

The interaction of unsaturated C₈-ring systems with ruthenium carbonyl clusters

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Abstract

The reactions of [Ru₃(CO)₁₂] with cyclooctene and cyclooctatetraene have been shown to proceed via different reaction pathways; cyclooctene, C₈H₁₄, causes cluster build-up with dehydrogenation of the ligand resulting in the formation of the hexaruthenium cyclooctyne carbido-cluster, [Ru₆C(CO)₁₅(μ₃-η¹:η¹:η²-C₈H₁₂)] **2**, whereas cyclooctatetraene, C₈H₈, results in cluster degradation with the formation of a binuclear complex [Ru₂(CO)₅(μ₂-η⁴:η⁴-C₈H₈)] **3**. Both species have been characterised by spectroscopic methods and their molecular structures established in the solid-state by single crystal X-ray diffraction analyses. © 1997 Elsevier Science S.A.

Keywords: Ruthenium; Carbonyl; Clusters; Cyclooctatetraene; Cyclooctene; Crystal structure

1. Introduction

The catalytic transformation of C₆ and C₈ cyclic hydrocarbons is of considerable industrial importance, and it is well established that metals such as platinum are highly effective in activating both C–H and C–C bonds within such molecules [1]. Studies of the adsorption and subsequent reactivity of C₆ ring systems such as cyclohexane, cyclohexene and cyclohexadiene have revealed that on a Pt(111) surface the dominating chemistry is their dehydrogenation to benzene [2]. Similarly, when unsaturated C₈ hydrocarbons such as cyclooctene, cycloocta-1,3-diene, and cycloocta-1,5-diene are chemisorbed on a Pt(111) surface, dehydrogenation again predominates, forming cyclooctatetraene, which at higher temperatures converts to benzene via a two-step intramolecular mechanism involving contraction of the cyclooctatetraene ring to form bicyclo[4.2.0]octa-1,3,5-triene, which then undergoes a retro[2 + 2] cyclisation to form benzene and acetylene [3]. One of the primary objectives of our current work is to mimic such behaviour on related cluster surfaces, and a series of recent experiments have established that a similar behaviour is observed when these organic moieties are bonded to deltahedral ruthenium and osmium clusters

(see for example Ref. [4]). For example, model compounds corresponding to the adsorption and successive dehydrogenation of cyclohexene, cyclohexadiene and benzene have been isolated. A feature of this work is the formation of enyl, dienyl, alkynyl, yne and ring-contraction derivatives indicating the cleavage of C–C bonds, as well as both saturated and unsaturated C–H bond activation [5,6].

We are currently investigating the interaction between C₈ hydrocarbons and metal carbonyl clusters with similar objectives in mind, and have recently reported that the reaction between [Ru₃(CO)₁₂] with cycloocta-1,3-diene leads to the formation of the cluster complexes [H₂Ru₃(CO)₉(μ₃-η¹:η²:η¹-C₈H₁₀)], [HRu₃(CO)₉(μ₃-η¹:η²:η²-C₈H₁₁)] [7], [Ru₄(CO)₁₂(η²-C₈H₁₀)], [Ru₄(CO)₁₂(η²:η²-C₈H₁₀)] [8], and [Ru₆(μ₃-H)(μ₄-η²-CO)₂(CO)₁₃(η⁵-C₈H₉)] [5] (see Scheme 1). The first two triangular clusters are structural isomers, differing only in the transfer of one hydrogen atom from the organic ligand to the metal core. The third and fourth tetranuclear butterfly clusters are also isomeric; the C₈H₁₀ ligand donates four and six electrons to the cluster cores respectively, thus giving rise to different total electron counts of 60 and 62. The final product is slightly more unusual, containing a doubly edge-bridged tetrahedral metal geometry with a tetrahydropentalene ligand derived from C–C bond activation and ring contraction.

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In a continuation of these studies we have investigated the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with other unsaturated cyclic C_8 hydrocarbons, and we now wish to report the results obtained when cyclooctene and cyclooctatetraene are employed.

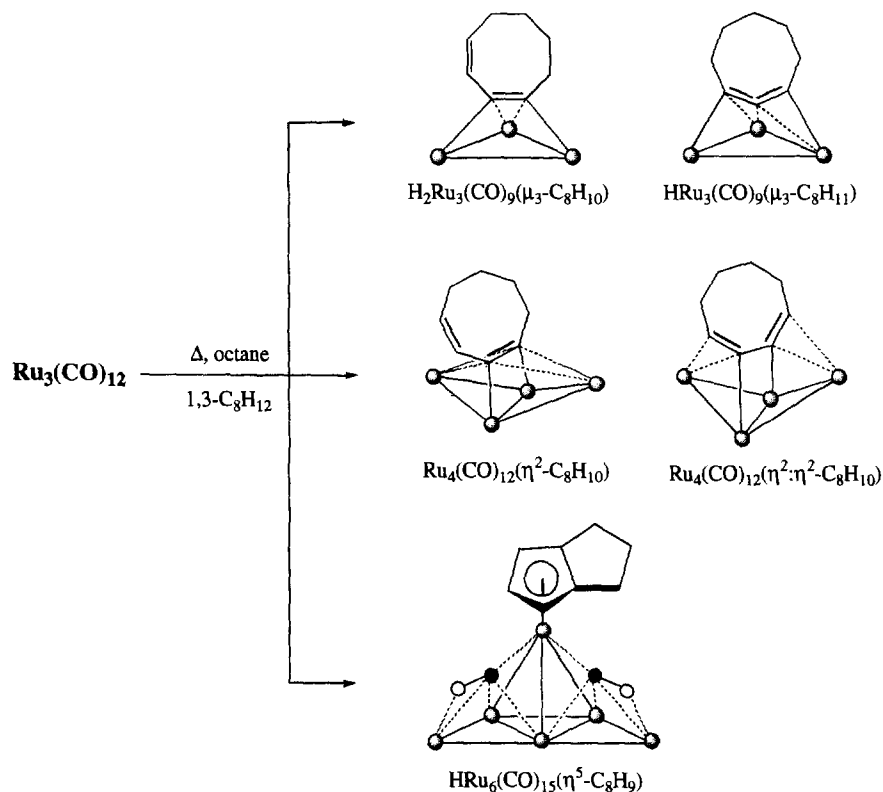
2. Results and discussion

When a solution of $[\text{Ru}_3(\text{CO})_{12}]$ in octane containing a slight excess of cyclooctene (C_8H_{14}) is heated to reflux (125°C) over a period of 5 h, two products are observed in moderate yields. These products are readily isolated by thin layer chromatography (tlc), and have been identified as the trinuclear cluster $[\text{H}_2\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_{12})]$ **1**, and the hexanuclear carbido-cluster $[\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_{12})]$ **2**. Compound **1** has previously been observed and fully characterised from a similar reaction where the thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ was carried out over a 92 h period using cyclooctene as the solvent [9]. However, this is the first observation of complex **2** which has been fully characterised in both solution and the solid-state by spectroscopic methods and a single-crystal X-ray diffraction analysis. In complexes **1** and **2** the cyclic olefin, having lost both vinylic H atoms, straddles a triangular face of the cluster, coordinating in the usual $\mu_3\text{-}\sigma\text{-}\sigma\text{-}\pi$ manner.

Compound **2** was initially characterised as

$[\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_3\text{-}\eta^2\text{-C}_8\text{H}_{12})]$ by comparison of its IR spectrum with those of the known alkyne cluster derivatives, $[\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_3\text{-}\eta^2\text{-RCCR}')] (R = R' = \text{H, Me, Et, Ph; } R = R' = \text{H and Ph, Me and Ph})$ [10]. The molecular formula was backed up by MS and ^1H NMR evidence, and its structure confirmed by single crystal X-ray diffraction analysis. The mass spectrum showed a parent peak at 1145 (calc. 1147) amu followed by peaks representing the sequential loss of several carbonyl groups. The ^1H NMR spectrum of **2** at room temperature exhibits three resonances of equal relative intensity at δ 3.22, 2.04 and 1.69 ppm. The resonances at δ 3.22 and 2.04 ppm are broad singlets suggesting a degree of fluxional behaviour, whereas the latter resonance at δ 1.69 ppm is a lot sharper and of multiplet character. This latter resonance is thought to correspond to those protons attached to the carbons on either side of the multiple bond. Coordination to the cluster unit through the olefinic bond will in turn restrict the movement of the carbons closest to this multiple bond to a greater extent than those further away. As a result it is thought that the protons on C(3L) and C(8L) (see Fig. 1) will give rise to a sharp multiplet resonance, whilst C(4L), C(7L) and C(5L), C(6L) may undergo a conformational change by 'flipping' of the ring, therefore making the protons appear equivalent.

The molecular structure of **2** in the solid-state is shown in Fig. 1 together with selected bond lengths and



Scheme 1. The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with cycloocta-1,3-diene in refluxing octane

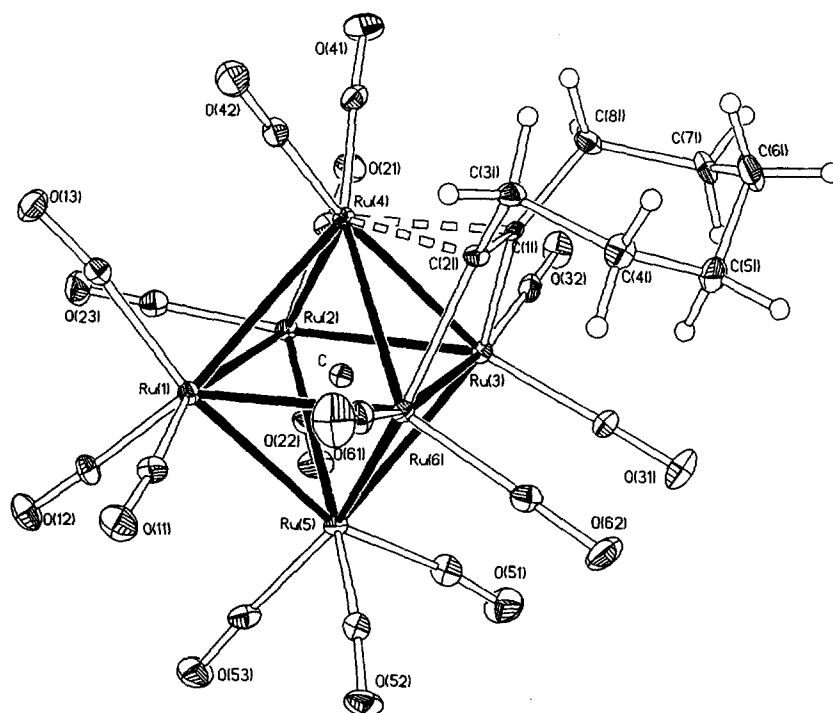


Fig. 1. Molecular structure of $[\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_3\text{-}\eta^1:\eta^1\text{-}\eta^2\text{-C}_8\text{H}_{12})]$ **2**, showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Principal bond distances (Å) and angles (deg) include: Ru(1)–Ru(2) 2.9127(8), Ru(1)–Ru(4) 2.9504(7), Ru(1)–Ru(5) 2.8497(7), Ru(1)–Ru(6) 2.9181(7), Ru(2)–Ru(3) 2.8977(7), Ru(2)–Ru(4) 2.9164(7), Ru(2)–Ru(5) 2.9199(8), Ru(3)–Ru(4) 2.7866(7), Ru(3)–Ru(5) 2.9909(7), Ru(3)–Ru(6) 2.8115(8), Ru(4)–Ru(6) 2.7874(7), Ru(5)–Ru(6) 2.9778(7), Ru(1)–C 2.071(6), Ru(2)–C 2.060(7), Ru(3)–C 2.003(6), Ru(4)–C 2.070(6), Ru(5)–C 2.047(6), Ru(6)–C 2.030(7), Ru(3)–C(1L) 2.070(6), Ru(4)–C(1L) 2.198(5), Ru(4)–C(2L) 2.190(6), Ru(6)–C(2L) 2.090(6), C(1L)–C(2L) 1.400(9), C(1L)–C(8L) 1.516(8), C(2L)–C(3L) 1.501(8), C(3L)–C(4L) 1.540(9), C(4L)–C(5L) 1.529(9), C(5L)–C(6L) 1.54(1), C(6L)–C(7L) 1.52(1), C(7L)–C(8L) 1.544(9), mean Ru–C_(CO) 1.903(7), mean C–O 1.143(9), Ru(3)–C(1L)–C(8L) 125.2(4), Ru(4)–C(1L)–C(8L) 125.2(4), Ru(4)–C(2L)–C(3L) 127.3(4), Ru(6)–C(2L)–C(3L) 123.7(4), C(1L)–C(2L)–C(3L) 123.8(4), C(2L)–C(1L)–C(8L) 124.7(6).

angles. The metal cluster framework consists of a distorted octahedron with Ru–Ru bond lengths ranging from 2.7866(7) to 2.9778(7) Å. An interstitial carbido atom occupies the central cavity and the organic ring straddles the Ru(3)–Ru(4)–Ru(6) triangular face interacting via its olefinic bond in a di- σ , π -manner. The coordination sphere of the cluster is completed by 15 carbonyl ligands which are all terminal and essentially linear.

The multiple bond of the C_8 moiety lies almost parallel to the Ru(3)–Ru(6) edge and a reduction of the formal bond order (as indicated by a C(1L)–C(2L) bond length of 1.400(9) Å) occurs upon coordination to the cluster in an alkyne manner which essentially involves σ -bonds to Ru(3) and Ru(6) (Ru(3)–C(1L) 2.070(6), Ru(6)–C(2L) 2.090(6) Å), and a π -interaction with Ru(4) (Ru(4)–C(1L) 2.198(5), Ru(4)–C(2L) 2.190(6) Å). All other C–C bonds lengths lie in the range 1.501(8) to 1.544(9) Å (mean 1.527 Å), and the cyclooctyne moiety adopts a chair conformation. This alkyne coordination mode has been seen on a number of occasions in cluster chemistry [11], and compound **2** has a structure closely related to those of $[\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_3\text{-}$

$\eta^2\text{-PhCCR}]$ (R = H, Ph), where the open chain alkyne ligands have been replaced by a cyclic C_8 moiety [10].

In contrast, the reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with cyclooctatetraene (C_8H_8) in refluxing octane over a 4 h period results in cluster degradation rather than build-up, with formation of one major dinuclear product, $[\text{Ru}_2(\text{CO})_5(\mu\text{-}\eta^4:\eta^4\text{-C}_8\text{H}_{12})]$ **3**. Characterisation of complex **3** has been achieved from spectroscopic evidence, and X-ray crystallographic studies have confirmed that the C_8H_8 ligand adopts a boat conformation, interacting with the two metal centres in a $\mu\text{-}\eta^4:\eta^4$ -manner.

The mass spectrum of complex **3** exhibits a strong parent peak at 447 (calc. = 446) amu followed by peaks corresponding to the loss of five CO groups in succession, and the ^1H NMR spectrum comprises of a singlet resonance at δ 4.77 ppm even at temperatures down to -70°C . This singlet resonance suggests the ring is undergoing a 'whizzing' process over the Ru–Ru bond, and its value of δ 4.77 ppm is significantly lower than that of the free ligand (δ 5.75 ppm) which is characteristic upon coordination of an organic moiety to a transition metal centre [12]. The molecular structure of **3** in

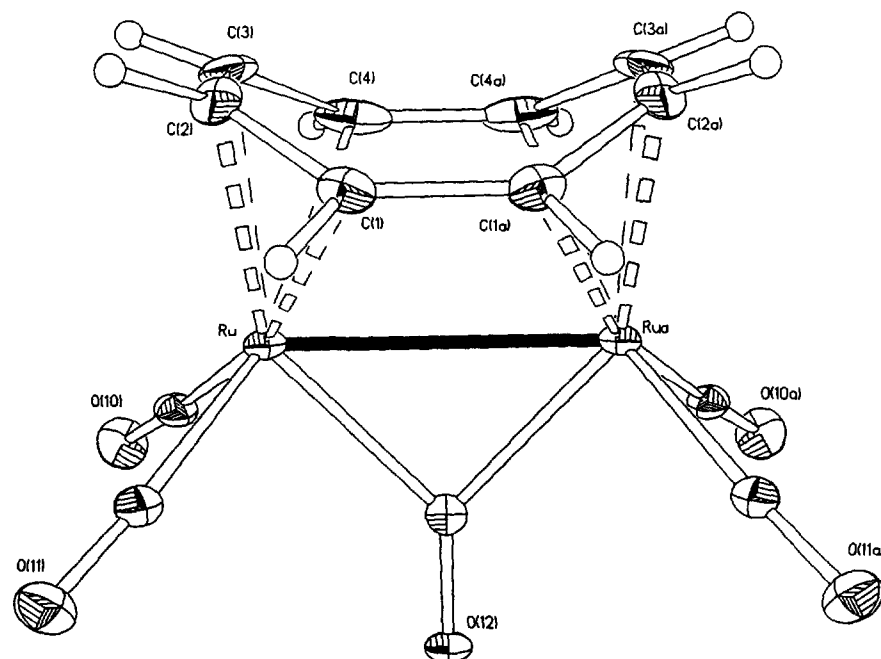


Fig. 2. Molecular structure of $[\text{Ru}_2(\text{CO})_5(\mu_2\text{-}\eta^4:\eta^4\text{-C}_8\text{H}_8)]$ **3**, showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms. Principal bond distances (Å) and angles (deg) include: Ru–Ru(a) 2.9362(9), Ru–C(1) 2.345(4), Ru–C(2) 2.240(4), Ru–C(3) 2.238(4), Ru–C(4) 2.323(5), C(1)–C(2) 1.401(6), C(1)–C(1a) 1.439(9), C(2)–C(3) 1.412(7), C(3)–C(4) 1.409(8), C(4)–C(4a) 1.45(1), Ru–C(12) 2.090(4), mean Ru–C_(terminal CO) 1.877(4), mean C–O 1.155(7), C(1)C(2)C(3)C(4)–C(1)C(1a)C(4a)C(4) 158.

the solid-state is illustrated in Fig. 2, together with relevant structural parameters. The molecule comprises of a diruthenium unit (Ru(1)–Ru(2) 2.936(1) Å), which is bridged by a cyclooctatetraene moiety. Each ruthenium atom also carries two terminal carbonyl ligands, and the final CO, which bridges the Ru–Ru bond, completes the structure. The most important feature of this molecule is the manner in which the C_8 ring bridges the two metal centres, with each ruthenium atom interacting with four carbon atoms of the bonded ring. An examination of this $\mu_2\text{-}\eta^4:\eta^4$ interaction reveals that the coordinated ring adopts a ‘boat’ conformation, convex with respect to the dimetallic unit, with an angle between the two diene-planes (C(1)–C(2)–C(3)–C(4) and C(1a)–C(2a)–C(3a)–C(4a)) and the central plane (C(1)–C(1a)–C(4a)–C(4)) of 158°. Each η^4 -diene unit interacts with a ruthenium atom via two long and two shorter interactions (Ru–C(1) 2.345(4), Ru–C(4) 2.323(5) vs. Ru–C(2) 2.240(4), Ru–C(3) 2.238(4) Å), and the mean C–C bond distances associated with the diene sections of the ring, i.e. C(1)–C(2), C(2)–C(3), and C(3)–C(4) are shorter than those linking the two diene units, i.e. C(1)–C(1a) and C(4)–C(4a) (mean 1.407(7) Å vs. 1.447(9) Å respectively). The molecule is bisected by a mirror plane which passes through the bridging carbonyl group and the centre of the C(1)–C(1a) and C(4)–C(4a) bonds.

Complex **3** may be compared with the analogous diiron complex, $[\text{Fe}_2(\text{CO})_5(\mu\text{-C}_8\text{H}_8)]$ [13]; however, the cyclooctatetraene bonding interaction differs slightly

between the two complexes due to a 45° twist in the orientation of the C_8 ring with respect to the underlying M–M unit (see Fig. 3). The diiron complex is also bisected by a mirror plane, but in this case the plane passes through two carbon atoms of the cyclooctatetraene ring as well as the bridging carbonyl group. These two carbon atoms sit at a distance of approximately 2.5 Å from each iron atom, compared with the other six carbon atoms which lie approximately 2.1 Å from their nearest Fe atom, thus forming two π -allyl-type interactions. Since the ligand must donate a total of eight electrons if the molecule is to obey the 18 electron rule, it is thought that two three-centre-two-electron bonds, extending over the two iron atoms and a carbon atom on the mirror plane, are formed.

^1H NMR of both the Fe and Ru complexes give rise to a singlet resonance, even at low temperature (–70 °C), thus suggesting the C_8 ring is undergoing

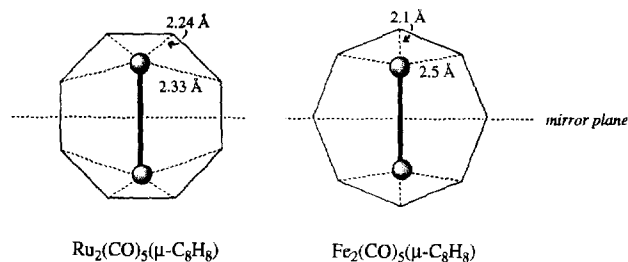


Fig. 3. Comparative views of the diruthenium and diiron complexes, $[\text{M}_2(\text{CO})_5(\mu\text{-C}_8\text{H}_8)]$, showing the different bonding interactions of the cyclooctatetraene ligand in the two complexes.

fluxional behaviour with a low energy barrier to rotation. The two different orientations observed in the solid-state show the ease with which such a rotation can occur, by providing snap-shots of the ligand as it rotates from a staggered configuration of the C-atoms with respect to the M-atoms (Ru complex) towards a conformation where opposite C-atoms eclipse the Ru-atoms (Fe complex). The different orientations adopted in the solid-state probably arise due to the relative sizes of the Fe and Ru atoms (Fe–Fe 2.742(3) c.f. Ru–Ru 2.936(1) Å); i.e. steric factors prevent each Fe atom from interacting with four C atoms, thus favouring the eclipsed conformation of the ligand.

3. Conclusion

A primary objective of this work has been to compare the interaction of cyclooctene and cyclooctatetraene with triangular faces of ruthenium clusters with their chemisorption on the elemental metal surface. In contrast to our previous observations, we find that dehydrogenation and ring-contraction is not a dominant aspect of these reactions; instead the chemistry appears to be dominated by cluster build-up (with C_8H_{14}) and cluster fragmentation (with C_8H_8). This is presumably associated with the electron donor capacities of the two ligands (four vs. eight electrons respectively); the greater the available electron density the more likely multi-site interaction at the same metal and hence fragmentation.

4. Experimental

4.1. General comments

All reactions were carried out with the exclusion of air under an atmosphere of dried nitrogen, using freshly distilled solvents. Product separation was achieved by tlc using glass plates supplied by Merck, pre-coated with a 0.25 mm layer of Kieselgel 60F₂₅₄. Eluents were mixed from standard laboratory-grade solvents. Infrared spectra were recorded in dichloromethane and/or hexane using NaCl cells (0.5 mm path length) on a Perkin–Elmer 1710 Series Fourier transform spectrometer, calibrated with carbon dioxide. Fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS50TC spectrometer. The instrument was run in positive mode, using CsI as calibrant. ¹H NMR spectra were recorded in CDCl₃ on a Bruker AM360 Fourier transform spectrometer, all chemical shifts being reported relative to internal TMS. [Ru₃(CO)₁₂] was prepared by the standard literature procedure [14], whilst cyclooctene (C₈H₁₄) and cyclooctatetraene (C₈H₈) were purchased from Aldrich Chemicals and used without further purification. Percentage yields are given on the basis of Ru content.

4.2. Preparation of [Ru₆C(CO)₁₅(μ₃-η¹:η¹:η²-C₈H₁₂)] 2

[Ru₃(CO)₁₂] (250 mg) was suspended in octane (50 ml) and excess cyclooctene (5 ml) added. The reaction mixture was heated to reflux for 5 h during which time the solution darkened quite substantially. The reaction was monitored by spot tlc and infrared spectroscopy, both of which indicated complete consumption of starting material after this time. The solvent was removed in vacuo and the products separated by tlc, eluting with a solution of dichloromethane–hexane (2:8, v/v). Two main bands were isolated and characterised, in order of elution, as [H₂Ru₃(CO)₉(μ₃-η²-C₈H₁₂)] **1** (yellow, 20%), and [Ru₆C(CO)₁₅(μ₃-η²-C₈H₁₂)] **2** (red-brown, 27%). Crystals of **2** were grown from dichloromethane at –25 °C. Spectroscopic data for **1**: IR (hexane): ν_{CO} 2104 w, 2075 vs, 2055 vs, 2040 s, 2024 s, 2014 s, 2006 m, 1987 m cm⁻¹; MS: M⁺ = 667 (calc. 666) amu. Spectroscopic data for **2**: IR (CH₂Cl₂): ν_{CO} 2087 w, 2042 vs, 2034 s(sh), 2020 m, 2009 m cm⁻¹; ¹H NMR (CDCl₃): δ 3.22 (s br, 4H), 2.03 (s br, 4H), 1.69 (m, 4H) ppm; MS: M⁺ = 1145 (calc. 1147) amu.

4.3. Preparation of [Ru₂(CO)₅(μ₂-η⁴:η⁴-C₈H₈)] 3

[Ru₃(CO)₁₂] (250 mg) was suspended in octane (50 ml) and excess cyclooctatetraene (5 ml) added. The reaction mixture was heated to reflux for 4 h after which spot tlc and infrared spectroscopy indicated the complete consumption of starting material. The solvent was removed in vacuo and one main band was isolated by tlc, eluting with a solution of dichloromethane–hexane (1:1, v/v) and characterised as [Ru₂(CO)₅(μ₂-η⁴:η⁴-C₈H₈)] **3** (yellow, 37%). Crystals of **3** were grown from dichloromethane at –25 °C. Spectroscopic data for **3**: IR (CH₂Cl₂): ν_{CO} 2034 m, 2005 s, 1963 m, 1797 w cm⁻¹; ¹H NMR (CDCl₃): δ 4.77 (s, 8H) ppm; MS: M⁺ = 447 (calc. 446) amu.

4.4. Crystal structure determination for compounds 2 and 3

4.4.1. Crystal data

2: C₂₄H₁₂O₁₅Ru₆, *M* = 1146.76, orthorhombic, space group *Pn*2₁, *a* = 18.141(2), *b* = 13.742(1), *c* = 11.955(2) Å, *U* = 2980.2(6) Å³, λ = 0.71073 Å, *Z* = 4, *D*_c = 2.556 mg m⁻³, red block 0.31 × 0.31 × 0.23 mm³, μ(Mo Kα) = 3.035 mm⁻¹, *F*(000) = 2160.

3: C₁₃H₈O₅Ru₂, *M* = 446.33, orthorhombic, space group *Pnam*, *a* = 7.582(2), *b* = 10.973(2), *c* = 15.696(4) Å, *U* = 1305.9(5) Å³, λ = 0.71073 Å, *Z* = 4, *D*_c = 2.270 mg m⁻³, yellow crystal 0.38 × 0.38 × 0.15 mm³, μ(Mo Kα) = 2.327 mm⁻¹, *F*(000) = 856.

4.4.2. Data collection and processing

All X-ray measurements were made on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device [15], graphite-monochromated Mo K α X-radiation: **2**; $T = 150$ K, ω - 2θ scans, 3580 unique data collected ($2\theta_{\max} = 50^\circ$, h 0 to 23, k -17 to 0, l 0 to 15), semi-empirical absorption correction applied [16], giving 3578 unique reflections with $I > 2\sigma(I)$ for use in all calculations. **3**; $T = 150$ K, ω - 2θ scans, 1186 unique data collected

Table 1

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2**

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Ru(1)	8919(1)	1770(1)	6425(1)	14(1)
Ru(2)	8462(1)	766(1)	8456(1)	14(1)
Ru(3)	7415(1)	-341(1)	7140(1)	13(1)
Ru(4)	7347(1)	1683(1)	7050(1)	12(1)
Ru(5)	9011(1)	-299(1)	6514(1)	15(1)
Ru(6)	7826(1)	650(1)	5180(1)	13(1)
O(11)	9413(3)	2248(4)	4049(5)	30(1)
O(12)	10528(2)	1836(4)	7110(5)	30(1)
O(13)	8697(3)	3925(3)	6934(5)	29(1)
O(21)	7465(3)	794(4)	10514(5)	32(1)
O(22)	9313(3)	-922(4)	9461(5)	32(1)
O(23)	9451(3)	2309(4)	9488(5)	34(1)
O(31)	6922(3)	-2147(4)	5881(5)	36(1)
O(32)	6698(3)	-1054(4)	9293(4)	33(1)
O(41)	6451(3)	2189(4)	9117(5)	33(1)
O(42)	7008(3)	3662(3)	6060(5)	32(1)
O(51)	8750(4)	-2469(4)	6985(6)	45(2)
O(52)	9354(3)	-652(4)	4064(5)	31(1)
O(53)	10665(3)	-538(4)	6912(6)	42(2)
O(61)	7806(3)	1922(4)	3094(5)	39(1)
O(62)	7423(3)	-1060(4)	3695(5)	35(1)
C(11)	9194(4)	2047(5)	4931(6)	22(1)
C(12)	9925(3)	1791(5)	6860(6)	19(1)
C(13)	8733(3)	3112(5)	6760(5)	18(1)
C(21)	7828(4)	795(5)	9744(6)	20(1)
C(22)	9017(3)	-309(5)	9002(6)	22(1)
C(23)	9085(4)	1747(5)	9089(6)	23(1)
C(31)	7103(4)	-1470(4)	6365(6)	20(1)
C(32)	6978(4)	-795(5)	8479(7)	22(1)
C(41)	6798(4)	2014(4)	8343(6)	22(1)
C(42)	7135(3)	2925(5)	6455(6)	21(1)
C(51)	8800(4)	-1643(5)	6831(6)	26(2)
C(52)	9158(4)	-479(5)	4947(7)	24(2)
C(53)	10052(4)	-441(5)	6792(6)	26(2)
C(61)	7824(4)	1450(5)	3884(6)	22(1)
C(62)	7570(4)	-406(5)	4259(6)	21(1)
C(1L)	6551(3)	535(4)	6625(5)	13(1)
C(2L)	6753(3)	1025(4)	5646(5)	14(1)
C(3L)	6213(3)	1513(5)	4878(6)	18(1)
C(4L)	5926(4)	812(5)	3972(6)	22(1)
C(5L)	5656(4)	-172(5)	4405(6)	27(2)
C(6L)	5047(4)	-129(6)	5305(7)	30(2)
C(7L)	5294(3)	-317(5)	6498(8)	29(2)
C(8L)	5771(3)	468(5)	7073(7)	21(1)
C	8175(4)	672(4)	6792(6)	15(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

Table 2

Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **3**

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}^a
Ru	9692(1)	215(1)	8435(1)	17(1)
C(1)	6788(5)	487(4)	7958(3)	25(1)
C(2)	6897(6)	-405(4)	8594(3)	30(1)
C(3)	8002(6)	-1440(4)	8599(3)	35(1)
C(3)	8002(6)	-1440(4)	8599(3)	35(1)
C(4)	9226(6)	-1765(4)	7963(4)	38(1)
C(10)	11747(6)	-261(4)	9008(3)	24(1)
C(11)	9600(5)	1686(4)	9052(3)	26(1)
C(12)	11291(7)	1000(5)	7500	21(1)
O(10)	12984(4)	-567(3)	9379(2)	32(1)
O(11)	9532(5)	2547(3)	9460(2)	40(1)
O(12)	12572(5)	1591(4)	7500	26(1)

^a U_{eq} is defined as one-third of the trace of the orthogonalised U_{ij} tensor.

($2\theta_{\max} = 45^\circ$, h -1 to 8, k -1 to 13, l -1 to 18), semi-empirical absorption correction applied, giving 1180 reflections with $I > 2\sigma(I)$ for use in all calculations.

4.4.3. Structure solution and refinement

The ruthenium atoms were located by automatic direct methods [17], and subsequent iterative cycles of least squares refinement and Fourier difference synthesis located all non-H atoms [18]. All non-H atoms were then refined (by least squares on F^2 using SHELX93 [18]) with anisotropic thermal parameters and H-atoms on C were included in the models at fixed, calculated positions.

In **2** at final convergence $R[I > 2\sigma(I)] = 0.0237$, $wR2 = 0.0577$ (all data), $S = 1.104$ for 406 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 0.654 or below $-0.826 \text{ e \AA}^{-3}$. In **3** at final convergence $R[I > 2\sigma(I)] = 0.0287$, $wR2 = 0.0740$ (all data), $S = 1.085$ for 106 refined parameters and the final ΔF synthesis showed no $\Delta\rho$ above 0.771 or below $-0.585 \text{ e \AA}^{-3}$. Atomic scattering factors were inlaid [18], molecular geometry calculations utilised CALC [19], and Fig. 1 and 2 were produced using SHELXTL PC [20].

Atom coordinates for **2** are given in Table 1, and those for **3** in Table 2. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and the remaining bond lengths and angles.

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