iso}$ ). About the Ru<sub>5</sub> core two difference map artefacts presented themselves in locations with some credibility as core hydrogen atoms. H(1) spans one of the two long Ru ··· Ru distances [Ru(3)–Ru(4) 3.036(1) Å] and refines satisfactorily in (*x*, *y*, *z*,  $U_{iso}$ ) to give Ru(3,4)–H(1) distances of 1.83(5), 1.80(4) Å and angle Ru(3)–H(1)–Ru(4) 113(2)°. The other, “H(2)”, also refines satisfactorily in (*x*, *y*, *z*,  $U_{iso}$ ) in a location spanning the Ru(3)–Ru(5) vector [Ru(3,5)–H(2) 2.02(5),



Table 9  
Crystal data and refinement details for 3, 4, 6 and 7

Compound	3	4	6	7
Formula	C <sub>63</sub> H <sub>42</sub> O <sub>12</sub> P <sub>4</sub> Ru <sub>5</sub> · CHCl <sub>3</sub>	C <sub>55</sub> H <sub>36</sub> NO <sub>11</sub> P <sub>3</sub> Ru <sub>5</sub>	C <sub>58</sub> H <sub>39</sub> O <sub>13</sub> P <sub>3</sub> Ru <sub>5</sub> · CHCl <sub>3</sub>	C <sub>57</sub> H <sub>37</sub> O <sub>11</sub> P <sub>3</sub> Ru <sub>5</sub>
MW	1739.7	1485.2	1661.6	1496.2
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic
Space groups	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	14.919(13)	24.230(14)	16.218(6)	17.382(5)
<i>b</i> (Å)	20.152(10)	13.535(4)	14.946(6)	15.559(9)
<i>c</i> (Å)	22.435(13)	19.749(11)	14.215(9)	10.531(5)
$\alpha$ (°)			94.10(4)	96.57(4)
$\beta$ (°)	91.57(6)	113.13(5)	107.71(4)	102.56(3)
$\gamma$ (°)			109.09(4)	94.45(4)
<i>V</i> (Å <sup>3</sup> )	6742	5956	3045	2742
<i>Z</i>	4	4	2	2
<i>D</i> <sub>c</sub> (g cm <sup>-3</sup> )	1.71	1.65	1.81	1.81
<i>F</i> (000)	3416	2904	1628	1464
$\mu$ (cm <sup>-1</sup> )	12.3	12.3	13.4	14.9
Crystal size (mm <sup>3</sup> )	0.33 × 0.10 × 0.14	0.09 × 0.23 × 0.38	0.05 × 0.17 × 0.19	0.38 × 0.07 × 0.50
<i>A</i> * (min, max)	1.12, 1.18	1.11, 1.17	1.07, 1.36	1.11, 1.96 (analytical)
2 $\theta$ <sub>max</sub> (°)	50	50	50	55
<i>N</i>	11922	10424	10475	12914
<i>N</i> <sub>0</sub>	5963	2278	7409	10300
<i>R</i>	0.048	0.079	0.056	0.031
<i>R</i> <sub>w</sub>	0.041	0.083	0.063	0.034

1.67(5) Å; Ru(3)–H(2)–Ru(5) 101(3)°] and, unlike H(1), is well out of the associated Ru<sub>3</sub> plane.

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