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## Cluster chemistry

### LXXI \*. Isomerisation of a pentanuclear ruthenium cluster by elimination of phenylphosphinidene from a tertiary phosphine. X-Ray structure of $\text{Ru}_5(\mu_5\text{-C}_2\text{Ph})(\mu_4\text{-PPh})(\mu\text{-PPh}_2)(\text{CO})_{13}$

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#### Abstract

Reactions of  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$  (**1**) in oxirane gave an isomer of **1**,  $\text{Ru}_5(\mu_5\text{-C}_2\text{Ph})(\mu_4\text{-PPh})(\mu\text{-PPh}_2)(\text{CO})_{13}$ , which has been formed by formal elimination of PPh from the  $\text{C}_2\text{PPh}_2$  ligand in **1** to the cluster, with concomitant cleavage of an Ru–Ru bond. The rhomboidal  $\text{Ru}_4$  core interacts with a  $\text{C}_2\text{Ph}$  ligand to give a trigonal prismatic  $\text{C}_2\text{Ru}_4$  arrangement, of which a triangular face is capped by the fifth Ru atom and a square face by the PPh group; the  $\text{Ru}_5$  skeleton has an envelope conformation. Notable is the short bond (1.965(6) Å) from the acetylide  $\text{C}_a$  to the edgebridging Ru atom, indicating some carbenic character for this carbon.

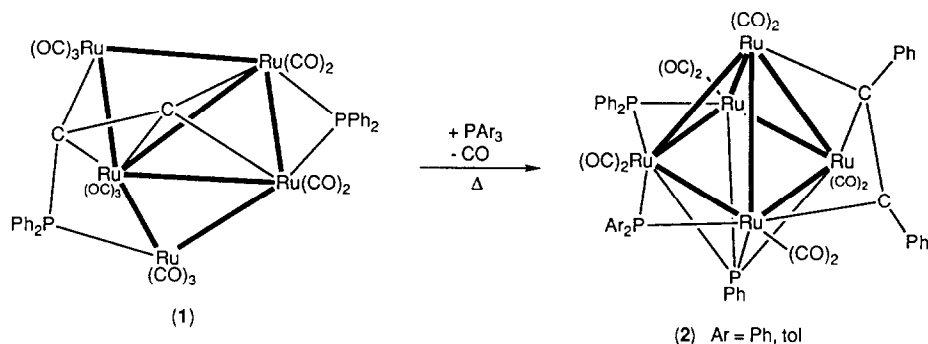
#### Introduction

In the reactions of  $\text{PAR}_3$  (Ar = Ph, tol) with  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$  (**1**) we found facile cleavage of P–C( $sp^2$ ) bonds occurred in both the coordinated  $\text{PAR}_3$  and  $\text{C}_2\text{PPh}_2$  ligands to give  $\text{Ru}_5(\mu_4\text{-PPh})(\mu_3\text{-PhC}_2\text{Ar})(\mu\text{-PPh}_2)(\mu\text{-PAR}_2)(\text{CO})_{10}$  (**2**; Ar = Ph, tol) (Scheme 1) [2]. Elimination of PPh occurred and migration of Ar from P to the ethynyl group afforded a cluster-bound alkyne. The net reaction on the cluster was:



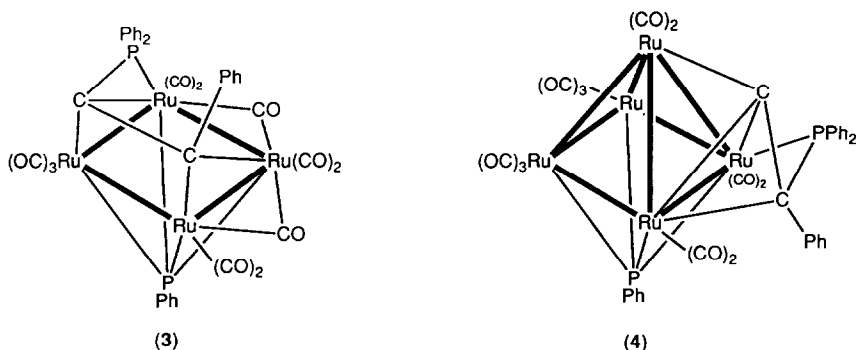
Similar migration of phenyl groups occurred during the thermolysis of  $\text{Ru}_5(\mu_4\text{-C}_2\text{Ph})(\mu\text{-PPh}_2)(\text{CO})_{14}$  to give  $\text{Ru}_5(\mu_4\text{-PPh})(\mu_3\text{-PhC}_2\text{Ph})(\text{CO})_{13}$  [3] and in a less

\* For Part LXX, see ref. 1.



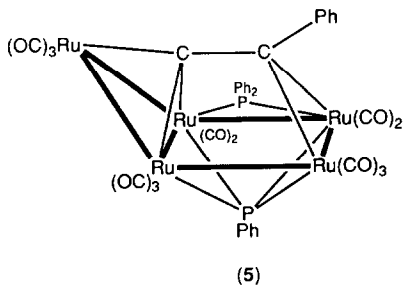
Scheme 1

well-defined way during the pyrolysis of  $\{\text{Ru}_3(\text{CO})_{11}\}_2(\mu\text{-dppa})$  ( $\text{dppa} = \text{C}_2(\text{PPh}_2)_2$ ), the products of which included the  $\mu_4$ -alkyne complex  $\text{Ru}_4(\mu_4\text{-PPh})(\mu_4\text{-PhC}_2\text{PPh}_2)(\mu\text{-CO})_2(\text{CO})_8$  (3) [4,5] and the  $\mu_4$ -vinylidene complex  $\text{Ru}_5(\mu_4\text{-PPh})\{\mu_3\text{-CCPh}(\text{PPh}_2)\}(\text{CO})_{12}$  (4) [5] in addition to 1 as the major product [4]. This paper describes an isomer of 1 which is formed by elimination of PPh from the  $\text{C}_2\text{PPh}_2$  ligand.



## Results and discussion

A reaction between 1 and oxirane (ethylene oxide) was carried out in benzene ( $100^\circ\text{C}/24\text{ h}$ ). The major product was obtained in only 15% yield as black crystals which were characterised by X-ray crystallography as an isomer of 1 of composition  $\text{Ru}_5(\mu_5\text{-C}_2\text{Ph})(\mu_4\text{-PPh})(\mu\text{-PPh}_2)(\text{CO})_{13}$  (5). A plot of the molecule is shown in Fig. 1, while Table 1 lists significant bond parameters.



The metal core consists of a rhombus of four Ru atoms, one edge of which is bridged by the fifth ruthenium to give an envelope-shaped cluster, similar to a 'step-site' on a metal surface. One side of the rhombus is capped by a  $\mu_4$ -PPh group, the opposite side by a phenylethynyl ligand.  $C_\alpha$  interacts strongly with Ru(1), resulting in an internal dihedral of  $108.40^\circ$  between the Ru(1)–Ru(2)–Ru(5) and Ru(2)–Ru(3)–Ru(4)–Ru(5) planes. A  $PPh_2$  group bridges an Ru–Ru edge adjacent to the flap. Coordination of the metal atoms is completed by 13 CO ligands, distributed two each to Ru(4) and Ru(5), and three each to the three remaining Ru atoms. There is a semi-bridging interaction between CO(52) and Ru(1) [Ru(1)–C(52) 2.596(8) Å; Ru(5)–C(52)–O(52)  $163.4(6)^\circ$ ], with a lesser displacement of CO(23) towards the same metal atom.

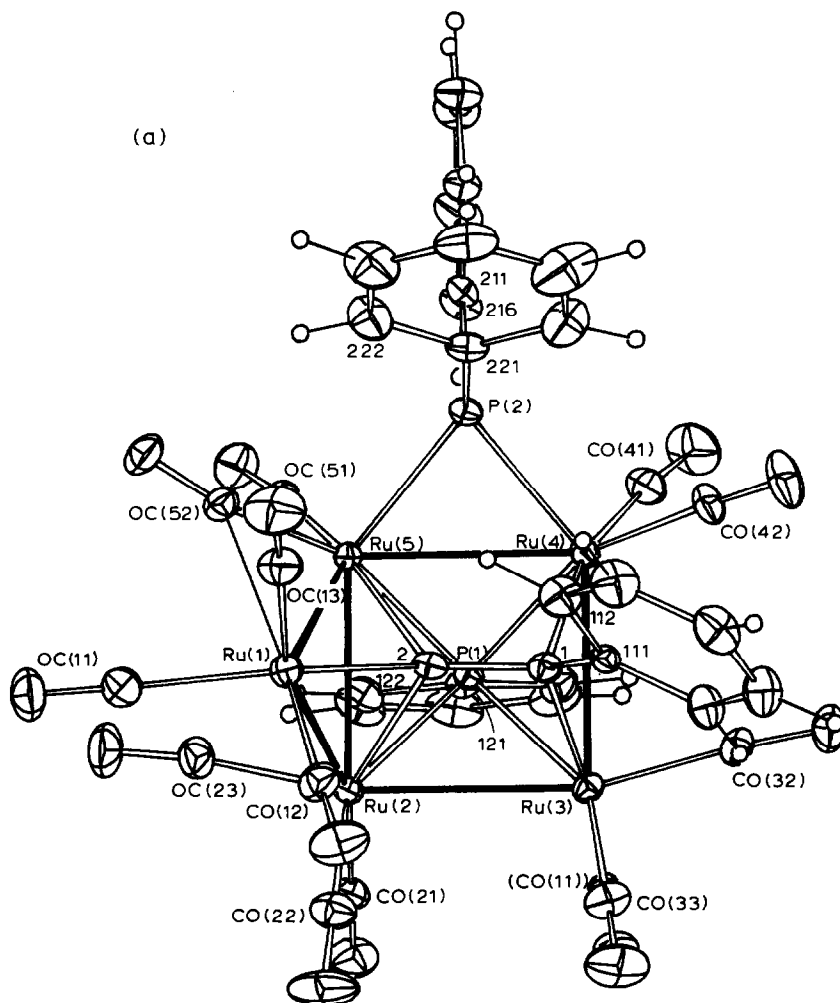


Fig. 1. Computer-generated plots of a molecule of  $Ru_5(\mu_5-C_2Ph)(\mu_4-PPh)(\mu-PPh_2)(CO)_{13}$  (5), (a) perpendicular to the Ru(5)–Ru(2)–Ru(3)–Ru(4) plane and (b) from the side of the  $Ru_4$  rhombus, showing atom numbering scheme. Non-hydrogen atoms are shown as 20% thermal ellipsoids; hydrogen atoms have arbitrary radii of 0.1 Å.

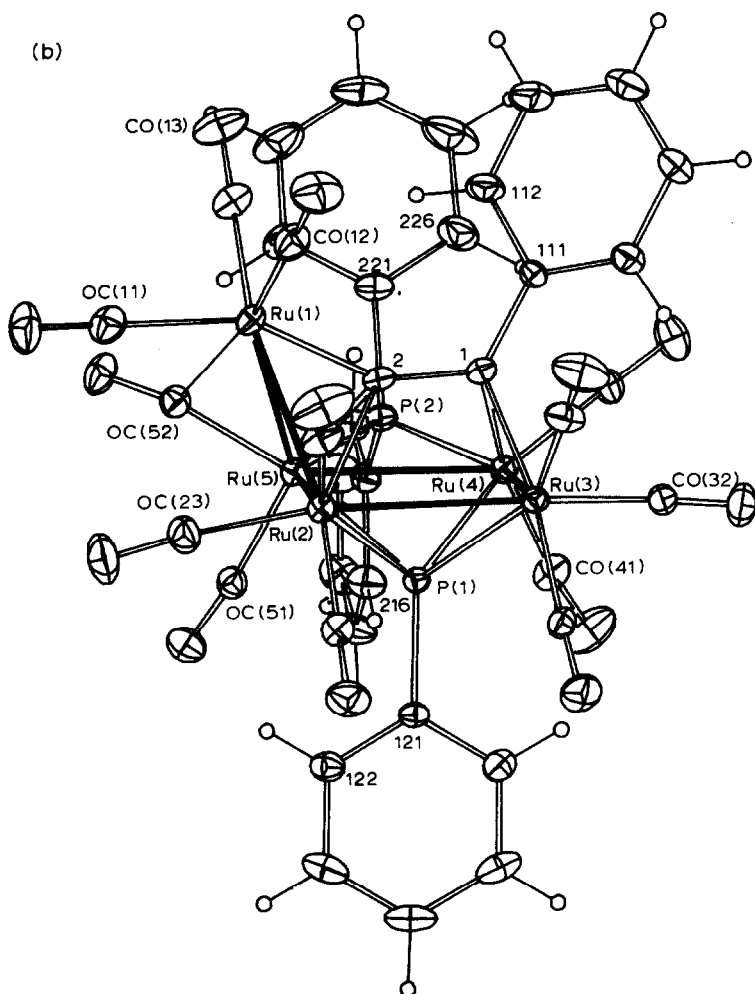


Fig. 1 (continued).

Within the core, Ru–Ru distances range from 2.829–2.913(1) Å, of which the shortest is Ru(2)–Ru(5), the hinge of the flap, and the longest Ru(2)–Ru(3). The PPh<sub>2</sub>-bridged Ru(4)–Ru(5) vector is 2.877(1) Å; Ru(1) asymmetrically bridges Ru(2)–Ru(5), being closer to Ru(5) by 0.034 Å.

The Ru<sub>4</sub> rhombus is asymmetrically capped by the PPh group, one bond, Ru(5)–P(1) [2.429(2) Å] being markedly longer than the other three [2.356–2.389(1) Å], as found in Ru<sub>5</sub>(μ<sub>4</sub>-PPh)(CO)<sub>15</sub> [6]. The PPh<sub>2</sub> group bridges Ru(4)–Ru(5) almost symmetrically.

The phenylethynyl fragment is attached to all five metal atoms. The strongest interaction is of C<sub>α</sub> with Ru(1) [1.965(6) Å], which is short enough to indicate a significant degree of multiple bond character. This carbon is less firmly attached to Ru(2) and Ru(5) [2.333, 2.222(6) Å, respectively]. The separation of C<sub>β</sub> from Ru(3) and Ru(4) is normal [2.182, 2.188(8) Å]. The C(1)–C(2) bond length is 1.395(8) Å.

Table 1

Significant bond lengths (Å) and angles (deg) in  $\text{Ru}_5(\mu_5\text{-C}_2\text{Ph})(\mu_4\text{-PPh})(\mu\text{-PPH}_2)(\text{CO})_{13}$  (**5**)

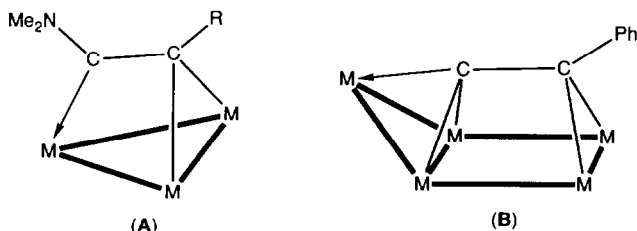
Ru(1)–Ru(2)	2.875(1)	Ru(5)–P(2)	2.299(2)
Ru(1)–Ru(5)	2.8406(9)		
Ru(2)–Ru(3)	2.913(1)	Ru(1)–C(2)	1.965(6)
Ru(2)–Ru(5)	2.829(1)	Ru(2)–C(2)	2.333(6)
Ru(3)–Ru(4)	2.847(1)	Ru(3)–C(1)	2.182(8)
Ru(4)–Ru(5)	2.877(1)	Ru(4)–C(1)	2.188(6)
		Ru(5)–C(2)	2.222(6)
Ru(2)–P(1)	2.389(1)		
Ru(3)–P(1)	2.356(2)	Ru(1)–C(52)	2.596(8)
Ru(4)–P(1)	2.370(1)	Ru(5)–C(52)	1.897(8)
Ru(4)–P(2)	2.281(2)		
Ru(5)–P(1)	2.429(2)	C(1)–C(2)	1.395(8)
Ru(2)–Ru(1)–Ru(5)	59.33(2)	Ru(4)–P(1)–Ru(5)	73.64(2)
Ru(2)–Ru(3)–Ru(4)	89.69(2)	Ru(2)–C(2)–Ru(5)	76.7(1)
Ru(3)–Ru(4)–Ru(5)	89.93(2)	Ru(3)–C(1)–Ru(4)	81.3(2)
Ru(4)–Ru(5)–Ru(2)	90.78(2)	Ru(1)–C(2)–C(1)	150.4(4)
Ru(5)–Ru(2)–Ru(3)	89.55(2)	Ru(2)–C(23)–O(23)	171.4(8)
Ru(1)–Ru(5)–Ru(2)	60.95(2)	Ru(1)–C(52)–O(52)	120.0(4)
Ru(1)–Ru(2)–Ru(5)	59.72(2)	Ru(5)–C(52)–O(52)	163.4(6)
		C(2)–C(1)–C(Ph)	122.1(6)
Ru–CO	range 1.875–1.981(8), av. 1.912 Å		
C–O	range 1.11–1.15(1), av. 1.135 Å		
P–C(Ph)	range 1.811–1.834(7), av. 1.822 Å		
Ru–C–O	range 171.4–178.4(8), av. 175.4°		

The geometry of the core of **5** can be described as a trigonal prism ( $\text{C}_2\text{Ru}_4$ ) capped on a triangular face by Ru(1) and on a square face by PPh. As described above, the ligands contribute a total of 50 electrons to the cluster, which is thus electron-precise, although formally Ru(5) is electron-rich and Ru(1) is electron-poor, the latter situation is partially compensated by the semi-bridging interactions with CO(23) and CO(52). Alternatively, the cluster is a 78 valence electron system, as expected for this open five-atom geometry.

The spectroscopic properties of **5** are consistent with the solid state structure. The IR  $\nu(\text{CO})$  spectrum contains only bands for terminal CO groups, while in the  $^{13}\text{C}$  NMR spectrum, the  $\text{C}_\alpha$  and  $\text{C}_\beta$  resonances are either in the CO region ( $\delta$  190–210) or in the phenyl region; a singlet at  $\delta$  147.6 may be due to one of these. The  $^1\text{H}$  NMR spectrum contains only resonances for the phenyl protons. The FAB mass spectrum contains a molecular ion at  $m/z$  1264, which fragments by loss of up to 13 CO ligands.

The bonding of the phenylethynyl group deserves further comment. The short Ru(1)–C(2) interaction is reminiscent of the interaction of the alkyne with the  $\text{Os}_3$  cluster in  $\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-HC}_2\text{NEt}_2)(\text{CO})_9$  [7], i.e. a carbenic interaction, which has been thoroughly examined by an Extended Hückel MO study [8]. In this complex, the  $\text{C}_2\text{Os}_3$  unit has a basket-like geometry with the carbon bearing the  $\text{NEt}_2$  group being attached to only one Os atom. The C–N bond has a bond order intermediate between a C–N single and a C=N double bond, and indeed, the system has been described as a dimetallamethyl(diethylamino)carbene (A). In the present case we

reverse the geometry, as in **B**, and propose a three-centre C(2)–Ru(2)–Ru(5) interaction. It is notable that the C(1)–C(2) bond is lengthened to about 1.4 Å in accord with the proposed description, and also that each ruthenium atom now achieves an 18-electron configuration.



The isomerisation of **1** has proceeded, at least formally, by a simple extrusion of PPh from the C<sub>2</sub>PPh<sub>2</sub> group to the cluster, with concomitant rupture of one of the 'internal' Ru–Ru bonds to form the cluster found in **5** (eq. 1).



Two possible routes for this cluster-mediated isomerisation are (i) by C(sp)–P bond cleavage to give (C<sub>2</sub> + PPh<sub>2</sub>), followed by Ph migration from PPh<sub>2</sub> to a carbon atom of the C<sub>2</sub> fragment, or (ii) by elimination of PPh directly from the PPh<sub>2</sub> group to the cluster. Studies of related reactions of **1**, to be described elsewhere, suggest that the former is more likely.

## Experimental

General experimental details [2] and the method of synthesis of **1** [5] are similar to those described previously.

### Reaction of Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)(CO)<sub>13</sub> with oxirane

A mixture of Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>PPh<sub>2</sub>)(μ-PPh<sub>2</sub>)(CO)<sub>13</sub> (100 mg, 0.079 mmol) and oxirane (1.1 g, 25 mmol) in benzene (15 cm<sup>3</sup>) was heated in a Carius tube at 100 °C for 24 h. The solvent was removed and the residue purified by preparative TLC (petroleum ether/acetone 10/3) to yield at least six bands. A major brown band (R<sub>f</sub> 0.7) was crystallised (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>Ph)(μ-PPh<sub>2</sub>)(μ<sub>4</sub>-PPh)(CO)<sub>13</sub> (**5**) (15 mg, 15%), m.p. > 300 °C (dec.). Found: C, 36.81; H, 1.65%; *M* (mass spectrometry), 1264. C<sub>30</sub>H<sub>20</sub>O<sub>13</sub>P<sub>2</sub>Ru<sub>5</sub> calc. C, 37.06; H, 1.59%; *M* 1264. IR: ν(CO) (cyclohexane) 2084s, 2061vs, 2040s, 2029vs, 2019s, 2005m, 1991m, 1982m, 1976m, 1924w cm<sup>-1</sup>. <sup>1</sup>H NMR: δ (CDCl<sub>3</sub>) 7.26–8.00 (m, 20H, Ph). <sup>13</sup>C NMR: δ (CDCl<sub>3</sub>) 190.6, 191.8, 194.0, 195.3, 199.0, 199.9, 202.1, 202.6, 208.0, 209.8, 210.1 (11 × s, CO); 147.6, 141.6, 139.3 (3 × s); 125.2–136.5 (m, Ph). FAB MS: 1264, [*M*]<sup>+</sup>; 1236–900, [*M* – *n*CO]<sup>+</sup> (*n* = 1–13). The remaining bands were obtained in trace amounts and have not been identified.

### Crystallography

A unique data set was measured at ca 295 K within the limit 2θ<sub>max</sub> = 50° using an Enraf-Nonius CAD4 diffractometer (2θ/θ scan mode; monochromatic Mo-K<sub>α</sub> radiation, λ = 0.71073 Å); 6937 independent reflections were obtained, 5759 with

Table 2

Non-hydrogen atomic coordinates and isotropic displacement parameters for Ru<sub>5</sub>(μ<sub>5</sub>-C<sub>2</sub>Ph)(μ<sub>4</sub>-PPh)(μ-PPh<sub>2</sub>)(CO)<sub>13</sub> (5)

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> (Å <sup>2</sup> )
Ru(1)	0.75187(5)	0.40935(2)	0.56770(3)	0.0385(2)
Ru(2)	0.60556(4)	0.32989(2)	0.60525(3)	0.0324(2)
Ru(3)	0.78043(5)	0.31917(2)	0.79536(3)	0.0318(2)
Ru(4)	0.99395(4)	0.27126(2)	0.79063(3)	0.0325(2)
Ru(5)	0.82273(4)	0.28545(2)	0.60339(3)	0.0299(2)
C(11)	0.6211(7)	0.4215(3)	0.4395(4)	0.056(4)
O(11)	0.5476(5)	0.4274(3)	0.3660(3)	0.084(3)
C(12)	0.7151(7)	0.4830(3)	0.6014(4)	0.057(4)
O(12)	0.6996(6)	0.5273(2)	0.6220(4)	0.091(4)
C(13)	0.8916(7)	0.4491(3)	0.5698(5)	0.059(4)
O(13)	0.9710(6)	0.4769(3)	0.5702(4)	0.098(4)
C(21)	0.4634(6)	0.2887(3)	0.6012(4)	0.044(3)
O(21)	0.3766(5)	0.2670(2)	0.5990(3)	0.071(3)
C(22)	0.5230(7)	0.4042(3)	0.6008(5)	0.061(4)
O(22)	0.4630(6)	0.4455(2)	0.5968(5)	0.106(4)
C(23)	0.5150(7)	0.3154(3)	0.4836(4)	0.059(4)
O(23)	0.4474(5)	0.3050(3)	0.4110(3)	0.093(4)
C(31)	0.6459(6)	0.2761(3)	0.8003(4)	0.043(3)
O(31)	0.5699(4)	0.2520(2)	0.8061(3)	0.067(3)
C(32)	0.9202(6)	0.2986(3)	0.9119(4)	0.047(3)
O(32)	0.9981(5)	0.2849(2)	0.9837(3)	0.071(3)
C(33)	0.7352(7)	0.3969(3)	0.8185(5)	0.056(4)
O(33)	0.7056(6)	0.4411(2)	0.8305(4)	0.093(4)
C(41)	1.0462(6)	0.1900(3)	0.8300(4)	0.055(4)
O(41)	1.0847(6)	0.1438(3)	0.8625(4)	0.098(4)
C(42)	1.1611(6)	0.2987(3)	0.8932(4)	0.052(3)
O(42)	1.2585(5)	0.3153(3)	0.9566(3)	0.091(3)
C(51)	0.7784(6)	0.2099(3)	0.5443(4)	0.043(3)
O(51)	0.7435(5)	0.1682(2)	0.5016(3)	0.065(3)
C(52)	0.8120(6)	0.3199(3)	0.5081(4)	0.044(3)
O(52)	0.8142(5)	0.3268(2)	0.4491(3)	0.062(3)
C(1)	0.9132(5)	0.3630(2)	0.7686(4)	0.035(3)
C(2)	0.8301(5)	0.3649(2)	0.6773(4)	0.033(3)
C(111)	1.0075(5)	0.4126(2)	0.8229(3)	0.031(3)
C(112)	1.0690(6)	0.4478(3)	0.7928(4)	0.055(4)
C(113)	1.1602(7)	0.4934(3)	0.8417(5)	0.072(4)
C(114)	1.1974(7)	0.5070(3)	0.9235(5)	0.069(4)
C(115)	1.1397(7)	0.4745(3)	0.9552(5)	0.066(4)
C(116)	1.0440(6)	0.4290(3)	0.9039(4)	0.053(3)
P(1)	0.7560(1)	0.24918(6)	0.69372(9)	0.0300(6)
C(121)	0.6831(5)	0.1745(2)	0.6797(4)	0.034(3)
C(122)	0.5800(6)	0.1536(3)	0.5979(4)	0.045(3)
C(123)	0.5198(6)	0.0984(3)	0.5869(5)	0.062(4)
C(124)	0.5618(7)	0.0644(3)	0.6585(5)	0.066(4)
C(125)	0.6659(8)	0.0839(3)	0.7414(5)	0.063(4)
C(126)	0.7257(6)	0.1396(3)	0.7515(4)	0.047(3)
P(2)	1.0558(1)	0.26955(7)	0.6984(1)	0.0335(7)
C(211)	1.1285(5)	0.2014(2)	0.6892(4)	0.036(3)
C(212)	1.2439(6)	0.2025(3)	0.6911(4)	0.044(3)
C(213)	1.2980(7)	0.1495(3)	0.6833(5)	0.061(4)
C(214)	1.2373(7)	0.0957(3)	0.6749(5)	0.065(4)

Table 2 (continued)

Atom	x	y	z	$U_{eq}$ (Å <sup>2</sup> )
C(215)	1.1238(7)	0.0932(3)	0.6739(5)	0.062(4)
C(216)	1.0696(6)	0.1453(3)	0.6809(4)	0.051(3)
C(221)	1.1723(6)	0.3272(3)	0.7077(4)	0.044(3)
C(222)	1.1499(7)	0.3516(4)	0.6337(5)	0.071(4)
C(223)	1.2424(8)	0.3932(4)	0.6415(6)	0.091(6)
C(224)	1.3520(8)	0.4111(3)	0.7195(6)	0.082(5)
C(225)	1.377(1)	0.3866(5)	0.7939(7)	0.112(7)
C(226)	1.2865(8)	0.3451(4)	0.7886(5)	0.076(5)

$I > 3\sigma(I)$  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  $|F|$  were 0.035, 0.041, respectively, statistical weights derivative of  $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$  being used. Computation used the XTAL 3.0 program system [9] implemented by S.R. Hall; neutral atom complex scattering factors were employed. Pertinent results are given in Fig. 1 and Tables 1 and 2. Structure factor amplitudes, thermal and hydrogen atom parameters and full non-hydrogen geometries are available from the authors.

#### Crystal data

$Ru_5(\mu_5-C_2Ph)(\mu_4-PPh)(\mu-PPh_2)(CO)_{13} \equiv C_{39}H_{20}O_{13}P_2Ru_5$ ,  $M = 1263.9$ . Monoclinic, space group  $P2_1/c$  (No. 14),  $a = 12.113(3)$ ,  $b = 22.198(5)$ ,  $c = 19.007(6)$  Å,  $\beta = 126.54(2)^\circ$ ,  $U = 4106.2$  Å<sup>3</sup>.  $D_c$  ( $Z = 4$ ) =  $2.04$  g cm<sup>-3</sup>.  $F(000) = 2432$ .  $\mu_{Mo} = 17.5$  cm<sup>-1</sup>. Specimen:  $0.40 \times 0.06 \times 0.52$  mm;  $A^*_{min,max} = 1.12, 2.07$ .

#### Acknowledgements

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