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Cluster chemistry

LXXX *. Reactions of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ with 1,3-butadiene: addition to C_α and formation of a μ_4-cyclohexenyne complex. X-Ray structures of $Ru_5\{\mu_4\text{-}CC(PPh_2)CH_2\text{-}\eta^3\text{-}CHCHCH_2\}(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{11}$, $Ru_5\{\mu_4\text{-}CC(PPh_2)CHCH{=}CHMe\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_9$ and $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)_2(CO)_{11}$

Chris J. Adams, Michael I. Bruce

Jordan Laboratories, Department of Physical and Inorganic Chemistry, University of Adelaide, Adelaide, South Australia 5001 (Australia)

Brian W. Skelton and Allan H. White

Department of Chemistry, University of Western Australia, Nedlands, Western Australia 6009 (Australia)

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Abstract

Reactions between $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (**1**) and 1,3-butadiene have given $Ru_5\{\mu_4\text{-}CC(PPh_2)CH_2\text{-}\eta^3\text{-}CHCHCH_2\}(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{11}$, (**7**), $Ru_5\{\mu_4\text{-}CC(PPh_2)CHCH{=}CHMe\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_9$ (**8**), and $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)_2(CO)_{11}$ (**9**), in addition to the previously described metallated benzoyldiphenylphosphine derivative, $Ru_4\{\mu_4\text{-}C_6H_3C(O)PPh_2\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$ (**6**). Complexes **7** and **8** contain isomeric tertiary phosphine ligands formed by addition of the 1,3-diene to C_α of the C_2PPh_2 ligand in **1**. The metal cores are based on square pyramidal Ru_5 clusters, but in **7**, two apical-basal Ru–Ru vectors are long, formally 1-e, bonds. In **9**, the cluster is an Ru-capped C_2Ru_4 octahedron, the two carbons forming part of a cyclohex-1-en-4-yne ligand generated by cycloaddition of the diene to a C_2 fragment with concomitant P–C bond cleavage. Complexes **7**, **8** and **9** were fully characterised by single crystal X-ray studies.

Introduction

We have described several reactions between the open Ru_5 cluster $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (1; Scheme 1) and olefins, in which the following types of

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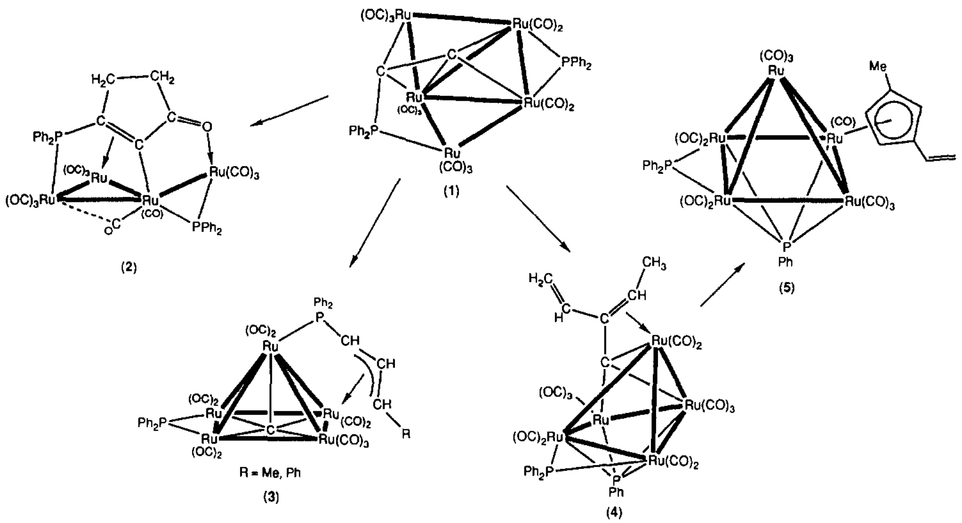
Correspondence to: Professor M.I. Bruce, Department of Physical and Inorganic Chemistry, University of Adelaide, PO Box 498, Adelaide, South Australia 5001.

* For Part LXXIX, see Ref. 1.



Scheme 1.

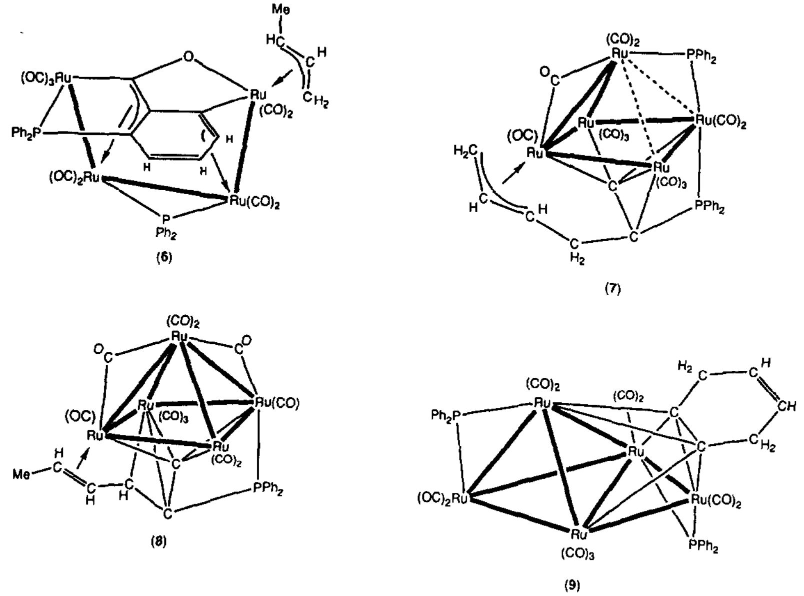
reactions were found [1,2]: (a) three-component cyclo-addition reactions incorporating the olefin, the intact C_2PPh_2 ligand and a molecule of CO to give **2**; (b) attack on C_α with concomitant cleavage of the C_α–C_β bond to give **3** [3]; (c) attack at C_α and cleavage of the P–C_α bond to give **4** [4]. A further reaction between **4** and excess olefin resulted in cycloaddition to form a substituted η-cyclopentadienyl ligand, as in **5** [4]. We have also reported that a related cyclo-addition reaction between **1** and 1,3-butadiene gave the tetranuclear complex **6** [1]. Here we describe three other complexes which we have isolated from the latter reaction and characterised by X-ray crystallography, which result from (i) a fourth type of reaction, involving addition at C_α to give two isomeric substituted tertiary phosphine ligands containing hydrocarbon chains which interact extensively with the cluster and (ii) cleavage of the P–C_α bond to give a C_2 fragment which is trapped by cyclo-addition of a butadiene molecule.

Results and discussion

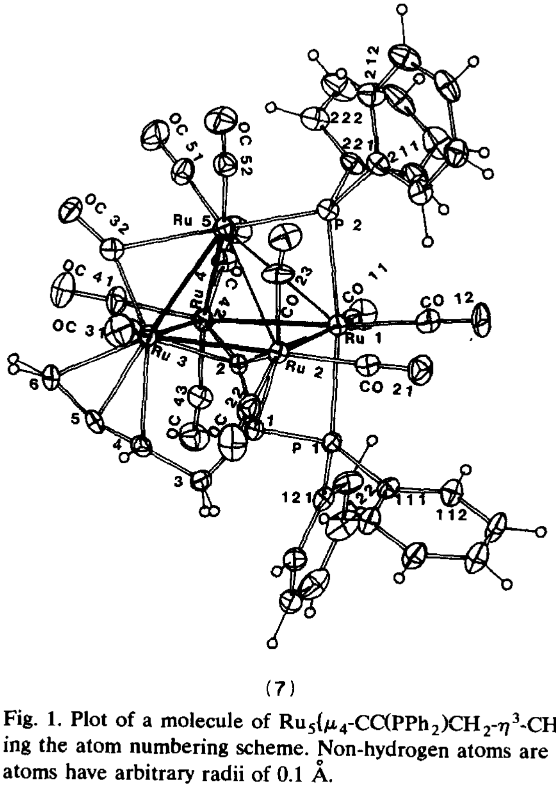
The reaction between **1** and 1,3-butadiene was carried out in benzene at 80°C for 10 h. Separation of the products by preparative TLC gave four complexes, of which **6** has been described previously [1]. Two relatively slow-moving bands contained black $Ru_5\{\mu_4\text{-}CC(PPh_2)CH_2\text{-}\eta^3\text{-}CHCHCH_2\}(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{11}$ (**7**) and dark greenish-black $Ru_5\{\mu_4\text{-}CC(PPh_2)CHCH{=}CHMe\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_9$ (**8**), while a red band with R_f 0.7 contained $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)_2(CO)_{11}$ (**9**). All three complexes were fully characterised by X-ray crystallographic studies, which will be described in turn.

Molecular structure of $Ru_5\{\mu_4\text{-}CC(PPh_2)CH_2\text{-}\eta^3\text{-}CHCHCH_2\}(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{11}$ *(7)*

A molecule of **7** is depicted in Fig. 1 and selected bond distances and angles are given in Table 1. The five ruthenium atoms form an envelope, the flap being bent over at an acute angle [65.08(4)°], held by the μ-PPh_2 group bridging Ru(1)–Ru(5);



Scheme 2.



(7)

Fig. 1. Plot of a molecule of $Ru_5\{\mu_4\text{-}CC(PPh_2)CH_2\text{-}\eta^3\text{-}CHCHCH_2\}(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{11}$ (7), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

Table 1

Selected bond lengths (Å) and angles (deg) for $Ru_5\{\mu_4\text{-CC(PPh}_2\text{)CH}_2\text{-}\eta^3\text{-CHCHCH}_2\}(\mu\text{-PPh}_2)(\mu\text{-CO})(CO)_{11}$ (7) and $Ru_5\{\mu_4\text{-CC(PPh}_2\text{)CHCH=CHMe}\}(\mu\text{-PPh}_2)(\mu\text{-CO})_2(CO)_9$ (8)

	7	8
Ru(1)-Ru(2)	2.900(2)	2.748(1)
Ru(1)-Ru(4)	2.962(1)	2.872(1)
Ru(1)-Ru(5)	3.215(2)	2.830(1)
Ru(2)-Ru(3)	2.852(2)	2.843(1)
Ru(2)-Ru(5)	3.209(2)	2.881(1)
Ru(3)-Ru(4)	2.925(2)	2.809(1)
Ru(3)-Ru(5)	2.763(1)	2.879(1)
Ru(4)-Ru(5)	2.762(2)	2.799(2)
Ru(1)-P(1)	2.397(3)	2.287(2)
Ru(1)-P(2)	2.362(3)	2.257(2)
Ru(2)-P(2)		2.269(2)
Ru(5)-P(2)	2.279(3)	
Ru(1)-C(2)	2.27(1)	2.234(4)
Ru(2)-C(2)	2.12(1)	2.063(4)
Ru(3)-C(2)	2.19(1)	2.105(4)
Ru(4)-C(2)	2.04(1)	2.171(4)
Ru(2)-C(1)	2.23(1)	
Ru(3)-C(4)	2.26(1)	2.439(8)
Ru(3)-C(5)	2.18(1)	2.253(7)
Ru(3)-C(6)	2.21(1)	
Ru(4)-C(1)		2.194(5)
Ru(4)-C(3)		2.161(6)
Ru(1)-C(51)		2.289(6)
Ru(3)-C(53)		2.254(7)
Ru(3)-C(32)	1.92(1)	
Ru(5)-C(53)		2.004(6)
Ru(5)-C(51)		1.990(6)
Ru(5)-C(32)	2.40(1)	
P(1)-C(1)	1.82(1)	1.795(5)
C(1)-C(2)	1.43(2)	1.445(7)
C(1)-C(3)	1.53(2)	1.435(8)
C(3)-C(4)	1.50(2)	1.473(8)
C(4)-C(5)	1.40(2)	1.395(9)
C(5)-C(6)	1.36(2)	1.533(9)
Ru-CO	1.83-1.94(1)	1.866-1.922(5)
	av. 1.90	av. 1.892
C-O	1.08-1.17(1)	1.121-1.184(7)
	av. 1.135	av. 1.139
P-C(Ph)	1.82-1.85(1)	1.812-1.818(6)
	av. 1.84	av. 1.817
Ru(1)-Ru(2)-Ru(3)	94.61(5)	92.28(4)
Ru(2)-Ru(3)-Ru(4)	87.38(5)	88.33(4)
Ru(1)-Ru(4)-Ru(3)	91.80(5)	90.42(4)
Ru(2)-Ru(1)-Ru(4)	85.81(5)	88.94(4)
Ru(1)-Ru(5)-Ru(3)	89.68(4)	89.86(4)
Ru(2)-Ru(5)-Ru(4)	83.51(5)	87.78(3)
Ru(1)-P(1)-C(1)	86.4(4)	82.4(2)

the core approximates a proto-square pyramid, one apical-basal edge of which is bridged by CO [asymmetrically, with Ru(3)–C(32) 1.92, Ru(5)–C(32) 2.40 Å] and another long, apparently non-bonding (but see below), vector by a PPh_2 ligand. A molecule of butadiene has added to C_α of the C_2PPh_2 ligand of **1** to form a $(\eta^3\text{-}C_3H_4)CH_2C(C)PPh_2$ ligand which is attached to the Ru_4 face of the cluster by an allylic interaction with Ru(3), the PPh_2 group bonded to Ru(1), C(1) bonded to Ru(2) and C(2) which is bonded to all four Ru atoms. The eleven remaining CO ligands are terminal.

There are several interesting features of the structure. The eight Ru–Ru separations range between 2.76 and 3.21 Å but fall into four groups:
(i) two bonds from Ru(5) to Ru(3) and Ru(4) [2.763(1), 2.762(2) Å, respectively], which are apical-basal bonds, the former being bridged by CO(32);
(ii) two bonds connecting basal Ru atoms bridged by C(1)–P(1) [2.900(2) Å] and by carbons C(1)–C(6) [2.852(2) Å];
(iii) two non-bridged basal Ru–Ru bonds [2.925(2) and 2.962(1) Å];
(iv) two long non-bonding separations between Ru(5) and Ru(1) and Ru(2) [3.215(2) and 3.209(2) Å, respectively].
The C_α–C_β moiety in **1**, now labelled C(1) and C(2), respectively, is also attached to the Ru_4 face. The former carbon forms a link between P(1) and the four-carbon allylic chain derived from the butadiene, and is attached to Ru(2) [2.23(1) Å], while C(2) more nearly resembles an alkylidyne carbon; the basal Ru–C(2) distances form a progression from 2.04(1) to 2.27(1) Å. The C(1)–C(2) bond length is 1.43(2) Å.

The electron count requires the hydrocarbon chain in the tertiary phosphine to donate seven electrons to the cluster; these come formally from the allyl group (three), from C(1) (one) and C(2) (three). Together with the 12 CO groups (24), the PPh_2 group (3), and the phosphine P atom (2), the cluster has a 76-cluster valence electron (c.v.e.) configuration.

Molecular structure of $Ru_5\{\mu_4\text{-}CC(PPh_2)CHCH{=}CHMe\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_9$ *(8)*

The structure of **8** is shown in Fig. 2, relevant bond parameters being collected in Table 1. The metal core forms a distorted square pyramid, with Ru–Ru distances ranging from 2.748 to 2.881(1) Å. Two apical-basal edges are bridged asymmetrically by CO groups [Ru(1)–C(51) 2.289(6), Ru(5)–C(51) 1.990(6), Ru(3)–C(53) 2.254(7), Ru(5)–C(53) 2.004(6) Å; Ru(5)–C(51)–O(51) 147.6(5), Ru(5)–C(53)–O(53) 145.6(5)°] and Ru(1)–Ru(2) is symmetrically bridged by the PPh_2 ligand [Ru(1)–P(2) 2.257(2), Ru(2)–P(2) 2.269(2) Å]. The remaining nine CO ligands are all terminal.

Atom C(2) caps the Ru_4 face, again with a uniform spread of Ru–C(2) distances: 2.063, 2.105, 2.171 and 2.234(4) Å; it is also attached to C(1) [1.445(7) Å]. These two atoms are part of the C_2PPh_2 ligand in **1**, C(2) still carrying the PPh_2 group which interacts with Ru(1) [Ru(1)–P(1) 2.287(2) Å]. A four-carbon chain derived from a butadiene molecule is bonded to C(1); the hydrocarbon interacts with Ru(4) via C(2)–C(1)–C(3) and with Ru(3) via the C(4)–C(5) double bond. However, the Ru(3)–C(4) distance is long at 2.439(6) Å, perhaps because of some strain in the rest of the chain. As with **7**, the six-carbon chain donates seven electrons to the cluster. Five of these obviously come from the C(4)–C(5) double

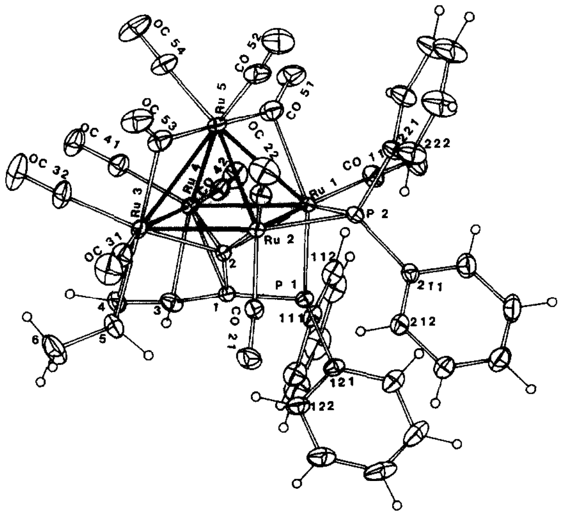


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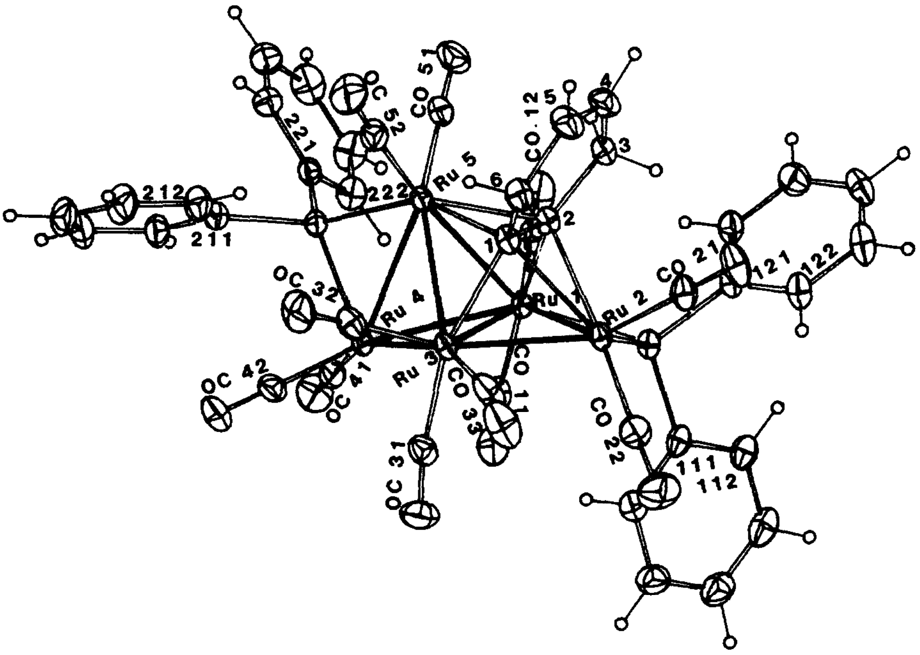
Fig. 2. Plot of a molecule of $Ru_5\{\mu_4\text{-}CC(PPh_2)CHCH{=}CHMe\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_9$ (**8**), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

bond and the alkylidyne C(2); the other two come from the C(1)–C(3) system. As a whole, the cluster has the expected 74-c.v.e. configuration.

The metal atom cores in **7** and **8** are similar, both being derived from square pyramids; two of the apical-basal edges in **7** are non-bonding. The usual cluster valence electron count associated with a square pyramid is 74, as found for **8**. Cleavage of two Ru–Ru bonds in **7** should increase the count to 78 c.v.e.; the observed count of only 76 c.v.e. suggests that the long Ru–Ru separations are formally each 1-e bonds.

Both complexes **7** and **8** have been formed by attack of butadiene on C_α of the C_2PPh_2 ligand in **1**. It is not possible to say whether an initial butadiene derivative is formed first, although the results that we have obtained in similar reactions with olefins, allene and allyl halides strongly suggest this to be the case [1–4]. Formation of the bond between C_α and the terminal carbon of the diene with concomitant rearrangement leads to formation of the η^3-allylic side chain found in **7**. In the case of **8**, isomerisation of the hydrocarbon chain by an H-atom shift has occurred. In **7**, the C(1)–C(2) fragment can be described as part of an alkylidyne or as a vinylidene, of which C(1) is substituted by C(3) and P(1). The C(1)–C(2) distance is consistent with the latter interpretation: a related complex is $Ru_5(\mu_4\text{-}PPh)\{\mu_3\text{-}CCPh(PPh_2)\}(CO)_{12}$, in which the analogous bond is 1.45(6) Å [5]. In **8**, however, C_α is involved in a multiple bond to C(3) [1.432(7) Å], so that the vinylidene description is not appropriate for the interaction between C(1)–C(2) and Ru(4). At present, we are unable to rationalise the long Ru(3)–C(4) distance, the asymmetry in the C(4)–C(5) bonding to Ru(3) possibly being influenced by the necessity for this double bond to occupy an axial site on Ru(3). The C–C bond lengths in the C(1)–C(5) chain suggest that some delocalisation of electron density occurs along this chain.



(9)

Fig. 3. Plot of a molecule of $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)_2(CO)_{11}$ (9), showing the atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

Molecular structure of $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)_2(CO)_{11}$ *(9)*

A molecule of 9 is shown in Fig. 3 and selected bond lengths and angles are listed in Table 2. The metal skeleton can be variously described as an edge-bridged tetrahedron or a wing-capped butterfly, although when the two atoms C(1)–C(2) are taken into account, the skeletal description simplifies to a C_2Ru_4 octahedron, an Ru_3 face of which is capped by Ru. Two Ru–Ru edges are bridged by μ-PPh_2 groups; the eleven CO groups are all terminal.

The eight Ru–Ru separations are between 2.692(1) and 2.9231(7) Å and fall into four groups, for which there is no obvious rationale. These are:
(i) the shortest, Ru(2)–Ru(3), is one of the uncapped wing edges;
(ii) three between 2.7694(7) and 2.7928(7) Å, comprising the PPh_2-bridged vector Ru(1)–Ru(2), one capped wing edge [Ru(1)–Ru(5)], and a non-bridged edge of the Ru_4 tetrahedron [Ru(3)–Ru(4)];
(iii) three between 2.830(1) and 2.8606(7) Å, comprising the other non-bridged edge of the Ru_4 tetrahedron, the non-bridged Ru(3)–Ru(5) capped wing edge, and the hinge, Ru(1)–Ru(3);
(iv) the longest bond is the PPh_2-bridged edge, Ru(4)–Ru(5), of the Ru_4 tetrahedron.
There are some curious asymmetries in these Ru–Ru separations. The two PPh_2-bridged Ru–Ru vectors differ by 0.15_4 Å, while there is a difference of 0.05_3 Å in the two hinge-wing tip distances involving Ru(4). These differences can be

Table 2

Selected bond lengths (Å) and angles (deg) for $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)_2(CO)_{11}$ (**9**)

Ru(1)–Ru(2)	2.7694(7)	Ru(1)–C(2)	2.156(4)
Ru(1)–Ru(3)	2.8606(7)	Ru(2)–C(1)	2.345(4)
Ru(1)–Ru(4)	2.830(1)	Ru(2)–C(2)	2.336(4)
Ru(1)–Ru(5)	2.7835(7)	Ru(3)–C(1)	2.146(4)
Ru(2)–Ru(3)	2.692(1)	Ru(5)–C(1)	2.233(4)
Ru(3)–Ru(4)	2.7928(7)	Ru(5)–C(2)	2.243(4)
Ru(3)–Ru(5)	2.8363(8)	C(1)–C(2)	1.424(6)
Ru(4)–Ru(5)	2.9231(7)	C(2)–C(3)	1.522(6)
Ru(1)–P(1)	2.315(1)	C(3)–C(4)	1.490(7)
Ru(2)–P(1)	2.268(1)	C(4)–C(5)	1.320(7)
Ru(4)–P(2)	2.223(1)	C(5)–C(6)	1.492(7)
Ru(5)–P(2)	2.300(1)	C(1)–C(6)	1.524(6)
Ru–CO	range 1.844–1.932(5), av. 1.889 Å		
C–O	range 1.128–1.155(6), av. 1.14 Å		
P–C(Ph)	range 1.817–1.832(5), av. 1.823 Å		
Dihedrals:	Ru(1)–Ru(2)–Ru(3)/Ru(1)–Ru(3)–Ru(4) 11.61(2)°		
	Ru(1)–Ru(2)–Ru(3)/Ru(1)–Ru(3)–Ru(5) 62.68(2)°		
	Ru(2)–C(1)–C(2)/Ru(5)–C(1)–C(2) 42.7(1)°		
	C(1–6)/Ru(2)–C(1)–C(2) 68.0(1)°		
	C(1–6)/Ru(5)–C(1)–C(2) 69.4(1)°		

related to the electron distribution within the cluster. It is interesting that the four atoms Ru(1,2,3,4) form an almost planar rhombus [dihedral 11.61(2)°]; the dihedral within the C_2-bridged butterfly is 117.32(2)°.

The two carbons C(1), C(2) form the usual μ-alkyne-M_4 cluster, in which the Ru–C distances form three sets:

(i) two at 2.146, 2.156(4) Å to the 'hinge' Ru atoms;

(ii) two at 2.233, 2.243(4) Å, to one wing-tip atom also attached to the face-capping Ru(4);

(iii) two at 2.336, 2.345(4) Å, to the other wing-tip atom, Ru(2).

The first two sets are within the normal separations found in related clusters, e.g. 2.16–2.26(1) Å in $Ru_4(\mu_4\text{-}C_2Ph_2)(CO)_{12}$ [6] or 2.16–2.27(1) Å in $Ru_4(\mu_4\text{-}C_2Me_2)(CO)_{12}$ [7].

The organic ligand, which is formally a cyclo-adduct of C_2 with butadiene, is μ_4-η^2-cyclohex-1-en-4-yne, a rare isomer of benzene. Within the organic ligand, C(1)–C(2) [1.424(6) Å] is similar to other examples of C_2Ru_4 clusters [6,7]. Other bonds around the six-membered ring show localisation, with the site of the double bond confirmed as C(4)–C(5) [1.320(7) Å]; the other C–C separations range between 1.490 and 1.524(6) Å.

It is difficult to account for the formation of **9** except in empirical terms. Cleavage of the P–C_α bond in **1** and Diels-Alder cycloaddition of butadiene to the C_2 moiety which is thus released gives an unusual C_6H_6 isomer which is stabilised on the cluster framework. Compared with **1**, which has seven, there is one more Ru–Ru bond in **9**, corresponding to a loss of two electrons from the attached ligands. As found with other C_2M_4 clusters (M = Fe, Ru, Os), the whole is two electrons deficient by the normal electron counting rules, although when considered as an Ru-capped C_2Ru_4 cluster, **9** has the expected 72-c.v.e. configuration [8]. Individual metal atoms are either electron-rich or -poor; these polarities may account for some of the discrepancies in Ru–Ru separations.

Spectroscopic properties

The NMR spectra of the three complexes are consistent with their solid-state structures. Thus, for **7**, four of the protons of the C_4 chain are centred at δ 2.85 (complex multiplet), with H(5) and H(6a) resonating at δ 4.19 and 3.32, respectively. In **8**, the H(5), Me, H(4) and H(3) signals are at δ 0.81, 2.03, 4.20 and 4.82, respectively. In the ^{13}C NMR spectra, the alkylidyne carbons C(2) are found at δ 304.6 and 261.1 in **7** and **8**, respectively, while C(1) occurs at relatively high field, at δ 61.0 for **7** and 51.3 for **8**. The carbon atoms of the butadiene-derived chain resonate between δ 38.3 and 92.7 (for **7**) and 23.0 and 84.5 (for **8**).

The CH_2 protons of the C_6 ring in **9** are found at δ 2.75 and 4.07, while the CH protons resonate as an AB quartet between δ 5.47 and 5.69. The ring carbons were found at δ 52.3 and 57.1 (C(3,6)), 125.0 and 125.1 (C(4,5)) and 164.6 (C(1,2)) in the ^{13}C NMR spectrum. In all cases, other resonances are assigned as recorded in the Experimental section.

Conclusions

The reactivity of **1** with olefins has been extended to the reaction with 1,3-butadiene. In addition to the previously described cluster-mediated three-component reaction which afforded a metallated benzoyldiphenylphosphine ligand [1], two other types of reaction have been found: (i) addition to C_α of the C_2PPh_2 ligand in **1** to give isomeric $Ph_2PC(C)CH_2$-η^3-$CHCHCH_2$ and $Ph_2PC(C)$-$CHCH{=}CHMe$ ligands, and (ii) formation of a cyclic C_6 ligand by cycloaddition of the 1,3-diene to the C_2 fragment with concomitant cleavage of the P–C_α bond. In the latter case, the rare C_6H_6 isomer cyclohex-1-en-3-yne is trapped in an Ru-capped C_2Ru_4 cluster.

Experimental

All reactions were carried out under dry, high purity nitrogen by standard Schlenk techniques. Solvents were dried and distilled before use. Elemental analyses were performed by the Canadian Microanalytical Service, Delta, B.C., Canada V4G 1G7. TLC was carried out on glass plates (20 × 20 cm) coated with silica gel (Merck 60 GF_{254}, 0.5 mm thick). Complex **1** was prepared by the literature method [5,9]. $Me_3NO \cdot 2H_2O$ (Aldrich) was dehydrated by sublimation (100°C/0.1 mmHg). 1,3-Butadiene was obtained commercially (Matheson) and used as received.

Instrumentation was as follows. IR: Perkin-Elmer 1700X FT IR; 683 double beam, NaCl optics; NMR: Bruker CXP300 or ACP300 (^{1}H NMR at 300.13 MHz, ^{13}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).

Table 3

Non-hydrogen atomic coordinates and isotropic thermal parameters for $Ru_5\{\mu_4\text{-}CC(PPh_2)CH_2\text{-}\eta^3\text{-}CHCHCH_2\}(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{11}$ (7)

Atom	x	y	z	U_{eq} (Å^2) [a]
Ru(1)	0.75572(4)	0.59677(4)	0.41051(4)	0.0376(3)
Ru(2)	0.71397(5)	0.52713(4)	0.52416(4)	0.0410(3)
Ru(3)	0.63514(5)	0.45631(4)	0.44707(5)	0.0435(4)
Ru(4)	0.68203(5)	0.51615(4)	0.32792(4)	0.0417(3)
Ru(5)	0.61886(5)	0.57919(4)	0.42257(5)	0.0429(4)
C(11)	0.7774(6)	0.6188(5)	0.3226(6)	0.050(5)
O(11)	0.7908(4)	0.6350(4)	0.2707(4)	0.069(4)
C(12)	0.8033(6)	0.6571(6)	0.4506(5)	0.049(5)
O(12)	0.8329(4)	0.6924(4)	0.4707(5)	0.083(4)
C(21)	0.7715(6)	0.5770(6)	0.5656(6)	0.050(5)
O(21)	0.8020(4)	0.6066(4)	0.5982(4)	0.077(4)
C(22)	0.7187(6)	0.4644(6)	0.5917(7)	0.069(6)
O(22)	0.7234(5)	0.4273(5)	0.6296(4)	0.099(5)
C(23)	0.6546(6)	0.5717(6)	0.5723(6)	0.062(6)
O(23)	0.6284(4)	0.5964(5)	0.6112(4)	0.080(4)
C(31)	0.6043(7)	0.4384(6)	0.5319(7)	0.064(6)
O(31)	0.5881(5)	0.4263(5)	0.5811(5)	0.095(5)
C(32)	0.5610(7)	0.4886(6)	0.4235(7)	0.066(6)
O(32)	0.5121(4)	0.4855(4)	0.4109(6)	0.089(5)
C(41)	0.6212(6)	0.4719(6)	0.2930(6)	0.062(6)
O(41)	0.5842(5)	0.4438(5)	0.2697(5)	0.093(5)
C(42)	0.6711(6)	0.5746(6)	0.2576(6)	0.051(5)
O(42)	0.6662(5)	0.6065(4)	0.2141(4)	0.082(4)
C(43)	0.7387(6)	0.4697(6)	0.2783(6)	0.054(5)
O(43)	0.7672(5)	0.4438(4)	0.2423(5)	0.080(4)
C(51)	0.5707(6)	0.5942(6)	0.3520(6)	0.062(6)
O(51)	0.5372(5)	0.6026(5)	0.3104(5)	0.099(5)
C(52)	0.5681(6)	0.6144(6)	0.4857(6)	0.058(6)
O(52)	0.5313(4)	0.6368(5)	0.5162(5)	0.082(5)
C(1)	0.7620(5)	0.4691(5)	0.4512(5)	0.036(4)
C(2)	0.7156(5)	0.5027(5)	0.4215(5)	0.040(4)
C(3)	0.7600(5)	0.3997(5)	0.4558(6)	0.049(5)
C(4)	0.6986(6)	0.3796(5)	0.4636(6)	0.050(5)
C(5)	0.6633(6)	0.3683(5)	0.4082(7)	0.058(5)
C(6)	0.6051(6)	0.3653(6)	0.4155(8)	0.075(6)
P(1)	0.8235(1)	0.5161(1)	0.4293(2)	0.042(1)
C(111)	0.8770(5)	0.5191(6)	0.4959(5)	0.045(4)
C(112)	0.9209(6)	0.5604(6)	0.4919(6)	0.055(5)
C(113)	0.9621(6)	0.5640(7)	0.5403(7)	0.071(6)
C(114)	0.9593(7)	0.5256(7)	0.5952(7)	0.078(7)
C(115)	0.9170(7)	0.4840(7)	0.6010(7)	0.070(6)
C(116)	0.8754(6)	0.4807(6)	0.5493(6)	0.059(5)
C(121)	0.8669(5)	0.4811(6)	0.3624(5)	0.044(4)
C(122)	0.8832(6)	0.5145(6)	0.3056(6)	0.064(6)
C(123)	0.9163(7)	0.4883(9)	0.2564(7)	0.084(7)
C(124)	0.9345(7)	0.430(1)	0.2628(8)	0.091(8)
C(125)	0.9200(7)	0.3975(7)	0.3198(9)	0.082(7)
C(126)	0.8865(6)	0.4222(6)	0.3684(6)	0.055(5)
P(2)	0.6758(2)	0.6632(1)	0.4107(1)	0.044(1)

Table 3 (continued)

Atom	x	y	z	U_{eq} (Å^2) [a]
C(211)	0.6659(6)	0.7206(5)	0.4779(6)	0.047(5)
C(212)	0.6183(6)	0.7604(6)	0.4708(6)	0.062(5)
C(213)	0.6074(7)	0.8024(6)	0.5171(7)	0.076(7)
C(214)	0.6424(8)	0.8077(6)	0.5709(7)	0.071(7)
C(215)	0.6895(7)	0.7709(6)	0.5796(6)	0.066(6)
C(216)	0.7007(6)	0.7260(6)	0.5319(6)	0.054(5)
C(221)	0.6751(6)	0.7168(5)	0.3393(5)	0.048(5)
C(222)	0.6308(7)	0.7242(6)	0.2953(7)	0.066(6)
C(223)	0.6357(9)	0.7657(7)	0.2419(8)	0.094(8)
C(224)	0.683(1)	0.7998(6)	0.2362(7)	0.086(8)
C(225)	0.7275(8)	0.7942(6)	0.2792(7)	0.083(7)
C(226)	0.7241(7)	0.7530(6)	0.3309(6)	0.067(6)
Cl(1) *	0.8527(4)	0.7706(4)	0.6353(4)	0.196(5)
Cl(2) *	0.9261(4)	0.6806(4)	0.6809(4)	0.220(5)
Cl(3) *	0.9578(3)	0.7542(4)	0.5745(6)	0.257(6)
C(0) *	0.906(1)	0.721(1)	0.617(1)	0.14(1)
Cl(1′) #	0.9993(4)	0.6409(4)	0.3447(4)	0.189(5)
Cl(2′) #	1.0003(4)	0.7631(5)	0.3559(6)	0.243(7)
Cl(3′) #	0.9025(4)	0.7118(5)	0.3189(6)	0.262(8)
C(0′) #	0.967(2)	0.706(2)	0.310(2)	0.17(1)

* Site occupancy factor = 0.875(6). # Site occupancy factor = 0.755(6). [a] $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a^*_i a^*_j (\mathbf{a}_i \cdot \mathbf{a}_j)$.

Reaction of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ with 1,3-butadiene

A solution of $Ru_5(\mu_5\text{-}C_2PPh_2)(\mu\text{-}PPh_2)(CO)_{13}$ (150 mg, 0.119 mmol) and 1,3-butadiene (2.0 g, 37 mmol) in benzene (15 ml) was heated in a Carius tube for 10 h at 80°C (tube oven). After cooling to room temperature the solvent was removed and the residue purified by preparative TLC (light petroleum/acetone 10/3) to give six bands. A red band (R_f 0.70) was recrystallised from CH_2Cl_2/MeOH to yield $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)_2(CO)_{11}$ (**9**) (33 mg, 22%), m.p. 194–202°C (dec.). Found: C, 37.87; H, 2.06%; M^+, 1262. $C_{41}H_{26}O_{11}P_2Ru_5 \cdot CH_2Cl_2$ calc.: C, 37.45; H, 2.10%; M, 1262. IR: ν(CO) (cyclohexane) 2080 vw, 2046 w, 2012 vs, 1987 m, 1967 w, 1955 w cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 2.61 (1H, d (br), J(HH) = 21 Hz, H(3) or H(6)), 2.88 (1H, dq, J(HH) = 21.4, 4.0 Hz, H(3) or H(6)), 4.00 (1H, dq, J(HH) = 21, 4 Hz, H(3) or H(6)), 4.14 (1H, d (br), J(HH) = 19 Hz, H(3) or H(6)), 5.47 (1H, d, J(HH) = 9.7 Hz, H(4) or H(5)), 5.69 (1H, d, J(HH) = 10.0 Hz, H(4) or H(5)), 7.13–7.81 (20H, m, Ph). ^{13}C NMR: δ ($CDCl_3$) 52.36 (d, J(CP) = 2.7 Hz, CH_2), 57.10 (s, CH_2), 124.96 (s, =CH), 125.10 (s, =CH), 127.97–132.75 (m, Ph), 138.61 (d, J(CP) = 25.8 Hz, *ipso* C), 138.99 (d, J(CP) = 25.4 Hz, *ipso* C), 141.65 (d, J(CP) = 35.6 Hz, *ipso* C), 143.05 (d, J(CP) = 35.6 Hz, *ipso* C), 164.60 (t, J(CP) = 8.3 Hz, CC), 192.89 (d, J(CP) = 10.8 Hz, CO), 193.43 (t, J(CP) = 6.3 Hz, CO), 193.66 (d, J(CP) = 8.4 Hz, CO), 195.84 (s, CO), 197.99 (s, CO), 198.92 (d, J(CP) = 4.8 Hz, CO), 201.71 (s, CO), 202.77 (d, J(CP) = 10.9 Hz, CO), 202.77 (t, J(CP) = 4.3 Hz, CO). FAB MS: 1262, M^+; 1234–954, $[M - n\text{CO}]^+$ (n = 1–11). A yellow band (R_f 0.50) was recrystallised from CH_2Cl_2/MeOH to yield $Ru_4\{\mu_4\text{-}C_6H_3C(O)PPh_2\}(\mu\text{-}PPh_2)(CO)_9(\eta^3\text{-}C_4H_7)$ (**6**) (24 mg, 17%), m.p. > 300°C (dec.), identified as described [1]. The product from a black band (R_f 0.40) was recrystallised (CH_2Cl_2/MeOH) to give $Ru_5\{\mu_4\text{-}CC(PPh_2)CH_2\text{-}\eta^3\text{-}CHCHCH_2\}(\mu\text{-}PPh_2)(\mu\text{-}CO)(CO)_{11}$ (**7**)

Table 4

Non-hydrogen atomic coordinates and isotropic thermal parameters for $Ru_5\{\mu_4\text{-}CC(PPh_2)CH\text{-}CH{=}CHMe\}(\mu\text{-}PPh_2)(\mu\text{-}CO)_2(CO)_9$ (**8**)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.18259(2)	0.71879(3)	0.70799(3)	0.0266(1)
Ru(2)	0.34198(2)	0.84730(3)	0.82092(3)	0.0279(1)
Ru(3)	0.30087(3)	1.02541(3)	0.71127(3)	0.0355(2)
Ru(4)	0.13533(3)	0.89711(3)	0.59818(3)	0.0333(2)
Ru(5)	0.31314(3)	0.82739(3)	0.57548(3)	0.0362(2)
C(11)	0.1202(4)	0.5806(5)	0.6597(5)	0.053(3)
O(11)	0.0831(4)	0.4952(4)	0.6332(6)	0.095(3)
C(21)	0.3416(4)	0.9112(4)	0.9714(4)	0.043(2)
O(21)	0.3387(4)	0.9554(4)	1.0593(4)	0.068(2)
C(22)	0.4750(4)	0.8395(5)	0.8401(5)	0.049(3)
O(22)	0.5546(3)	0.8310(4)	0.8479(5)	0.084(3)
C(31)	0.4068(4)	1.0909(5)	0.8161(5)	0.055(3)
O(31)	0.4706(4)	1.1347(4)	0.8749(5)	0.089(3)
C(32)	0.3250(5)	1.1264(5)	0.6064(6)	0.068(3)
O(32)	0.3398(5)	1.1839(5)	0.5405(5)	0.107(4)
C(41)	0.1471(4)	0.9813(5)	0.4780(4)	0.051(3)
O(41)	0.1509(4)	1.0351(4)	0.4068(4)	0.070(2)
C(42)	0.0230(4)	0.8170(5)	0.5170(4)	0.047(2)
O(42)	−0.0410(3)	0.7703(4)	0.4602(4)	0.069(2)
C(51)	0.2064(5)	0.7099(5)	0.5185(5)	0.061(3)
O(51)	0.1695(4)	0.6464(4)	0.4417(4)	0.080(3)
C(52)	0.4139(4)	0.7439(6)	0.5679(6)	0.066(3)
O(52)	0.4775(4)	0.6984(5)	0.5607(6)	0.104(4)
C(53)	0.4181(4)	0.9486(5)	0.6321(5)	0.059(3)
O(53)	0.4982(3)	0.9841(5)	0.6279(4)	0.088(3)
C(54)	0.3146(4)	0.8659(6)	0.4231(5)	0.062(3)
O(54)	0.3155(4)	0.8850(5)	0.3330(4)	0.096(3)
P(1)	0.06483(8)	0.7723(1)	0.8127(1)	0.0346(5)
C(111)	−0.0637(3)	0.7489(4)	0.7703(4)	0.042(2)
C(112)	−0.1031(4)	0.6767(5)	0.6765(5)	0.054(3)
C(113)	−0.2016(5)	0.6664(6)	0.6443(6)	0.069(4)
C(114)	−0.2589(4)	0.7248(7)	0.7027(7)	0.082(4)
C(115)	−0.2193(4)	0.7976(6)	0.7963(7)	0.076(4)
C(116)	−0.1229(4)	0.8085(5)	0.8297(6)	0.060(3)
C(121)	0.0698(3)	0.7769(4)	0.9665(4)	0.042(2)
C(122)	0.1063(5)	0.8695(5)	1.0378(5)	0.057(3)
C(123)	0.1099(5)	0.8710(6)	1.1549(5)	0.073(4)
C(124)	0.0746(6)	0.7809(8)	1.2004(5)	0.087(5)
C(125)	0.0365(5)	0.6886(7)	1.1301(6)	0.080(4)
C(126)	0.0370(4)	0.6862(5)	1.0132(5)	0.060(3)
P(2)	0.29491(9)	0.6716(1)	0.8314(1)	0.0352(5)
C(211)	0.2663(4)	0.6211(4)	0.9641(4)	0.040(2)
C(212)	0.2906(4)	0.6809(5)	1.0704(5)	0.051(3)
C(213)	0.2682(5)	0.6374(5)	1.1692(5)	0.066(4)
C(214)	0.2245(6)	0.5361(6)	1.1644(6)	0.075(4)
C(215)	0.1999(6)	0.4746(5)	1.0603(7)	0.075(4)
C(216)	0.2209(5)	0.5178(5)	0.9612(6)	0.062(3)
C(221)	0.3716(4)	0.5763(4)	0.7823(5)	0.048(3)

Table 4 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(222)	0.4514(5)	0.5638(6)	0.8522(6)	0.074(4)
C(223)	0.5123(6)	0.4937(8)	0.8164(8)	0.106(6)
C(224)	0.4930(7)	0.4351(8)	0.7094(8)	0.106(6)
C(225)	0.4146(6)	0.4460(6)	0.6406(7)	0.085(4)
C(226)	0.3541(5)	0.5159(5)	0.6755(6)	0.062(3)
C(1)	0.1155(3)	0.9013(4)	0.7804(4)	0.036(2)
C(2)	0.2146(3)	0.8941(3)	0.7624(4)	0.030(2)
C(3)	0.0781(4)	0.9883(5)	0.7343(5)	0.048(3)
C(4)	0.1472(5)	1.0866(5)	0.7389(5)	0.059(3)
C(5)	0.2189(5)	1.1226(4)	0.8282(6)	0.057(3)
C(6)	0.2568(7)	1.2419(6)	0.8547(9)	0.103(6)

(22 mg, 14%), m.p. > 300°C (dec.). Found: C, 38.39; H, 2.11%; M^+, 1290. $C_{42}H_{26}O_{12}P_2Ru_5 \cdot 0.5CH_2Cl_2$ calc.: C, 38.31; H, 2.04%; M, 1290. IR: ν(CO) (cyclohexane) 2057 w, 2036 vs, 2010 vs, 1992 m, 1972 m, 1951 w, 1897 w cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 2.74–2.93 (4H, m, H(3,4,6b)), 3.32 (1H, d, J(HH) = 6.4 Hz, H(6a)), 4.19 (1H, dt, J(HH) = 10.5, 6.6 Hz, H(5)), 6.88–7.97 (20H, m, Ph). ^{13}C NMR: δ ($CDCl_3$) 38.29 (s, C(3)), 41.71 (s, C(6)), 61.01 (d, J(CP) = 14.1 Hz, C(1)), 62.49 (d, J(CP) = 18.3 Hz, C(4)), 92.69 (s, C(5)), 127.26–134.39 (m, Ph), 137.20 (d, J(CP) = 46.8 Hz, *ipso* C), 140.47 (d, J(CP) = 37.7 Hz, *ipso* C), 146.67 (d, J(CP) = 31.4 Hz, *ipso* C), 192.74 (d, J(CP) = 5.7 Hz, CO), 195.53 (s, CO), 195.94 (s, CO), 198.00 (d, J(CP) = 6.2 Hz, CO), 198.18 (d, J(CP) = 6.6 Hz, CO), 200.10 (d, J(CP) = 5.1 Hz, CO), 201.48 (d, J(CP) = 6.6 Hz, CO), 201.32 (d, J(CP) = 5.5 Hz, CO), 205.56 (d, J(CP) = 6.3 Hz, CO), 218.42 (d, J(CP) = 21 Hz, CO), 304.61 (s, C(2)). FAB MS: 1290, M^+; 1262–954, $[M - n\text{CO}]^+$ (n = 1–12). A dark green band (R_f 0.35) was recrystallised (CH_2Cl_2/MeOH) to give crystals of $Ru_5\{\mu_4\text{-}CC(PPh_2)CHCH{=}CHMe\}(\mu\text{-}PPh_2)(CO)_{11}$ (**8**) (21 mg, 14%), m.p. 222–225°C (dec.). Found: C, 38.76; H, 2.08%; M^+, 1262. $C_{41}H_{26}O_{11}P_2Ru_5 \cdot CH_2Cl_2$ calc.: C, 39.02; H, 2.08%; M, 1292. IR: ν(CO) (cyclohexane) 2060 m, 2025 (sh), 2018 vs, 1998 m, 1982 w, 1961 m cm^{-1}. ^{1}H NMR: δ ($CDCl_3$) 0.81 (1H, dq, J(HH) = 10.7, 5.7 Hz, H(5)), 2.03 (3H, d, J(HH) = 5.8 Hz, CH_3), 4.20 (1H, dt, J(HH) = 10.6, 3.3 Hz, H(4)), 4.82 (1H, d, J(HH) = 3.4 Hz, H(3)), 6.12 (2H, dd, J(HH) = 12.9, 7.2 Hz, Ph), 6.60 (2H, td, J(HH) = 7.8, 2.9 Hz, Ph), 6.97–7.99 (16H, m, Ph). ^{13}C NMR: δ ($CDCl_3$) 23.29 (s, CH_3), 42.74 (s, C(5)), 51.29 (s, C(1)), 54.60 (s, C(4)), 84.55 (d, J(CP) = 5.4 Hz, C(3)), 128.21–133.23 (m, Ph), 145.47 (d, J(CP) = 30.7 Hz, *ipso* C), 148.84 (d, J(CP) = 32.2 Hz, *ipso* C), 191.62 (s, CO), 191.71 (s, CO), 194.04 (s, CO), 198.03 (s, CO), 201.55 (s, CO), 201.64 (s, CO), 207.02 (s, CO), 207.24 (d, J(CP) = 5.1 Hz, CO), 261.13 (t, J(CP) = 7.1 Hz, C(2)). FAB MS: 1262, M^+; 1234–954, $[\text{M} - n\text{CO}]^+$ (n = 1 – 11). The products from two other bands were formulated from their FAB mass spectra as $Ru_5(CO)_n$(dppa)(butadiene) (n = 10 or 11; *ca.* 8 mg, 5%) and $Ru_3(CO)_9$(dppa)(butadiene) (*ca.* 5 mg, 4%) (dppa = elements of $C_2(PPh_2)_2$), but crystals suitable for X-ray studies could not be obtained.

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

Table 5

Non-hydrogen atomic coordinates and isotropic thermal parameters for $Ru_5(\mu_4\text{-}C_6H_6)(\mu\text{-}PPh_2)_2(CO)_{11}$ (9)

Atom	x	y	z	U_{eq} (Å^2)
Ru(1)	0.10140(1)	0.72882(2)	0.93347(3)	0.03680
Ru(2)	0.03165(1)	0.80598(2)	0.76464(4)	0.04178
Ru(3)	0.03380(1)	0.67400(2)	0.71171(4)	0.04076
Ru(4)	0.08631(1)	0.58929(2)	0.90543(4)	0.04106
Ru(5)	0.15264(1)	0.66672(2)	0.70844(3)	0.03907
C(11)	0.0671(2)	0.6901(2)	1.0952(5)	0.0572
O(11)	0.0468(2)	0.6734(2)	1.1973(3)	0.0839
C(12)	0.1713(2)	0.7368(2)	1.0218(5)	0.0608
O(12)	0.2149(2)	0.7434(2)	1.0746(5)	0.1028
C(21)	0.0372(2)	0.8886(2)	0.6744(5)	0.0648
O(21)	0.0411(2)	0.9394(2)	0.6203(4)	0.0961
C(22)	−0.0426(2)	0.8257(3)	0.7920(6)	0.0739
O(22)	−0.0894(2)	0.8402(2)	0.8060(5)	0.1147
C(31)	−0.0189(2)	0.6370(2)	0.8411(5)	0.0629
O(31)	−0.0543(2)	0.6232(2)	0.9149(4)	0.0947
C(32)	0.0370(2)	0.6037(2)	0.5750(5)	0.0685
O(32)	0.0370(2)	0.5635(2)	0.4913(4)	0.1041
C(33)	−0.0273(2)	0.7146(3)	0.6126(6)	0.0766
O(33)	−0.0676(2)	0.7276(2)	0.5497(5)	0.1152
C(41)	0.1008(2)	0.5484(2)	1.0779(5)	0.0618
O(41)	0.1097(2)	0.5235(2)	1.1835(4)	0.0916
C(42)	0.0518(2)	0.5101(2)	0.8473(5)	0.0595
O(42)	0.0314(2)	0.4619(2)	0.8088(4)	0.0869
C(51)	0.2272(2)	0.6881(2)	0.7496(5)	0.0624
O(51)	0.2728(1)	0.7023(2)	0.7762(5)	0.0923
C(52)	0.1722(2)	0.6434(2)	0.5251(5)	0.0673
O(52)	0.1845(2)	0.6325(2)	0.4127(4)	0.1078
P(1)	0.06304(5)	0.83212(5)	0.9832(1)	0.0482
C(111)	0.0104(2)	0.8407(2)	1.1195(5)	0.0559
C(112)	0.0138(2)	0.8894(2)	1.2244(5)	0.0637
C(113)	−0.0271(3)	0.8927(3)	1.3254(5)	0.0782
C(114)	−0.0703(3)	0.8475(3)	1.3249(6)	0.0893
C(115)	−0.0739(2)	0.7992(3)	1.2253(6)	0.0811
C(116)	−0.0337(2)	0.7950(3)	1.1240(5)	0.0672
C(121)	0.1038(2)	0.9083(2)	1.0010(4)	0.0494
C(122)	0.0804(2)	0.9688(2)	0.9599(5)	0.0652
C(123)	0.1108(3)	1.0271(2)	0.9670(5)	0.0804
C(124)	0.1653(2)	1.0266(2)	1.0147(5)	0.0770
C(125)	0.1885(2)	0.9674(3)	1.0575(6)	0.0806
C(126)	0.1584(2)	0.9087(2)	1.0531(5)	0.0620
P(2)	0.16863(5)	0.56472(5)	0.8122(1)	0.0449
C(211)	0.1689(2)	0.4856(2)	0.7182(5)	0.0540
C(212)	0.1529(2)	0.4804(3)	0.5791(5)	0.0735
C(213)	0.1498(3)	0.4186(3)	0.5142(6)	0.0920
C(214)	0.1631(3)	0.3614(3)	0.5910(7)	0.1010
C(215)	0.1776(2)	0.3665(3)	0.7274(7)	0.0864
C(216)	0.1803(2)	0.4276(2)	0.7941(6)	0.0695
C(221)	0.2320(2)	0.5570(2)	0.9196(5)	0.0488
C(222)	0.2359(2)	0.5826(3)	1.0546(5)	0.0650

Table 5 (continued)

Atom	x	y	z	U_{eq} (Å^2)
C(223)	0.2846(2)	0.5802(3)	1.1305(6)	0.0836
C(224)	0.3312(2)	0.5526(3)	1.0741(6)	0.0899
C(225)	0.3298(2)	0.5271(3)	0.9412(7)	0.0850
C(226)	0.2802(2)	0.5301(3)	0.8628(5)	0.0652
C(1)	0.0926(2)	0.7434(2)	0.6260(4)	0.0482
C(2)	0.1248(2)	0.7728(2)	0.7369(4)	0.0448
C(3)	0.1660(2)	0.8288(2)	0.7068(5)	0.0549
C(4)	0.1725(2)	0.8438(3)	0.5553(5)	0.0704
C(5)	0.1418(3)	0.8166(3)	0.4541(5)	0.0766
C(6)	0.0956(2)	0.7677(2)	0.4751(5)	0.0606
C(0)	−0.1932(6)	0.7205(7)	0.820(1)	0.288
Cl(1)	−0.2072(1)	0.6320(2)	0.8177(3)	0.2135
Cl(2)	−0.1905(2)	0.7573(2)	0.9599(3)	0.2440

Mo-K_α radiation, λ 0.7107$_3$ Å); N independent reflections were obtained, N_0 with $I > 3\sigma(I)$ being considered 'observed' and used in the full matrix least squares refinement after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z, U_{iso})_H$ were included constrained at estimated values. Conventional residuals R, R' on $|F|$ are quoted, statistical weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 2.6 program system [10] implemented by S.R. Hall;

Table 6

Crystal data and refinement details for **7**, **8** and **9**

	7	8	9
Formula	$C_{42}H_{26}O_{12}P_2Ru_5 \cdot \sim 1.6CHCl_3$	$C_{41}H_{26}O_{11}P_2Ru_5$	$C_{41}H_{26}O_{11}P_2Ru_5 \cdot CH_2Cl_2$
MW	1481	1262	1346.9
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pbca*	$P\bar{1}$	$P2_1/n$
a (Å)	23.254(3)	14.110(11)	23.829(6)
b (Å)	21.916(5)	12.770(8)	20.033(6)
c (Å)	19.942(11)	11.842(5)	9.557(3)
α (deg)	–	96.26(4)	–
β (deg)	–	94.61(5)	90.92(2)
γ (deg)	–	97.99(6)	–
U (Å^3)	10136	2091	4561
Z	8	2	4
D_c (g cm^{-3})	1.93	2.00	1.96
F(000)	5734	1220	2608
Crystal size (mm)	0.17×0.33×0.20	0.41×0.07×0.20	0.15×0.36×0.15
A^* (min, max)	1.29, 1.37	1.12, 1.48	1.58, 1.67
μ (cm^{-1})	16.2	17.1	18.0
$2\theta_{max}$ (deg)	50	60	65
N	8925	12149	16255
N_o	5276	8271	8832
R	0.056	0.036	0.038
R_w	0.054	0.036	0.036

neutral atom complex scattering factors were employed. Pertinent results are given in the Figures and Tables. Tables of structure factor amplitudes, thermal and hydrogen atom parameters, and full non-hydrogen geometries are available from the authors.

Abnormal features / variations in procedure

7. Data were approximately scaled to compensate for decomposition of *ca.* 20% during measurement. This may have been associated with partial loss of chloroform solvate molecules, modelled in the refinement with populations 0.875(6), 0.755(6), respectively and with high thermal motion. Hydrogen atoms associated with the ligand were located in difference maps.

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