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## Cluster chemistry

**LXXIV. \* Reactions between  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$  and allyl halides: cluster cleavage and three-component addition reactions. Crystal structures of  $\text{Ru}_4\{\mu_4\text{-C}_2\text{PPh}_2\text{Ru}(\text{CO})_2(\eta\text{-C}_3\text{H}_5)(\mu\text{-Cl})\}(\mu\text{-PPh}_2)(\text{CO})_{10}$  and  $\text{Ru}_5\{\mu_5\text{-CCC}(\text{O})\text{CH}_2\text{CH}=\text{CH}_2\}(\mu\text{-PPh}_2)_2(\mu\text{-Br})(\text{CO})_{11}$**

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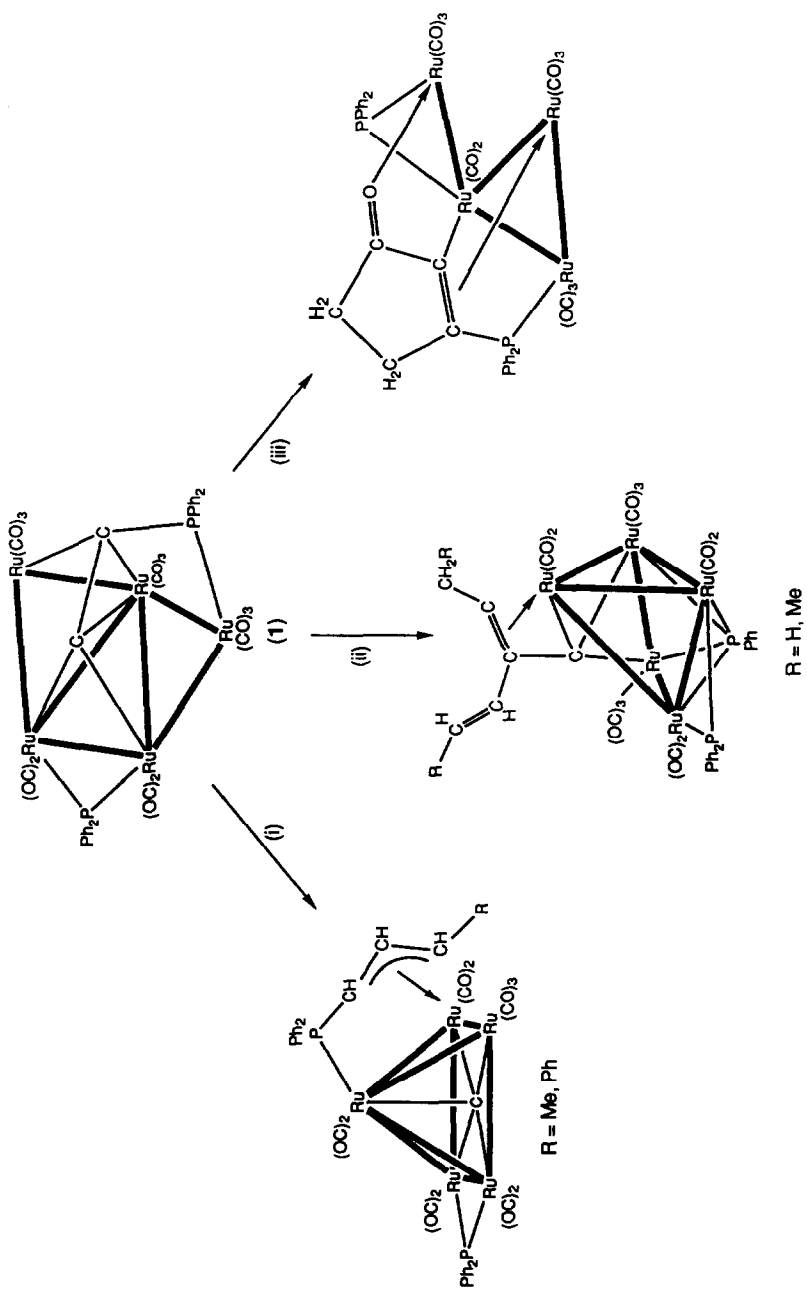
### Abstract

Reactions between  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$  and  $\text{CH}_2=\text{CHCH}_2\text{X}$  ( $\text{X} = \text{Cl}, \text{Br}$ ) have given two types of cluster complex which have been characterised by X-ray diffraction studies. In the first, **2-X**, an  $\text{RuX}(\text{CO})_2(\eta\text{-C}_3\text{H}_5)$  moiety, is attached by X and  $\text{PR}_3$  bridges to an  $\text{Ru}_4\{\mu_4\text{-C}_2\text{PPh}_2\}(\mu\text{-PPh}_2)(\text{CO})_{10}$  cluster. The second, **3-X**, is isomeric with **2-X** and contains an  $\text{Ru}_5$  core which is a metallated rhombus; the organic ligand, which has been formed by linking of CO,  $\text{C}_2$  and  $\text{C}_3\text{H}_5$  groups, bridges all five Ru atoms. Likely routes to these complexes are discussed.

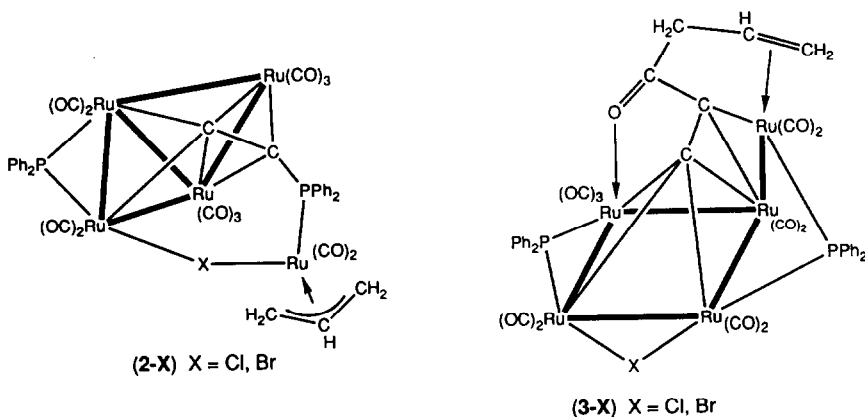
### Introduction

The complex  $\text{Ru}_5(\mu_5\text{-C}_2\text{PPh}_2)(\mu\text{-PPh}_2)(\text{CO})_{13}$  (**1**) is very reactive and recent papers have described the variety of reactions it undergoes with olefins [2,3]. These have been characterised as (i) addition to  $\text{C}_\beta$  with associated cleavage of the  $\text{C}_\alpha\text{-C}_\beta$  bond [2]; (ii) addition to the  $\text{C}_2$  unit with cleavage of the  $\text{C}_\beta\text{-P}$  bond [3]; (iii) incorporation of the phosphino-acetylide ligand with the olefin and CO in new types of cluster-bound tertiary phosphine ligands (Scheme 1) [3]. As an extension of

\* For Part LXXIII, see ref. 1.



Scheme 1



these experiments, we decided to investigate the reactions of allyl halides with **1**. From these, we have isolated and crystallographically characterised two types of complex, one formed by extrusion of an Ru atom from the Ru<sub>5</sub> cluster, and the other by addition of the allyl group and CO to the C<sub>2</sub> fragment.

## Results

The reactions between **1** and allyl chloride or bromide proceed quite slowly (20–24 hours, refluxing CH<sub>2</sub>Cl<sub>2</sub>). Two isomeric complexes, **2-Cl** and **3-Cl**, were isolated from the reaction of allyl chloride with **1** in 42 and 19% yields, respectively; similarly, allyl bromide gave complexes **2-Br** and **3-Br**. Of these, the brown chloro complex **2-Cl** and the orange bromo derivative **3-Br** were identified by X-ray studies as Ru<sub>4</sub>{μ<sub>4</sub>-C<sub>2</sub>PPh<sub>2</sub>Ru(CO)<sub>2</sub>(η-C<sub>3</sub>H<sub>5</sub>)(μ-X)}(μ-PPh<sub>2</sub>)(CO)<sub>10</sub> (**2**) and Ru<sub>5</sub>{μ<sub>5</sub>-CCC(O)CH<sub>2</sub>CH=CH<sub>2</sub>}(μ-PPh<sub>2</sub>)<sub>2</sub>(μ-X)(CO)<sub>11</sub> (**3**), respectively (X = Cl or Br). Two isomeric forms of **2-Br** are present in solution, but could not be separated by thin layer chromatography. No interconversion between **2-Br** and **3-Br** was noted after heating in refluxing CH<sub>2</sub>Cl<sub>2</sub> for 20 hours.

*Molecular structure of Ru<sub>4</sub>{μ<sub>4</sub>-C<sub>2</sub>PPh<sub>2</sub>Ru(CO)<sub>2</sub>(η-C<sub>3</sub>H<sub>5</sub>)(μ-Cl)}(μ-PPh<sub>2</sub>)(CO)<sub>10</sub> (**2-Cl**)*

A plot of a molecule of **2-Cl** is shown in Fig. 1 and selected bond parameters are collected in Table 1. The major feature is a butterfly Ru<sub>4</sub> cluster to which is attached the diphenylphosphino-acetylide ligand by the C<sub>2</sub> moiety in the μ-η<sup>2</sup>(⊥) mode, of which C(2) interacts with all four Ru atoms [Ru–C(2) 2.015–2.323(4) Å]. The Ru–Ru bonds range from 2.759–2.891(1) Å, the shortest being bridged by the η<sup>2</sup>-C<sub>2</sub> fragment, the longest being the other two bonds involving Ru(5). A PPh<sub>2</sub> group bridges the Ru(2)–Ru(3) vector [Ru(2)–P(2) 2.287(1), Ru(3)–P(2) 2.266(1) Å]. Ten CO groups are distributed two each to Ru(2) and Ru(3), and three each to Ru(4) and Ru(5).

The fifth metal atom is attached to the Ru<sub>4</sub> cluster via a donor bond from P(1) to Ru(1) [Ru(1)–P(1) 2.358(1) Å] and a Cl atom which bridges the Ru(1)···Ru(2) non-bonded vector [Ru(1)–Cl(1) 2.455(1), Ru(2)–Cl(1) 2.559(1) Å]; the Ru–Cl–Ru

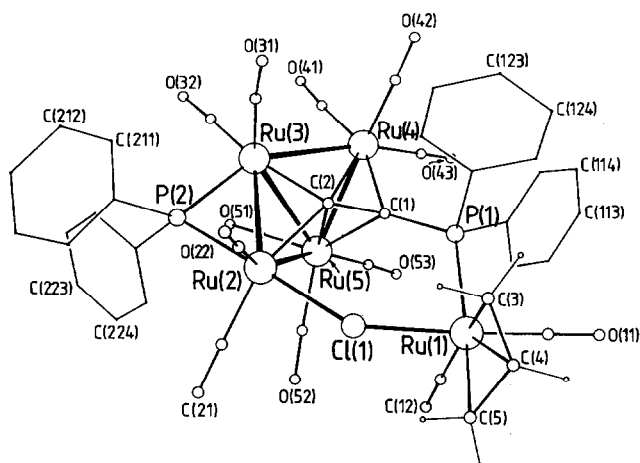


Fig. 1. Computer-generated plot of a molecule of  $\text{Ru}_4(\mu_4\text{-C}_2\text{PPh}_2\text{Ru}(\text{CO})_2(\eta\text{-C}_3\text{H}_5)(\mu\text{-Cl}))(\mu\text{-PPh}_2)(\text{CO})_{10}(2\text{-Cl})$ , showing atom numbering scheme.

angle of  $137.2(1)^\circ$  is presumably dictated by the geometric constraints of the rest of the molecule, rather than reflecting the preferred bonding tendencies of the Cl ligand. Other groups attached to Ru(1) are the allyl ligand [Ru(1)–C(3,5) (outer) 2.218, 2.273(5); Ru(1)–C(4) (inner) 2.211(4) Å; cf. Ru–C(outer) 2.236, 2.324(4) and 2.214(7), 2.258(8) Å; Ru–C(inner) 2.194(3) and 2.130(8) Å in  $\text{RuCl}(\eta^3\text{-C}_5\text{H}_7)(\text{PMe}_3)_3$  [4] and  $\text{Ru}(\eta\text{-C}_3\text{H}_5)(\text{NO})(\text{PPh}_3)_2$  [5], respectively] and two CO groups. The mononuclear part of this complex is thus a phosphine-substituted  $\text{RuCl}(\text{CO})_3(\eta\text{-C}_3\text{H}_5)$  system, the P and Cl donors taking up *cisoid* positions about the pseudo-octahedral Ru centre.

The chlorine ligand is involved in a bridging three-electron interaction with Ru(1)–Ru(2) and the addition of the allyl group formally adds three electrons to the

Table 1

Selected bond distances (Å) for 2-Cl

Ru(2)–Ru(3)	2.785(1)	Ru(1)–C(3)	2.218(5)
Ru(2)–Ru(5)	2.891(1)	Ru(1)–C(4)	2.211(4)
Ru(3)–Ru(4)	2.795(1)	Ru(1)–C(5)	2.273(5)
Ru(3)–Ru(5)	2.887(1)	Ru(2)–C(2)	2.214(4)
Ru(4)–Ru(5)	2.759(1)	Ru(3)–C(2)	2.015(3)
Ru(1)–P(1)	2.358(1)	Ru(4)–C(1)	2.150(4)
Ru(2)–P(2)	2.287(1)	Ru(4)–C(2)	2.323(4)
Ru(3)–P(2)	2.266(1)	Ru(5)–C(1)	2.278(3)
Ru(1)–Cl(1)	2.455(1)	Ru(5)–C(2)	2.106(4)
Ru(2)–Cl(1)	2.559(1)	P(1)–C(1)	1.769(3)
		C(1)–C(2)	1.355(5)
Ru–CO:	range, 1.850(5)–1.925(4), av. 1.898 Å		
C–O:	range, 1.125(6)–1.151(6), av. 1.14 Å		
P–C(Ph):	range, 1.808(4)–1.831(3), av. 1.818 Å		

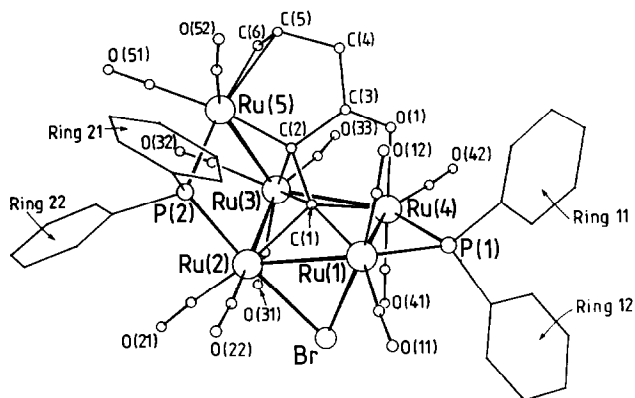


Fig. 2. Computer-generated plot of a molecule of  $\text{Ru}_5\{\mu_5\text{-CCC(O)CH}_2\text{CH=CH}_2\}(\mu\text{-PPh}_2)_2(\mu\text{-Br})(\text{CO})_{11}$  (3-Br), showing atom numbering scheme.

cluster. Compared with **1**, a carbonyl ligand has also been lost, the net change being the addition of four electrons, resulting in the cleavage of two M–M bonds.

#### *Molecular structure of $\text{Ru}_5\{\mu_5\text{-CCC(O)CH}_2\text{CH=CH}_2\}(\mu\text{-PPh}_2)_2(\mu\text{-Br})(\text{CO})_{11}$ (3-Br)*

Figure 2 is a computer-generated plot of **3-Br** and selected bond parameters are given in Table 2. The metal core is a metallated  $\text{Ru}_4$  rhombus [Ru–Ru 2.828–2.937(4) Å], of which atoms Ru(1)–Ru(4) are asymmetrically attached to C(1) [Ru–C 2.06–2.32(4) Å]. Two of the edges of the square are bridged by a  $\text{PPh}_2$  group [Ru(1)–P(2) 2.296, Ru(4)–P(1) 2.290(9) Å] and the Br atom [Ru(1)–Br 2.581, Ru(2)–Br 2.620(4) Å], while the second  $\text{PPh}_2$  group bridges the non-bonded Ru(2)···Ru(5) vector [Ru(2)–P(2) 2.312, Ru(5)–P(2) 2.362(9) Å]. Two CO ligands are bonded to each Ru except Ru(3), which has three. A semi-bridging interaction is found for CO(32) situated between Ru(3) and Ru(5) [Ru(3)C(32)O(32) 163(3)°, Ru(3)–C(32) 1.91(3) Å, Ru(5)–C(32) 2.70 Å].

An acyclic ligand composed of the allyl group, a CO molecule and the  $\text{C}_2$  fragment is attached to four of the metal atoms. Of the carbons, C(1) forms strong bonds to Ru(1), Ru(2) and Ru(3) [2.06–2.12(4) Å]; the interaction with Ru(4) is much weaker [2.32(4) Å]. Atom C(2) also forms strong bonds with Ru(3) and Ru(5) [2.13, 2.07(4) Å, respectively]. The distance between the C(1) carbon and the least-squares plane through Ru(1)Ru(2)Ru(3)Ru(4) (deviations 0.20, –0.19, 0.19, –0.20 Å, resp.) is 0.74 Å. The C(1)–C(2) system is best described as a  $\mu_5$ -acetylide, although the strong bonding of C(1) to three of the four Ru atoms in the rhombus shows that it has some methylidyne character [6]. Atom C(2) is also bonded to the four carbon unit C(3)–C(4)–C(5)–C(6), of which the C(5)–C(6) double bond is  $\pi$ -bonded to Ru(5) [C(5)–C(6) 1.33, Ru(5)–C(5), C(6) 2.38, 2.42(3) Å]; these distances are very long (cf. values of 2.24(2) Å found in  $\text{Ru}_3(\mu\text{-CH}_2=\text{CHC}_6\text{H}_4\text{PPh}_2)(\text{CO})_{10}$  [7]); for a closer approach, the C(3)–C(4)–C(5) angle would be less than the 107° found here. Atoms C(2), Ru(5), C(1) and C(3) are coplanar (sum of angles around C(2) is 359.9°).

Within the organic ligand, the C–C distances suggest significant double bond character for C(1)–C(2), C(2)–C(3) and C(5)–C(6) [1.47(5), 1.42(4), 1.34(4) Å,

Table 2

Selected bond distances (Å) and angles (deg.) for 3-Br

Ru(1)–Ru(2)	2.828(4)	Ru(1)–Ru(4)	2.849(4)
Ru(2)–Ru(3)	2.937(4)	Ru(3)–Ru(5)	2.889(4)
Ru(3)–Ru(4)	2.870(4)	Ru(2)–P(1)	2.312(9)
Ru(5)–P(1)	2.362(9)	Ru(1)–P(2)	2.296(9)
Ru(4)–P(2)	2.290(9)	Ru(1)–Br	2.581(4)
Ru(2)–Br	2.260(4)	Ru(1)–C(1)	2.08(4)
Ru(2)–C(1)	2.06(4)	Ru(3)–C(1)	2.12(4)
Ru(4)–C(1)	2.32(4)	Ru(3)–C(2)	2.13(3)
Ru(5)–C(2)	2.07(3)	Ru(5)–C(5)	2.38(3)
Ru(5)–C(6)	2.42(3)	Ru(4)–O(1)	2.11(2)
C(1)–C(2)	1.47(5)	C(2)–C(3)	1.42(4)
C(3)–C(4)	1.55(5)	C(4)–C(5)	1.58(4)
C(5)–C(6)	1.34(4)	C(3)–O(1)	1.26(3)
Ru(2)Ru(1)Ru(4)	89.2(1)	Ru(1)Ru(2)Ru(3)	89.5(1)
Ru(2)–Ru(3)–Ru(4)	86.7(1)	Ru(4)Ru(3)Ru(5)	114.7(1)
Ru(2)Ru(3)Ru(5)	82.1(1)	Ru(1)Ru(4)Ru(3)	90.4(1)
Ru(2)P(1)Ru(5)	109.8(3)	Ru(1)P(2)Ru(4)	76.8(3)
Ru(1)C(1)Ru(3)	150(2)	Ru(2)C(1)Ru(4)	131(2)
Ru(3)C(2)Ru(5)	87(1)	C(1)Ru(3)C(2)	40(1)
Ru(5)C(5)C(4)	107(2)	C(5)Ru(5)C(6)	32(1)
Ru(4)O(1)C(3)	112(2)	Ru(1)BrRu(2)	65.9(1)
C(1)C(2)C(3)	117(3)	C(2)C(3)C(4)	122(3)
C(3)C(4)C(5)	107(3)	C(4)C(5)C(6)	125(3)
Ru–CO:	range 1.77(4)–1.95(4), av. 1.86 Å		
C–O:	range 1.13(4)–1.20(4), av. 1.16 Å		
P–C(Ph):	range 1.81(2)–1.86(2), av. 1.84 Å		

resp.], while C(3)–C(4) and C(4)–C(5) are normal single bonds [1.55(5), 1.58(4) Å, resp.]. The oxygen atom is attached to C(3) and forms a donor bond to Ru(4) [Ru(4)–O(1) 2.11(2) Å; Ru(4)–O(1)–C(4) 112(2)°]; these values are comparable with those found in Ru<sub>2</sub>(μ-H)(μ-bza)(CO)<sub>6</sub> (bzaH = benzylideneacetone) [2.103(7) Å and 111.0(6)°] [8].

The bromine ligand is involved in a bridging three-electron interaction with Ru(1)–Ru(2) and the allyl group formally provides two electrons to the cluster. The C<sub>2</sub> unit contributes the same number of electrons as in **1**, but a PPh<sub>2</sub> group has gone from a 2e to 3e donor after cleavage of the P–C bond. The CO incorporated into the ligand is still a two-electron donor, but now through the oxygen atom. Compared with **1**, a carbonyl ligand has also been lost, the net change being the addition of four electrons, resulting in the cleavage of two M–M bonds. Cluster 3-Br is an 80-electron, 10-SEP compound, this assessment being obtained within PSEP theory by condensing the electron counts for a four-membered ring and a binuclear unit (i.e. 64 + 34 – 18 = 80).

### Spectroscopic properties

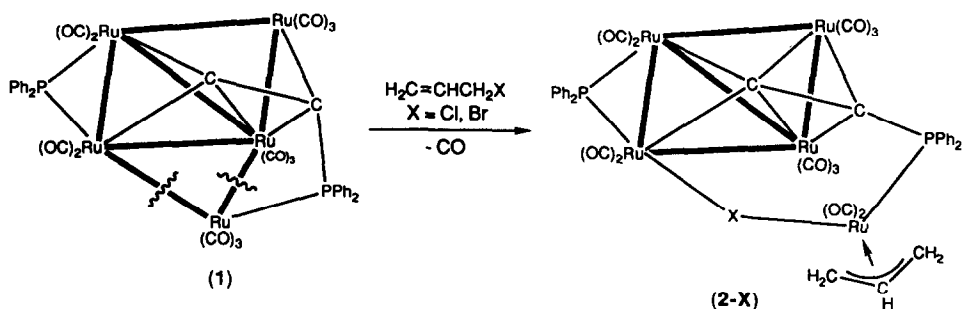
The IR spectra for 3-Cl and 3-Br were very similar, and suggest that the two complexes have related structures, but with a μ-Cl in 3-Cl replacing the μ-Br in 3-Br. Very weak bands at 1535 cm<sup>-1</sup> (3-Cl) and 1534 cm<sup>-1</sup> (3-Br) were assigned to the

coordinated ketonic carbonyls; a band was found at  $1588\text{ cm}^{-1}$  for a similar group in  $\text{Ru}_4\{\mu_4\text{-}\eta^2\text{-O, P-C}_5\text{H}_4\text{O(PPh}_2)\}\mu\text{-PPh}_2\text{(CO)}_{11}$  [2]. The IR spectra for **2-Cl** and **2-Br** are also closely related. No evidence was found for ketonic or bridging CO groups in these spectra. Molecular ions were found in the FAB mass spectra at  $m/z$  1313 for **2-Cl** and **3-Cl**, and at  $m/z$  1357 for **2-Br** and **3-Br**. Complexes of type **2** fragmented by loss of only seven carbonyl groups; an ion  $[\text{M} - \text{CO} - \text{allyl}]^+$  was also found in the latter spectra. Ions formed by loss of up to 12 CO groups were found in the mass spectra of complexes **3**.

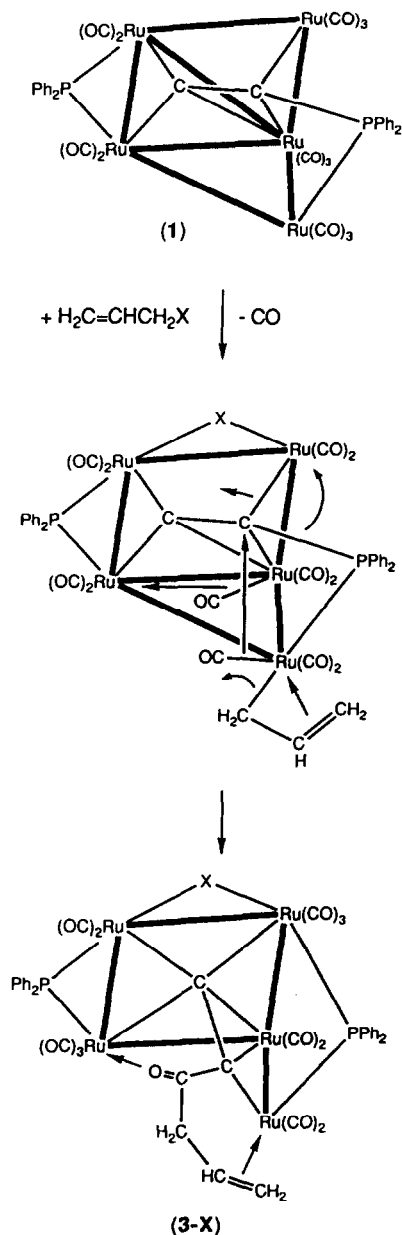
The  $^1\text{H}$  NMR spectra of complexes **3** were similar, the inequivalent protons of the allyl group giving rise to a five-resonance pattern. The low field multiplet was assigned to the proton on C(5), the three doublets (in order of increasing field) to the *syn* proton on C(4), the *anti* proton on C(4) and the *syn* proton on C(6), while the doublet of doublets was assigned to the *anti* proton on C(6) on the basis of coupling constant and chemical shift data. A complex pattern of ten resonances was observed for the allyl protons in both **2-Cl** and **2-Br**. Two multiplets were found at approximately  $\delta$  4.4. Of the other eight signals, two doublets showed H–H coupling, two doublets showed P–H coupling, two doublets of doublets showed both H–H and P–H coupling, and two multiplets were unresolved. The intensity of these resonances suggested the presence of two isomers of each complex in solution, in a ratio of ca 2 : 1 for **2-Cl** and ca 1 : 1 for **2-Br** (in  $\text{C}_6\text{D}_6$ ). The chemical shifts of the protons were quite different from those in the orange complexes and are consistent with the solid state structural feature of an olefinic  $\eta^2\text{-CH}_2=\text{CHCH}_2$  interaction with a phosphorus-bound ruthenium.

The  $^{31}\text{P}$  resonances of the  $\mu\text{-PPh}_2$  groups in the two isomers of **2** were at  $\delta$  65.5, 60.8 (**2-Cl**) and 67.2, 60.9 (**2-Br**); for **3**, the signals for the  $\text{PPh}_2$  groups bridging the non-bonded  $\text{Ru}(2) \cdots \text{Ru}(5)$  vector in **3-Cl** and **3-Br** appeared at  $\delta$  54.9 and 57.3, respectively. Signals for the  $\mu\text{-PPh}_2$  groups bridging Ru–Ru bonds were found in the range  $\delta$  249.8–271.3 for each of the complexes.

The formation of **2** is shown in Scheme 2. Coordination of allyl halide to Ru(1) in **1** is followed by its oxidative addition across the Ru(2)–Ru(5) bond and loss of CO. This results in Ru(5) becoming detached from the rest of the cluster, being attached only by the bridging halide and the P atom of the tertiary phosphine. The formation of **3** is not so straightforward, but probably involves addition of the allyl halide to Ru(5), migration of the  $\eta$ -allyl group to CO and addition of the resulting acyl to the  $\text{C}_2$  unit with concomitant cleavage of the C(*sp*)–P(1) bond (Scheme 3). Atom C(2)



Scheme 2



Scheme 3

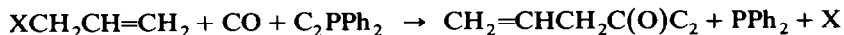
becomes tightly bonded to the Ru<sub>4</sub> cluster at this stage, with P(1) moving to Ru(4); the halide atom bridges Ru(1)–Ru(4) vector. It is not possible to determine the precise order in which these transformations occur.

### Conclusions

Reactions between 1 and allyl halides have given two types of complex: 2, in which an RuCl(CO)<sub>3</sub>(η-C<sub>3</sub>H<sub>5</sub>) moiety is attached to an Ru<sub>4</sub> cluster via Cl and PR<sub>3</sub>



bridges, and **3**, which contains a novel  $\mu_5$  ligand formed from one CO, the C<sub>2</sub> and allyl groups of the reactants:



## Experimental

### General conditions

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

**Reagents:** Complex **1** was prepared as previously described [9]. Me<sub>3</sub>NO · 2H<sub>2</sub>O (Aldrich) was dehydrated by sublimation (100 °C/0.1 mm Hg).

**Instrumentation:** IR: Perkin-Elmer 1700X FT IR; 683 double beam, NaCl optics; NMR: Bruker CXP300 (<sup>1</sup>H NMR at 300.13 MHz, <sup>13</sup>C NMR at 75.47 MHz, <sup>31</sup>P NMR at 121.49 MHz); <sup>31</sup>P chemical shifts are relative to external 85% H<sub>3</sub>PO<sub>4</sub>. Spectra recorded in non-deuterated solvents used an external concentric tube containing D<sub>2</sub>O for field lock. FAB MS: VG ZAB 2HF (FAB MS, using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

### Reaction between **1** and allyl chloride

Allyl chloride (250 mg, 3.29 mmol) and **1** (50 mg, 0.040 mmol) were refluxed in CH<sub>2</sub>Cl<sub>2</sub> (30 mL) for 20 h. After cooling, the solvent was removed under reduced pressure and the residue was purified by TLC (petroleum spirit/CH<sub>2</sub>Cl<sub>2</sub> 3/2). Two bands were collected: the first brown band (*R<sub>f</sub>* 0.50) was crystallised (CH<sub>2</sub>Cl<sub>2</sub>/MeOH) by slow evaporation to give light brown crystals of Ru<sub>4</sub>{ $\mu_4$ -C<sub>2</sub>PPh<sub>2</sub>Ru(CO)<sub>2</sub>( $\eta$ -C<sub>3</sub>H<sub>5</sub>)( $\mu$ -Cl)}( $\mu$ -PPh<sub>2</sub>)(CO)<sub>10</sub> (**2-Cl**) (22 mg, 42%), m.p. 225–226 °C. Anal. Found: C, 37.14; H, 1.94; *M<sub>r</sub>*, 1312 (mass spectrometry, 1313 = [*M* + H]<sup>+</sup>). C<sub>41</sub>H<sub>25</sub>ClO<sub>12</sub>P<sub>2</sub>Ru<sub>5</sub> calcd.: C, 37.52; H, 1.92%; *M<sub>r</sub>*, 1312. IR (cyclohexane):  $\nu$ (CO) 2069w, 2058(sh), 2049vs, 2032(sh), 2020(sh), 2015s, 2005m, 1991s, 1980m, 1956vw, 1942vw cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>; signals for two isomers marked \*, †; ratio \*: † = 2:1):  $\delta$  8.1–6.6 (m, 20H, Ph); 4.52 (m, CH); 3.87 (d, *J*(HH) = 7.6 Hz, CH<sub>2</sub>†); 3.55 (m, CH<sub>2</sub>†); 3.28 (m, 1H, CH<sub>2</sub>\*); 3.15 (dd, *J*(HP) = 13.0, *J*(HH) = 5.0 Hz, CH<sub>2</sub>\*); 3.02 (dd, *J*(HP) = 13.0, *J*(HH) = 5.0 Hz, CH<sub>2</sub>†); 2.21 (d, *J*(HP) = 12.9 Hz, CH<sub>2</sub>†); 2.12 (d, *J*(HH) = 8.0 Hz, CH<sub>2</sub>\*); 1.87 (d, *J*(HP) = 13.0 Hz, CH<sub>2</sub>\*). FAB MS: 1313, [*M*]<sup>+</sup>; 1285–1117, [*M* - *n*CO]<sup>+</sup> (*n* = 1–7); 1244, [*M* - CO - allyl]<sup>+</sup>.

A second band (*R<sub>f</sub>* 0.37, orange) was collected and crystallised (CH<sub>2</sub>Cl<sub>2</sub>/petroleum spirit) giving orange crystals of Ru<sub>5</sub>{ $\mu_5$ -CCC(O)CH<sub>2</sub>CH=CH<sub>2</sub>}( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>( $\mu$ -Cl)(CO)<sub>11</sub> (**3-Cl**) (10 mg, 19%), m.p. 200 °C (dec.). Anal. Found: C, 37.39; H, 2.09; *M<sub>r</sub>*, 1312 (mass spectrometry, 1313 = [*M* + H]<sup>+</sup>). C<sub>41</sub>H<sub>25</sub>ClO<sub>12</sub>P<sub>2</sub>Ru<sub>5</sub> calcd.: C, 37.52; H, 1.92%; *M<sub>r</sub>*, 1312. IR (cyclohexane):  $\nu$ (CO) 2060m, 2043(sh), 2038s, 2032s, 2026(sh), 1992s, 1987(sh), 1975w, 1951vw, 1928vw, 1535vw cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>):  $\delta$  8.2–6.7 (m, 20H, Ph); 3.57 (m, 1H, CH); 3.36 (d, *J*(HH) = 8.7 Hz, 1H, CH<sub>2</sub>); 2.92 (d, *J*(HP) = 14.9 Hz, 1H, CH<sub>2</sub>); 2.23 (d, *J*(HP) = 19.3 Hz, 1H,

CH<sub>2</sub>); 1.96 (dd,  $J(\text{HP}) = 19.3$ ,  $J(\text{HH}) = 8.0$  Hz, 1H, CH<sub>2</sub>). FAB MS: 1313, [M]<sup>+</sup>; 1285–977, [M – nCO]<sup>+</sup> ( $n = 1–12$ ).

#### Reaction between 1 and allyl bromide

Allyl bromide (500 mg, 4.13 mmol) and 1 (130 mg, 0.10 mol) were heated in refluxing CH<sub>2</sub>Cl<sub>2</sub> (20 mL) for 24 h. After cooling, the solvent was removed under reduced pressure and the residue was purified by TLC (petroleum spirit/CH<sub>2</sub>Cl<sub>2</sub> 3/2). Two bands were collected: the major brown band ( $R_f$  0.60) was rechromatographed (TLC: petroleum spirit/Et<sub>2</sub>O/CH<sub>2</sub>Cl<sub>2</sub> 16/2/1) to give a band ( $R_f$  0.47) which was precipitated from CH<sub>2</sub>Cl<sub>2</sub>/cyclohexane as a brown powder of Ru<sub>4</sub>{μ<sub>4</sub>-C<sub>2</sub>PPh<sub>2</sub>Ru(CO)<sub>2</sub>(η-C<sub>3</sub>H<sub>5</sub>)(μ-Br)}(μ-PPh<sub>2</sub>)(CO)<sub>10</sub>·0.5C<sub>6</sub>H<sub>12</sub> (2-Br) (24 mg, 18%), m.p. 145–147 °C. Anal. Found: C, 37.58; H, 2.30;  $M_r$ , 1357 (mass spectrometry). C<sub>41</sub>H<sub>25</sub>BrO<sub>12</sub>P<sub>2</sub>Ru<sub>5</sub>·0.5C<sub>6</sub>H<sub>12</sub> calcd.: C, 37.78; H, 2.23%;  $M_r$  (unsolvated), 1357. IR (cyclohexane): ν(CO) 2068w, 2056(sh), 2049vs, 2016(sh), 2014s, 2004w, 1992m, 1980w, 1956vw cm<sup>-1</sup>. <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>; signals for two isomers marked \*, †; ratio \*: † = 1 : 1): δ 7.9–6.8 (m, 20H, Ph); 4.45 (m, CH\*); 4.31 (m, CH†); 3.83 (d,  $J(\text{HH}) = 7.5$  Hz, CH<sub>2</sub>†); 3.44 (m, CH<sub>2</sub>†); 3.29 (dd,  $J(\text{HP}) = 13.1$ ,  $J(\text{HH}) = 5.2$ , CH<sub>2</sub>\*); 3.11 (dd + m,  $J(\text{HP}) = 12.2$ ,  $J(\text{HH}) = 5.4$  Hz, CH<sub>2</sub>\*†); 2.32 (d,  $J(\text{HP}) = 13.1$  Hz, CH<sub>2</sub>†); 2.15 (d,  $J(\text{HH}) = 6.3$  Hz, CH<sub>2</sub>\*); 1.97 (d,  $J(\text{HP}) = 13.1$  Hz,

Table 3

Crystal data and refinement details for 2-Cl and 3-Br

Compound	2-Cl	3-Br
Formula	C <sub>41</sub> H <sub>25</sub> ClO <sub>12</sub> P <sub>2</sub> Ru <sub>5</sub>	C <sub>41</sub> H <sub>25</sub> BrO <sub>12</sub> P <sub>2</sub> Ru <sub>5</sub> ·0.5CH <sub>2</sub> Cl <sub>2</sub>
MW	1312.4	1399.32
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$
<i>a</i> , Å	9.990(2)	12.92(1)
<i>b</i> , Å	11.789(2)	18.66(1)
<i>c</i> , Å	20.100(5)	19.13(1)
<i>α</i> , deg.	96.37(2)	90
<i>β</i> , deg.	96.11(2)	106.33(8)
<i>γ</i> , deg.	106.32(2)	90
<i>U</i> , Å <sup>3</sup>	2234.4(8)	4426(6)
<i>T</i> , °C	–110	–110
<i>Z</i>	2	4
<i>D<sub>c</sub></i> , g cm <sup>-3</sup>	1.95	2.10
<i>F</i> (000)	1268	2692
Crystal size, mm	0.36 × 0.22 × 0.21	0.23 × 0.19 × 0.11
<i>A</i> * (min, max)	0.739, 0.836	0.670, 0.743
<i>μ</i> , cm <sup>-1</sup>	18	28
<i>θ</i> limits, deg.	1.5–24	2–20
No. data collected	7234	4675
No. unique data	7007	4101
Criterion used	$I > 2\sigma(I)$	$I > 2.5\sigma(I)$
No. data used	6055	2043
<i>g</i>	0.000144	0.00198
<i>R</i>	0.0256	0.0649
<i>R<sub>w</sub></i>	0.0250	0.0643

Table 4

Non-hydrogen atomic coordinates for  $\text{Ru}_4\{\mu_4\text{-C}_2\text{PPh}_2\text{Ru}(\text{CO})_2(\eta\text{-C}_3\text{H}_5)(\mu\text{-Cl})\}(\mu\text{-PPh}_2)(\text{CO})_{10}$  (2-Cl)

Atom	x	y	z	$U_{\text{eq}}$
Ru(1)	0.12415(3)	-0.18890(3)	0.05857(2)	0.019
Ru(2)	0.23781(3)	0.10708(3)	0.24738(2)	0.016
Ru(3)	0.40037(3)	0.05700(3)	0.35576(2)	0.018
Ru(4)	0.51259(3)	-0.11757(3)	0.29879(2)	0.018
Ru(5)	0.50783(3)	0.06904(3)	0.22790(2)	0.016
P(1)	0.2559(1)	-0.2359(1)	0.15070(5)	0.017
P(2)	0.3339(1)	0.2247(1)	0.34920(5)	0.019
Cl(1)	0.1000(1)	-0.0233(1)	0.13723(5)	0.027
C(1)	0.3557(4)	-0.1195(3)	0.2157(2)	0.017
C(2)	0.3305(4)	-0.0400(3)	0.2632(2)	0.016
C(3)	-0.0853(5)	-0.2910(4)	0.0826(3)	0.034
C(4)	-0.1012(5)	-0.2738(4)	0.0145(3)	0.035
C(5)	-0.0642(5)	-0.1615(4)	-0.0056(3)	0.033
C(11)	0.1505(5)	-0.3142(4)	0.0026(2)	0.036
C(12)	0.2712(5)	-0.0714(4)	0.0268(2)	0.029
C(21)	0.2063(4)	0.2330(4)	0.2033(2)	0.025
C(22)	0.0564(5)	0.0707(4)	0.2749(2)	0.027
C(31)	0.2733(5)	-0.0368(4)	0.4039(2)	0.031
C(32)	0.5380(5)	0.1288(4)	0.4324(2)	0.033
C(41)	0.6593(5)	-0.0554(4)	0.3749(2)	0.029
C(42)	0.4234(5)	-0.2556(4)	0.3375(2)	0.029
C(43)	0.6312(4)	-0.1898(3)	0.2513(2)	0.022
C(51)	0.6483(5)	0.1909(4)	0.2894(2)	0.025
C(52)	0.4586(5)	0.1623(4)	0.1620(2)	0.026
C(53)	0.6438(5)	0.0231(4)	0.1784(2)	0.025
O(11)	0.1670(4)	-0.3919(3)	-0.0319(2)	0.057
O(12)	0.3535(4)	-0.0010(3)	0.0061(2)	0.045
O(21)	0.1893(4)	0.3095(3)	0.1762(2)	0.039
O(22)	-0.0515(3)	0.0473(3)	0.2918(2)	0.045
O(31)	0.1873(4)	-0.1007(3)	0.4269(2)	0.047
O(32)	0.6199(4)	0.1744(3)	0.4790(2)	0.060
O(41)	0.7504(4)	-0.0237(3)	0.4195(2)	0.049
O(42)	0.3701(4)	-0.3363(3)	0.3620(2)	0.045
O(43)	0.7111(3)	-0.2263(3)	0.2263(2)	0.031
O(51)	0.7406(3)	0.2611(3)	0.3227(2)	0.034
O(52)	0.4489(3)	0.2204(3)	0.1204(2)	0.036
O(53)	0.7261(3)	0.0004(3)	0.1479(2)	0.040
C(111)	0.4640(3)	-0.2657(2)	0.0765(1)	0.023
C(112)	0.5591(3)	-0.3224(2)	0.0525(1)	0.030
C(113)	0.5724(3)	-0.4255(2)	0.0771(1)	0.029
C(114)	0.4905(3)	-0.4717(2)	0.1257(1)	0.026
C(115)	0.3954(3)	-0.4150(2)	0.1496(1)	0.023
C(116)	0.3822(3)	-0.3119(2)	0.1250(1)	0.019
C(121)	0.1027(3)	-0.2960(2)	0.2579(1)	0.030
C(122)	0.0049(3)	-0.3726(2)	0.2902(1)	0.038
C(123)	-0.0577(3)	-0.4916(2)	0.2611(1)	0.037
C(124)	-0.0225(3)	-0.5339(2)	0.1997(2)	0.034
C(125)	0.0754(3)	-0.4573(2)	0.1674(1)	0.027
C(126)	0.1380(3)	-0.3383(2)	0.1965(1)	0.020
C(211)	0.1491(3)	0.1970(2)	0.4458(1)	0.043
C(212)	0.0442(3)	0.2251(2)	0.4797(1)	0.065
C(213)	-0.0010(3)	0.3233(2)	0.4664(1)	0.063
C(214)	0.0586(3)	0.3933(2)	0.4192(1)	0.056

Table 4 (continued)

Atom	x	y	z	$U_{eq}$
C(215)	0.1635(3)	0.3651(2)	0.3854(1)	0.037
C(216)	0.2088(3)	0.2669(2)	0.39879(1)	0.027
C(221)	0.5355(3)	0.4249(2)	0.4193(1)	0.027
C(222)	0.6429(3)	0.5334(2)	0.4271(1)	0.032
C(223)	0.6836(3)	0.5849(2)	0.3703(1)	0.029
C(224)	0.6170(3)	0.5279(2)	0.3058(1)	0.027
C(225)	0.5097(3)	0.4194(2)	0.2980(1)	0.024
C(226)	0.4689(3)	0.3679(2)	0.3547(1)	0.019
H(31)	-0.106(5)	-0.239(4)	0.115(2)	0.039
H(32)	-0.101(5)	-0.376(4)	0.94(2)	0.039
H(41)	-0.121(5)	-0.346(4)	-0.025(2)	0.039
H(51)	-0.074(5)	-0.100(4)	0.025(2)	0.039
H(52)	-0.056(5)	-0.146(4)	-0.048(2)	0.039

$\text{CH}_2^*$ ). FAB MS: 1357,  $[M]^+$ ; 1329–1161,  $[M - n\text{CO}]^+$  ( $n = 1-12$ ); 1288–1036,  $[M - n\text{CO} - \text{C}_3\text{H}_5]^+$  ( $n = 1-10$ ).

The other minor band ( $R_f$  0.40, orange) was collected and crystallised ( $\text{CH}_2\text{Cl}_2/\text{petroleum spirit}$ ) giving orange cubes of  $\text{Ru}_5\{\mu_5\text{-CCC(O)CH}_2\text{CH=CH}_2\}(\mu\text{-PPh}_2)_2(\mu\text{-Br})(\text{CO})_{11}(\text{3-Br})$  (7 mg, 5%), m.p. 230–232°C. Anal. Found: C, 35.53; H, 1.96;  $M_r$ , 1357 (mass spectrometry).  $\text{C}_{41}\text{H}_{25}\text{BrO}_{12}\text{P}_2\text{Ru}_5 \cdot 0.5\text{CH}_2\text{Cl}_2$  calcd: C, 35.62; H, 1.87%;  $M_r$  (unsolvate), 1357. IR (cyclohexane):  $\nu(\text{CO})$  2059w, 2038s, 2031s, 2026(sh), 1995(sh), 1989m, 1975w, 1955vs, 1925vw  $\text{cm}^{-1}$ . IR ( $\text{CH}_2\text{Cl}_2$ ):  $\nu(\text{CO})$  1534vw  $\text{cm}^{-1}$ .  $^1\text{H NMR}$  ( $\text{C}_6\text{D}_6$ ):  $\delta$  8.3–6.9 (m, 20H, Ph); 5.26 (s, 1H,  $\text{CH}_2\text{Cl}_2$ ); 3.56 (m, 1H, CH); 3.35 (d,  $J(\text{HH}) = 8.9$  Hz, 1H,  $\text{CH}_2$ ); 2.94 (d,  $J(\text{HP}) = 13.9$  Hz, 1H,  $\text{CH}_2$ ); 2.24 (d,  $J(\text{HP}) = 19.4$  Hz, 1H,  $\text{CH}_2$ ); 1.96 (dd,  $J(\text{HP}) = 19.2$ ,  $J(\text{HH}) = 7.8$  Hz, 1H,  $\text{CH}_2$ ). FAB MS: 1357,  $[M]^+$ ; 1329–1021,  $[M - n\text{CO}]^+$  ( $n = 1-12$ ). A large base-line was also observed in the TLC separation.

No change was observed when either 2-Br or 3-Br was heated in refluxing  $\text{CH}_2\text{Cl}_2$  for 48 h.

### Crystallography

Both complexes formed dark red crystals from toluene/hexane (2-Cl) or  $\text{CH}_2\text{Cl}_2/\text{hexane}$  (3-Br); the quality of the latter was not ideal giving wide peak profiles. The space groups were defined by precession photography, and accurate cell dimensions and intensity data were collected with a Nicolet P3 diffractometer using  $\omega$ -scans with monochromated  $\text{Mo-K}\alpha$  X-radiation ( $\lambda = 0.7107$  Å). The data were corrected for absorption using an empirical  $\theta$ -scan technique.

The structures were solved by direct methods and routinely developed and refined. In the final cycles of full-matrix least squares refinement all non-hydrogen atoms (in 2-Cl), but only the Ru and Br atoms (in 3-Br) were assigned anisotropic temperature factors. Other atoms were treated isotropically. The phenyl groups were treated as rigid rings ( $D(\text{C-H})$  1.40 Å); for 2-Cl only, the aryl H atoms were included in calculated positions with a common tied temperature factor. Also in 2-Cl, the allyl H atoms were located as the highest peaks in the penultimate difference map and were included in the refinement with unrestricted positional

Table 5

Non-hydrogen atomic coordinates for  $\text{Ru}_5(\mu_5\text{-CCC(O)CH}_2\text{CH=CH}_2)(\mu\text{-PPh}_2)_2(\mu\text{-Br})(\text{CO})_{11}$  (**3-Br**)

Atom	x	y	z	Atom	x	y	z
Ru(1)	0.0324(2)	0.1703(1)	0.9075(1)	C(42)	0.228(3)	0.185(2)	0.740(2)
Ru(2)	-0.1443(2)	0.0899(1)	0.8233(1)	O(42)	0.292(2)	0.196(2)	0.708(1)
Ru(3)	-0.0808(2)	0.1262(1)	0.6918(1)	C(51)	-0.382(3)	0.218(2)	0.670(2)
Ru(4)	0.1228(2)	0.1692(2)	0.7878(1)	O(51)	-0.463(2)	0.211(1)	0.561(1)
Ru(5)	-0.2514(2)	0.2303(1)	0.6749(1)	C(52)	-0.299(3)	0.307(2)	0.712(2)
Br(1)	0.0372(3)	0.0323(2)	0.8994(2)	O(52)	-0.325(2)	0.359(1)	0.738(1)
P(1)	0.2063(7)	0.1953(5)	0.9074(5)	C(111)	0.259(2)	0.337(1)	0.8866(8)
P(2)	-0.2948(7)	0.1548(5)	0.7617(5)	C(112)	0.289(2)	0.407(1)	0.9095(8)
C(1)	-0.052(3)	0.170(2)	0.798(2)	C(113)	0.310(2)	0.425(1)	0.9830(8)
C(2)	-0.096(3)	0.226(2)	0.743(2)	C(114)	0.302(2)	0.373(1)	1.0336(8)
C(3)	-0.026(2)	0.282(2)	0.735(2)	C(115)	0.273(2)	0.303(1)	1.0107(8)
C(4)	-0.068(3)	0.352(2)	0.693(2)	C(116)	0.252(2)	0.285(1)	0.9372(8)
C(5)	-0.176(2)	0.333(2)	0.634(2)	C(121)	0.418(2)	0.150(1)	0.944(1)
C(6)	-0.186(3)	0.284(2)	0.581(2)	C(122)	0.510(2)	0.116(1)	0.988(1)
O(1)	0.075(1)	0.276(1)	0.7591(9)	C(123)	0.503(2)	0.075(1)	1.047(1)
C(11)	0.045(3)	0.161(20)	1.011(2)	C(124)	0.405(2)	0.068(1)	1.063(1)
O(11)	0.05792	0.159(1)	1.071(1)	C(125)	0.313(2)	0.101(1)	1.019(1)
C(12)	0.006(3)	0.266(2)	0.909(2)	C(126)	0.320(2)	0.142(1)	0.959(1)
O(12)	-0.016(2)	0.325(1)	0.911(1)	C(211)	-0.283(1)	0.246(1)	0.882(1)
C(21)	-0.216(2)	0.002(2)	0.792(2)	C(212)	-0.322(1)	0.300(1)	0.918(1)
O(21)	-0.248(2)	-0.055(1)	0.774(1)	C(213)	-0.429(1)	0.321(1)	0.894(1)
C(22)	-0.188(3)	0.089(2)	0.907(2)	C(214)	-0.498(1)	0.290(1)	0.832(1)
O(22)	-0.221(2)	0.085(1)	0.959(1)	C(215)	-0.459(1)	0.236(1)	0.795(1)
C(31)	-0.054(3)	0.025(2)	0.698(2)	C(216)	-0.351(1)	0.214(1)	0.820(1)
O(31)	-0.039(2)	-0.034(1)	0.691(1)	C(221)	-0.428(2)	0.061(1)	0.663(1)
C(32)	-0.204(2)	0.112(2)	0.610(2)	C(222)	-0.507(2)	0.008(1)	0.640(1)
O(32)	-0.261(2)	0.094(1)	0.557(1)	C(223)	-0.567(2)	-0.013(1)	0.686(1)
C(33)	0.007(3)	0.155(2)	0.634(2)	C(224)	-0.549(2)	0.018(1)	0.755(1)
O(33)	0.055(2)	0.164(1)	0.590(1)	C(225)	-0.470(2)	0.071(1)	0.777(1)
C(41)	0.170(3)	0.080(2)	0.801(2)	C(226)	-0.409(2)	0.092(1)	0.731(1)
O(41)	0.204(2)	0.020(1)	0.801(1)	Cl(1)	0.934(1)	0.002(1)	0.4953(9)
				Cl(2)	0.850(2)	0.009(1)	0.402(1)

parameters and with a common tied temperature factor. In **3-Br**, the penultimate difference map showed two peaks with significant electron density and these were included as half-weighted Cl atoms from a solvent molecule in the lattice. There were no shifts in the final cycles greater than  $0.5\sigma$  (**2-Cl**) or  $0.3\sigma$  (**3-Br**), and the final difference maps showed no features larger than  $0.6$  (**2-Cl**) or  $1.0 e \text{ \AA}^{-3}$  (**3-Br**). All calculations were performed using the SHELX programmes [10]; for  $R_w$ ,  $w = [\sigma^2(F) + gF^2]^{-1}$ . Crystal data and refinement details are summarised in Table 3. Non-hydrogen fractional atomic coordinates are given in Tables 4 (**2-Cl**) and 5 (**3-Br**). Tables of anisotropic thermal parameters and final structure factors are available from the authors.

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