

Preparation, Characterisation, Molecular and Crystal Structure of the Octaruthenium Arene Clusters $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-arene})]$ (arene = C_6H_6 or $\text{C}_{16}\text{H}_{16}$)[†]

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Two octaruthenium arene clusters, $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-arene})]$ (arene = C_6H_6 **1** or $\text{C}_{16}\text{H}_{16}$ **2**), have been isolated from the thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ in octane, in the presence of cyclohexene (C_6H_{10}) or [2.2]paracyclophane ($\text{C}_{16}\text{H}_{16}$), respectively. Both compounds **1** and **2** have been characterised in the solid state by single-crystal X-ray diffraction and their molecular and crystal structures determined. The reaction of **2** with CO resulted in conversion to the carbido cluster $[\text{Ru}_6\text{C}(\text{CO})_{14}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16})]$ and $[\text{Ru}_3(\text{CO})_{12}]$ in quantitative amounts. Compound **1** did not react in the same way but yielded both $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$ and $[\text{Ru}_4\text{H}_2(\text{CO})_{13}]$.

Despite several review articles concerned with the synthesis, structure and theoretical aspects of arene cluster compounds,¹ the chemistry of arene clusters with nuclearity higher than six has not been well developed, and relatively few arene cluster derivatives have been structurally characterised in the solid state. The heptaruthenium complex $[\text{Ru}_7(\text{CO})_{15}(\mu_4\text{-PPh})(\eta^6\text{-C}_6\text{H}_5\text{Me})]$ has been reported as the product (although only in extremely low amounts) of the thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with PPhH_2 in toluene.² Similarly, when $[\text{Ru}_3(\text{CO})_{12}]$ is treated with PPh_2H in refluxing toluene the octaruthenium complex $[\text{Ru}_8(\text{CO})_{19}(\mu_8\text{-P})(\mu\text{-}\sigma\text{:}\eta^6\text{-C}_6\text{H}_5\text{CH}_2)]$ may be isolated as a minor product.³ The metal framework of this complex forms a square antiprism in which a P(phosphide) atom occupies the interstitial site, and the benzyl group bridges two ruthenium atoms. Others have shown that the dropwise addition of $[\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-S})]$ in toluene to a similar solution of $[\text{Ru}_3(\text{CO})_{12}]$ heated to reflux yields the octaruthenium complex $[\text{Ru}_8(\text{CO})_{17}(\mu_4\text{-S})_2(\eta^6\text{-C}_6\text{H}_5\text{Me})]$ which contains two fused square-pyramidal units of ruthenium atoms bridged by the two sulfur atoms.⁴ The only other example of an octametallarene cluster is found in the mixed-metal species $[\text{Cu}_2\text{Ru}_6(\text{CO})_{16}(\eta^2\text{-C}_6\text{H}_5\text{Me})_2]$ which has been prepared by treating $[\text{Ru}_6(\text{CO})_{18}]^{2-}$ with $[\text{Cu}(\text{MeCN})_4]^-$ in acetone.⁵ In the mixed-metal species an octahedral ruthenium core bicapped on opposite faces by the copper atoms, *viz.* a *trans*-dicapped octahedron, is observed and each copper atom bears a toluene ligand bound in η^2 fashion.

We have recently reported,⁶ in preliminary form, the synthesis and structural characterisation of the octaruthenium complex $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-C}_6\text{H}_6)]$. This cluster forms an octahedron capped by two additional ruthenium atoms on two triangular faces sharing a common vertex, *viz.* a *cis*-dicapped octahedron. The benzene ligand is η^6 -bound to the only octahedron vertex not belonging to the capped triangular faces. With the synthesis of this complex we have been able to demonstrate that the synthetic route to arene clusters,

successfully applied to the synthesis of many different cluster species of nuclearity up to six, could also be used to expand the cluster nuclearity. In this respect we were also interested in exploring the possibility of isolating high-nuclearity clusters containing [2.2]paracyclophane. This ligand has been shown to bind to hexa- and tri-nuclear cluster cores as benzene does, and is able to adopt either the η^6 -terminal or the $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2$ -face bonding mode.⁷

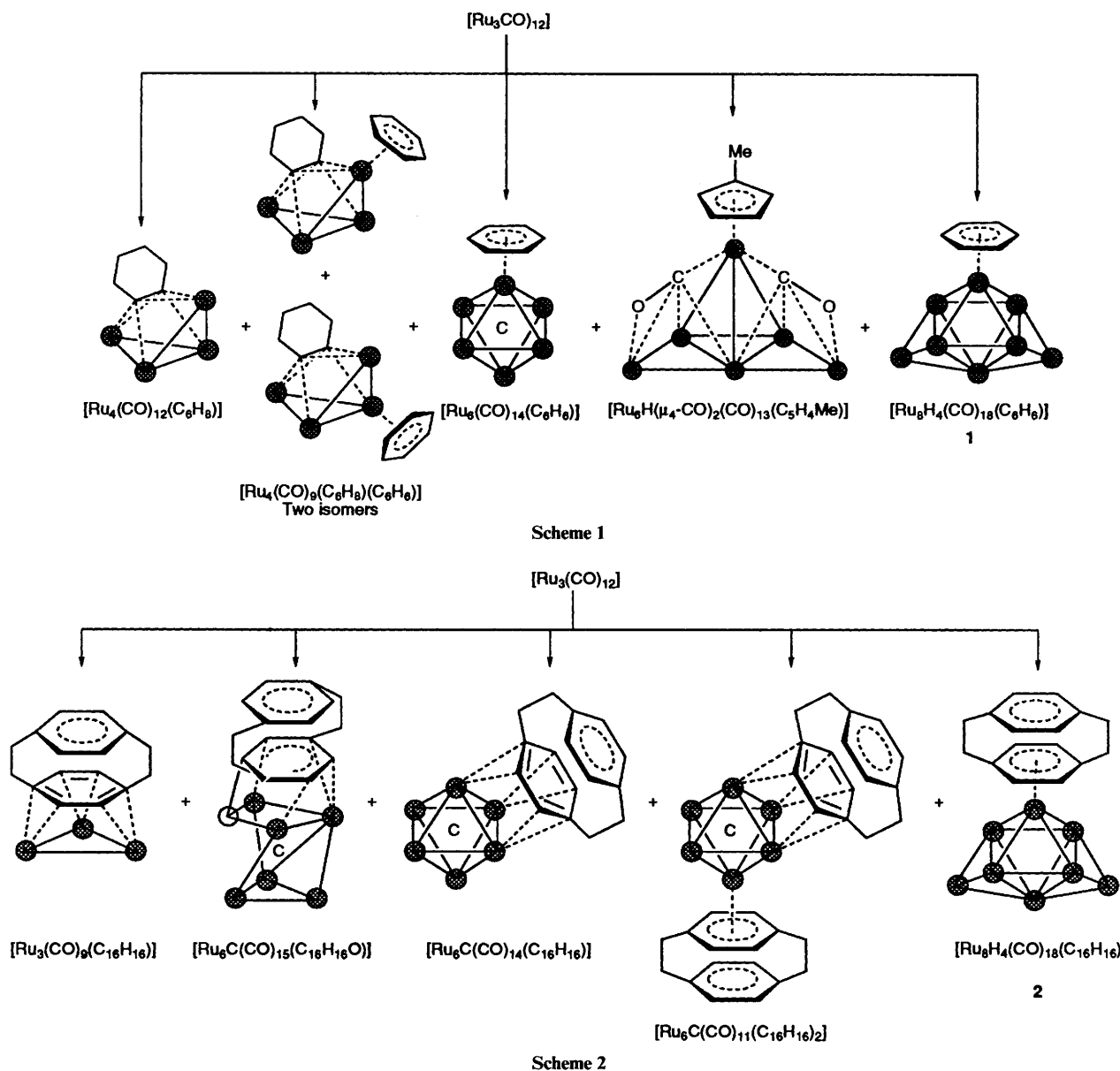
In this paper we describe the synthesis and full structural characterisation in solution and in the solid state of the two new octaruthenium clusters $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-arene})]$ (arene = C_6H_6 **1** or $\text{C}_{16}\text{H}_{16}$ **2**). Compound **1** is isolated from the thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ in octane in the presence of cyclohexene (C_6H_{10}), and compound **2** is obtained when the thermolysis is carried out in the presence of [2.2]paracyclophane ($\text{C}_{16}\text{H}_{16}$). A detailed discussion of the molecular structures of **1** and **2** in the solid state, as determined by single-crystal X-ray diffraction, is also reported. The molecular organization in the solid state is also investigated in order to ascertain the preferential packing motifs of the type observed in crystals of other arene clusters.^{1a,8}

The distribution and location of the four H(hydride) atoms is also of interest. Although the use of X-ray diffraction methods poses some well known limitations to an exact location of these atoms on the surface of high-nuclearity clusters, we have gathered convincing evidence from Fourier synthesis and from an analysis of the ligand distribution to identify the location of all four hydride atoms on the cluster periphery. The H(hydride) atoms are found either in edge- or face-bridging positions thus reproducing the situation observed by neutron diffraction for the dianion $[\text{Os}_{10}\text{H}_4(\text{CO})_{24}]^{2-}$.⁹

Results and Discussion

The thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ in octane containing C_6H_{10} affords a range of products (see Scheme 1) with cluster nuclearities ranging from four to eight, *viz.* $[\text{Ru}_4(\text{CO})_{12}(\mu_4\text{-C}_6\text{H}_8)]$,^{10a} $[\text{Ru}_4(\text{CO})_9(\mu_4\text{-C}_6\text{H}_8)(\eta^6\text{-C}_6\text{H}_6)]$,^{10a,b} $[\text{Ru}_6\text{H}(\mu_4\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_4\text{Me})]$,¹¹ $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$ ¹² and $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-C}_6\text{H}_6)]$ **1**. Both $[\text{Ru}_4(\text{CO})_{12}(\mu_4\text{-C}_6\text{H}_8)]$ and the hexaruthenium carbido cluster have been reported previously, the former as a product from the reaction of

[†] Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv-xxx.



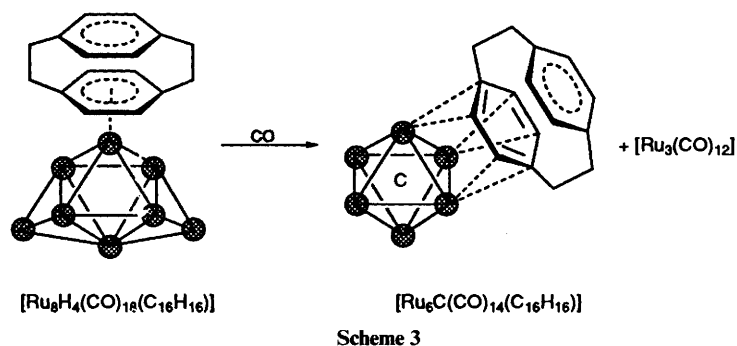
[Ru₃(CO)₁₂] with cyclohexa-1,3-diene in refluxing octane,¹⁰ and the latter by a number of routes including an extended thermolysis in benzene.^{1,2a}

In a similar reaction involving the thermolysis of [Ru₃(CO)₁₂] in octane, but containing an excess of [2.2]paracyclophane, clusters with nuclearities ranging from three to eight have been isolated (see Scheme 2). These products comprise [Ru₃(CO)₉(μ₃-η²:η²:η²-C₁₆H₁₆)],⁷ [Ru₆C(CO)₁₅(μ₃-σ:η²:η²-C₁₆H₁₆O)],¹³ [Ru₆C(CO)₁₄(μ₃-η²:η²:η²-C₁₆H₁₆)], [Ru₆C(CO)₁₁(μ₃-η²:η²:η²-C₁₆H₁₆)(η⁶-C₁₆H₁₆)],⁷ and [Ru₈H₄(CO)₁₈(η⁶-C₁₆H₁₆)] **2**.

Compounds **1** and **2** were characterised by IR, mass and ¹H NMR spectroscopies. Their IR spectra are similar, the profile in the CO stretching region being almost identical, with frequencies belonging to **2** occurring at slightly lower wavenumbers. The mass spectra of both compounds afford parent ions (*m/z* 1394 **1** or 1524 **2**) and are followed by peaks which correspond to the sequential loss of several carbonyl groups. The ¹H NMR spectrum of **1** exhibits three singlet resonances at δ 5.40, -17.80 and -19.26 with relative intensities 3:1:1. The first signal is readily assigned to the C-H protons of the benzene ring whilst the two singlets of very low frequency correspond to the four hydridic

protons. A total electron count of 110 is required for an octaruthenium cluster with the metal-atom topology observed in the solid-state structure (see below) and apart from the 18 CO ligands and six-electron donor benzene group, four electrons are required which are formally donated by the four hydride ligands. The ¹H NMR spectrum of **2** is slightly more complicated because of the cyclophane unit, with resonances observed at δ 6.78 (s), 4.51 (s), 3.18 (m), 2.85 (m), -17.80 and -19.40 with relative intensities of 2:2:2:2:1:1, respectively. The singlets at δ 6.78 and 4.51 are taken to correspond to the ring protons of the unattached and co-ordinated rings, respectively. The multiplets at δ 3.18 and 2.85 may be attributed to the protons in the CH₂CH₂ linkages, the former from those neighbouring the unbound ring, the latter nearest to the bound ring. As in **1**, four hydrides give rise to the signals at δ -17.80 and -19.40.

It is noteworthy that the ring protons of these compounds arise at remarkably low frequency for arenes in terminal bonding mode. Considering the benzene cluster **1** in relation to a series of comparable clusters there appears to be an inverse relationship between cluster nuclearity and chemical shift. Thus, [Ru₅C(CO)₁₂(η⁶-C₆H₆)] exhibits a singlet resonance at δ 5.93,¹⁴ [Ru₆C(CO)₁₄(η⁶-C₆H₆)] at δ 5.56^{12b}



and in **1** the resonance is observed at δ 5.40. It would appear from these preliminary results that the extent of the benzene-cluster interaction may be a function of cluster size and these observations may shed further light on the complexities of interactions on the bulk surface. We believe these differences in chemical shift arise from the electron-accepting capability of the cluster unit and hope to delineate this phenomenon by preparing and characterising a range of higher nuclearity benzene clusters.

We have studied the reactions of both **1** and **2** with CO; compound **2** reacts with a steady stream of CO in dichloromethane at room temperature to produce [Ru₃(CO)₁₂] and [Ru₆C(CO)₁₄(μ_3 - η^2 : η^2 : η^2 -C₁₆H₁₆)] quantitatively (see Scheme 3). While [Ru₃(CO)₁₂] may derive from the recombination of ruthenium carbonyl fragments generated from the degradative carbonylation of the two capping ruthenium atoms attached to the octahedral cage, the formation of [Ru₆C(CO)₁₄(μ_3 - η^2 : η^2 : η^2 -C₁₆H₁₆)] is less easy to visualise. Clearly the migration of the cyclophane from a terminal position to a face-capping site is required (a process quite common in these systems) but the encapsulation of a carbido atom into the octahedral cavity is also necessary. Further studies of this reaction are currently underway. However, it is noteworthy that a similar rearrangement has been observed in the reaction of the octahedral dianion [Ru₆(CO)₁₈]²⁻ with trifluoromethanesulfonic anhydride which quantitatively yields [Ru₆C(CO)₁₇].¹⁵

In a similar reaction involving compound **1** with CO in dichloromethane [Ru₄H₄(CO)₁₂] and [Ru₄H₂(CO)₁₃] have been isolated, together with two other compounds in much lower yield which have not, as yet, been identified.

Molecular Structures of Complexes 1 and 2 in the Solid State.—The molecular structures of **1** and **2** in the solid state have been determined by single crystal X-ray diffraction. Due to the formation of very small crystals and to instability under X-ray exposure, data for species **2** have been collected using a FAST diffractometer (see Experimental section). The structures of **1** and **2** together with the corresponding labelling schemes are shown in Fig. 1(a) and 1(b), respectively.

Relevant structural parameters are reported in Table 1. The two molecules share fundamental structural features and will be described together. The octaruthenium cluster framework can be described as an octahedron capped by two additional metal atoms on two triangular faces sharing a common vertex, *viz.* the metal-atom framework is a *cis*-capped octahedron. The Ru–Ru bond distances range from 2.746(1) to 3.057(1) Å in **1** and from 2.748(3) to 3.059(3) Å in **2**. Both the benzene ligand in **1** and the C₁₆H₁₆ ligand in **2** are η^6 bound to the octahedron vertex not involved in bonding with the two capping ruthenium atoms. The metal core geometry can be formally derived by removal of two capping atoms from that of the tetracapped octahedral metal framework shared by [Ru₁₀HC(CO)₂₄]^{-17a,b} or [Ru₁₀C(CO)₂₄]^{-17a,c} and observed also in a number of osmium derivatives.¹⁸ The *cis*-dicapped octahedral core has been previously observed only for the osmium cluster anion

Table 1 Relevant structural parameters (Å) for **1** and **2**

| | 1 | 2 |
|--|----------------------|---|
| Ru(1)–Ru(2) | 3.025(1) | 3.044(3) |
| Ru(1)–Ru(3) | 3.001(1) | 2.976(3) |
| Ru(1)–Ru(4) | 2.963(1) | 2.986(3) |
| Ru(1)–Ru(6) | 3.057(1) | 3.046(3) |
| Ru(1)–Ru(7) | 3.056(1) | 3.059(3) |
| Ru(1)–Ru(8) | 2.818(1) | 2.799(3) |
| Ru(2)–Ru(3) | 2.808(1) | 2.805(3) |
| Ru(2)–Ru(5) | 2.855(1) | 2.790(3) |
| Ru(2)–Ru(6) | 2.870(1) | 2.792(3) |
| Ru(2)–Ru(7) | 2.785(1) | 2.767(3) |
| Ru(3)–Ru(4) | 2.912(1) | 2.972(3) |
| Ru(3)–Ru(5) | 2.861(1) | 2.858(3) |
| Ru(3)–Ru(8) | 2.746(1) | 2.752(3) |
| Ru(4)–Ru(5) | 2.885(1) | 2.931(3) |
| Ru(4)–Ru(6) | 2.796(1) | 2.784(3) |
| Ru(4)–Ru(8) | 2.757(1) | 2.748(3) |
| Ru(5)–Ru(6) | 2.861(1) | 2.820(3) |
| Ru(6)–Ru(7) | 2.770(1) | 2.823(3) |
| Mean Ru–C(CO _{terminal}) | 1.882(5) | 1.87(2) |
| Mean Ru–C(CO _{bridging}) | 2.139(5) | 2.15(2) |
| Mean C–O | 1.136(6) | 1.15(2) |
| Ru(5)–C(19) | 2.201(5) | 2.27(2) |
| Ru(5)–C(20) | 2.225(5) | 2.21(2) |
| Ru(5)–C(21) | 2.198(5) | 2.40(2) |
| Ru(5)–C(22) | 2.206(5) | 2.24(2) |
| Ru(5)–C(23) | 2.212(5) | 2.20(1) |
| Ru(5)–C(24) | 2.207(5) | 2.37(2) |
| Mean C(sp ²)–C(sp ²) | 1.40(1) | 1.43(2) (μ_3 -bound ring) 1.39(2) ('free' ring) |
| Mean C(sp ²)–C(sp ³) | | 1.53(2) |
| Mean H(1)–Ru | 1.84(1) ^a | 1.86(2) ^a |
| Mean H(2)–Ru | 1.82(1) ^a | 1.78(2) ^b |
| Mean H(4)–Ru | | 1.78(2) ^b |
| H(3)–Ru(1) | 1.62(1) ^b | 1.71(2) ^a |
| H(3)–Ru(7) | 1.69(1) ^b | 2.14(2) ^a |

^a Experimental value. ^b Hydride position calculated with XHYDEX.¹⁶

[Os₈(CO)₂₂]²⁻^{19a} and for the mixed neutral cluster [Os₆Pt₂(CO)₁₇(C₈H₁₂)₂].^{19b} All these complexes share the same number of valence shell electrons, *i.e.* 110.

Sixteen out of the 18 carbonyl ligands are terminally bound, three on each capping atom and two on each ruthenium atom of the octahedral core. Two symmetrically bridging CO ligands span two opposite Ru edges connecting the capped triangles. In both complexes the arene is apically bound. The presence of the interring bridges in the C₁₆H₁₆ ligand in compound **2** is reflected in the deviation from planarity of the rings [see Fig. 1(b)] and in the pattern of Ru–C distances (see Table 1). A similar deviation from planarity towards a boat conformation of the rings is also present in free C₁₆H₁₆.²⁰ The Ru–C(21) and Ru–C(24) bond lengths are 2.40(2) and 2.37(2) Å, respectively, whereas the remaining four distances range from 2.20(1) to 2.27(2) Å. No distortion is observed for the benzene ring in **1**,

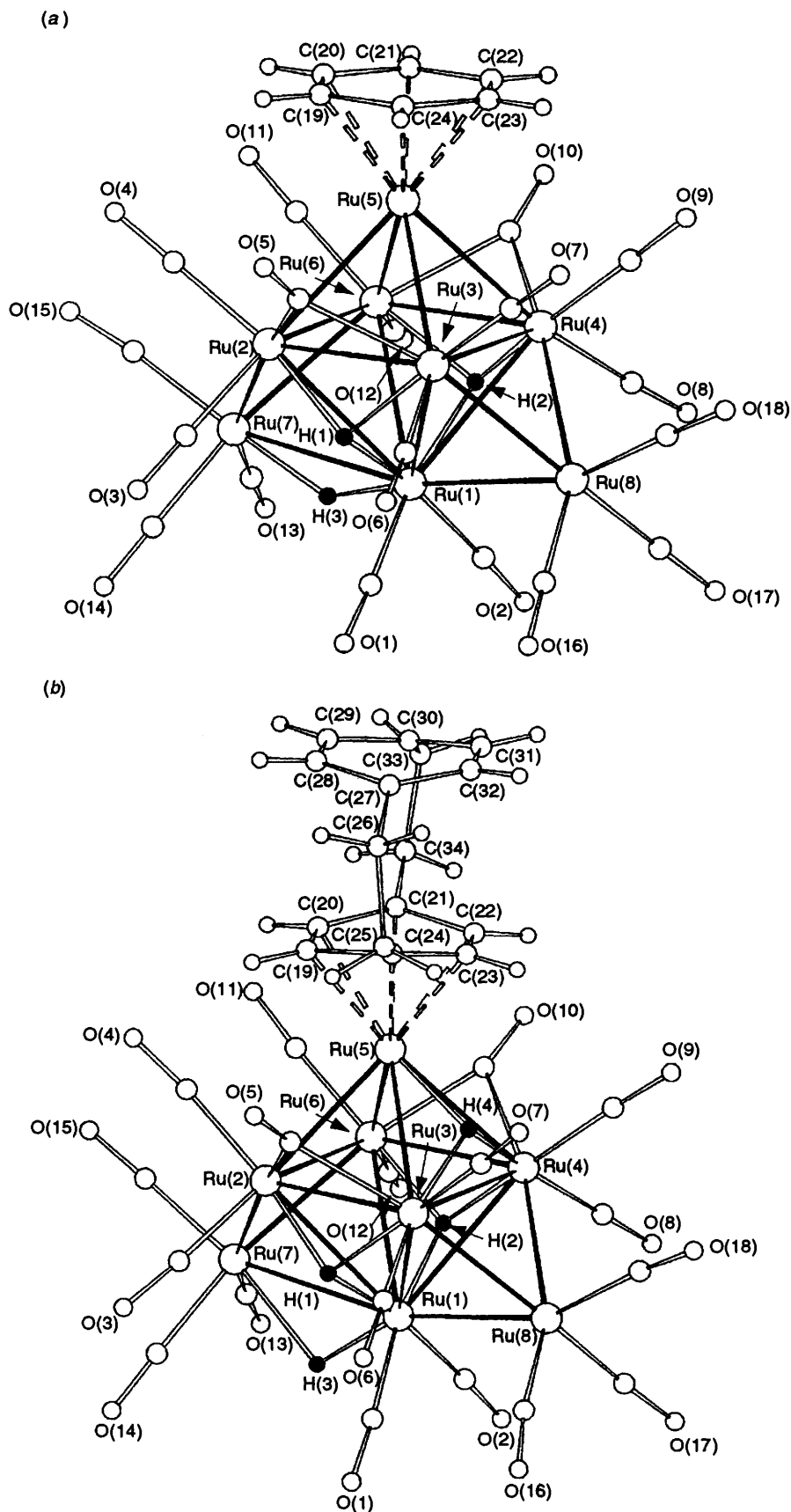


Fig. 1 Molecular structures of complexes **1** (a) and **2** (b) showing the atomic labelling scheme; the C atoms of the CO ligands bear the same numbering as the corresponding O atoms, the H(hydride) atom positions as determined *via* Fourier syntheses and/or *via* XHYDEX are shown (see Experimental section)

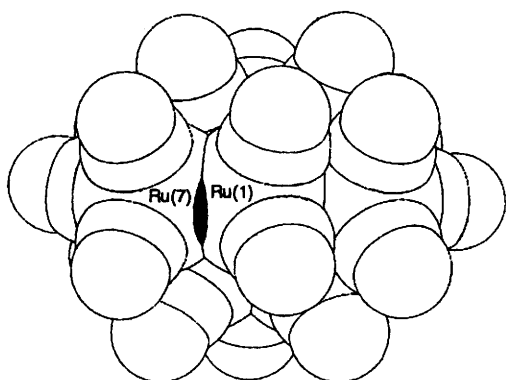


Fig. 2 The large niche in the ligand envelope of **1** which is believed to accommodate one of the H(hydride) ligands. Note how the CO ligands bend away from the metal-metal bond

where the Ru-C(C_6) distances are markedly shorter [mean Ru-C 2.208(5) Å] with respect to the short Ru-C(C_6) distances in **2**.

The hydride location deserves some comment. In **1** only two of the four hydride atoms [H(1) and H(2)] were observed experimentally and they triply bridge the Ru triangular faces adjacent to the capped ones. Their positions were verified using the program XHYDEX,¹⁶ which also indicated a third hydride bridging one of the longest Ru-Ru edges [Ru(1)-Ru(7)]. The position of this hydride could also be inferred by the presence of a large niche in the ligand envelope accompanied by a pronounced distortion of the CO ligands, which are bent away from the metal-metal bond as shown in Fig. 2. The location of the fourth hydride is more critical, due to the absence of preferential cavities in the ligand coverage and of a clear-cut potential energy minimum on the cluster surface; this atom is probably disordered over different cluster sites. A similarly complicated distribution of the hydrides has been observed in the neutron diffraction study at 20 K on the dianion [Os₁₀H₄(CO)₂₄]²⁻⁹ where the hydride ligands were located on the cluster surface, two in μ_3 and two in doubly bridging sites. The hydride distribution in **2** is comparable to that observed in **1**. Two of the four hydrides in **2** were located from a Fourier-difference synthesis: as observed in **1**, H(3) is doubly bridging the Ru(1)-Ru(7) edge, while H(1) is μ_3 bound to the Ru(1)-Ru(2)-Ru(3) triangular face of the octahedron. From a graphic examination of the outer cluster surface and from potential-energy calculations using the program XHYDEX¹⁶ two other suitable positions were found for the remaining two H(hydride) atoms; H(2) is triply bridging the opposite triangular face with respect to H(1), as observed in **1**, while H(4) is probably located on the Ru(3)-Ru(4)-Ru(5) metal triangle. The H(hydride) distribution on the metal frame is consistent with the pseudo *m* symmetry of the molecule, as shown in Fig. 3. By analogy with compound **2** and for similar symmetry considerations, it might be suggested that the fourth hydride ligand in **1** is disordered over the two faces adjacent to the capped Ru₃ triangles and sharing the Ru(5) vertex.

Crystal Structures of Complexes 1 and 2.—Crystalline arene clusters have been shown to pack according to only a few, well defined, packing motifs. These are dictated by the need to optimise the intermolecular interlocking of flat arene fragments with cylindrical carbonyl ligands. It has been demonstrated that organometallic clusters form essentially molecular crystals, *viz.* crystals held together by van der Waals interactions of the type commonly observed in organic solids. The basic packing motifs observed in crystalline arene clusters are: (i) arene-arene interactions of the graphitic type, *i.e.* with benzene or other arenes belonging to neighbouring molecules layered on top of each other at a separation of *ca.* 3.5 Å; (ii) carbonyl-carbonyl interactions based on the intimate interlocking of tricarbonyl

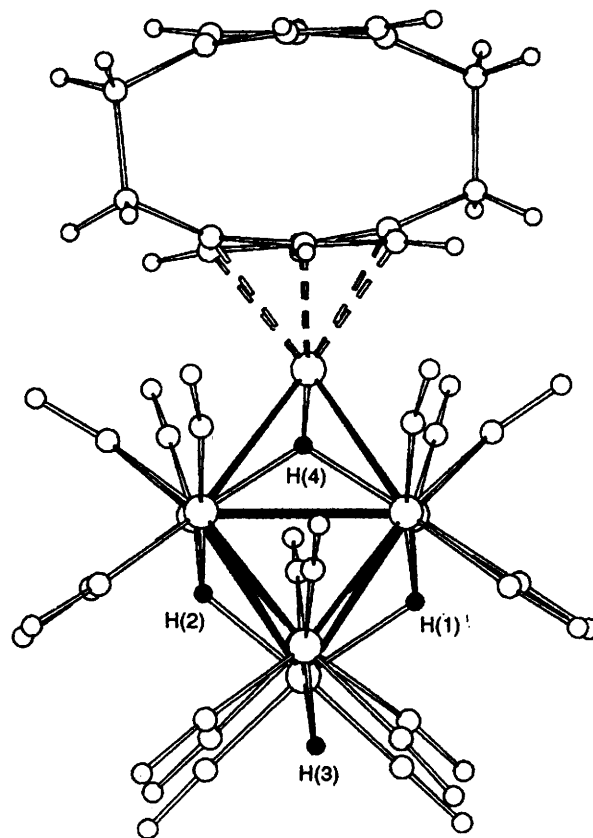


Fig. 3 A side view of compound **2**, showing the molecular pseudo *m* symmetry

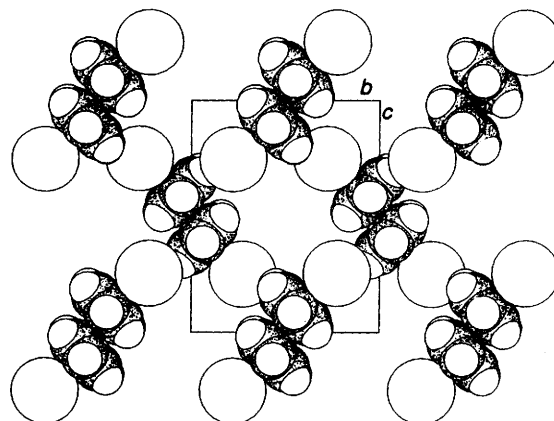


Fig. 4 Crystal packing of compound **1** along the *a* axis. The CO ligands are omitted for clarity. Large spheres represent the centre of mass of the metal frame

or tetracarbonyl units commonly observed in carbonyl cluster systems; and (iii) carbonyl-arene interactions most often based on intricate networks of C-H...O hydrogen bonding. This latter type of interaction has been observed in a number of other ionic and neutral organometallic systems. Hydrogen bonding of the O-H...O and C-H...O types in organometallic systems has been recently subjected to systematic investigations.²¹

In spite of the size and complexity of compound **1**, the molecules arrange themselves in pairs throughout the crystal (see Fig. 4) with the benzene ligands facing each other in a graphitic fashion (distance between the ring planes 3.32 Å), as observed in a number of transition-metal arene clusters. On the opposite side of the cluster with respect to the benzene moiety six carbonyl ligands, terminally bound to the long Ru(7)-Ru(1)-Ru(8) 'edge', interlock in a parallel fashion with the same edge of

a neighbouring molecule generated by an inversion centre (see Fig. 5), as previously observed for one of the 'tetrahedron' edges of $[\text{Os}_{10}\text{H}_2\text{C}(\text{CO})_{24}]$.¹⁷

The crystal structure of compound **2** is constituted of molecules arranged in piles along the *b* axis, as shown in Fig. 6. The interstices among the clusters are filled with toluene molecules; each solvent molecule is 'inserted' into the cavity formed by four terminal carbonyl ligands bound to the Ru–Ru edge which bears the doubly bridging H(hydride), as shown in Fig. 7.

Experimental

All reactions were carried out under an atmosphere of dinitrogen. Subsequent work-up of products was carried out using standard laboratory-grade solvents without precautions to exclude air. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform spectrometer, mass spectra were obtained by positive fast atom bombardment on a Kratos MS50TC and ¹H NMR spectra were recorded using a Bruker AM360 spectrometer. Products were isolated by thin-layer chromatography (TLC) using plates supplied by Merck coated with Silicagel-60.

The cluster $[\text{Ru}_3(\text{CO})_{12}]$ was prepared according to the literature method.²² Cyclohexene (C_6H_{10}) and [2.2]paracyclophane ($\text{C}_{16}\text{H}_{16}$) were purchased from Fluka chemicals and used without further purification.

Thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with Cyclohexene in Octane.—The compound $[\text{Ru}_3(\text{CO})_{12}]$ (250 mg) was suspended in octane (30 cm³) and excess cyclohexene (2 cm³) was added. The reaction mixture was heated to reflux for 6 h during which time the solution darkened considerably. The reaction was monitored by spot TLC which indicated the complete consumption of the starting material after this time. The solvent was removed *in vacuo* and the products separated by TLC, using a solution of dichloromethane–hexane (3:7) as eluent. Five bands were extracted and characterised by spectroscopy (in order of elution) as $[\text{Ru}_4(\text{CO})_{12}(\mu_4\text{-C}_6\text{H}_8)]$ (red, 18%), $[\text{Ru}_4(\text{CO})_9(\mu_4\text{-C}_6\text{H}_8)(\eta^6\text{-C}_6\text{H}_6)]$ (red, 4%), $[\text{Ru}_6\text{H}(\mu_4\text{-CO})_2\text{-}(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ (brown, 8%), $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-C}_6\text{H}_6)]$ **1** (brown, 10%) and $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$ (brown, 14%).

Spectroscopic data for **1**. IR (CH_2Cl_2): ν_{CO} 2091m, 2080m, 2066vs, 2031s, 2006w (sh), 1966w, 1922w cm⁻¹. ¹H NMR (CDCl_3): δ 5.40 (s, 6 H), –17.80 (s, 2 H), –19.26 (s br, 2 H). Mass spectrum (*m/z*): M^+ 1394 (calc. 1394).

Thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with [2.2]Paracyclophane in Octane.—A suspension of $[\text{Ru}_3(\text{CO})_{12}]$ (500 mg) in octane (30 cm³) containing a large excess of [2.2]paracyclophane (200 mg) was heated to reflux for 3 h. Five products were formed from the reaction. The solvent was removed from the reaction solution under reduced pressure, and the products separated by column chromatography, using a solution of dichloromethane–hexane (3:7) as eluent. In order of elution, the products were characterised by spectroscopy as $[\text{Ru}_3(\text{CO})_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16})]$ (yellow, 10%), $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-C}_{16}\text{H}_{16})]$ **2** (brown, 3%), $[\text{Ru}_6\text{C}(\text{CO})_{14}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16})]$ (red, 25%), $[\text{Ru}_6\text{C}(\text{CO})_{15}(\mu_3\text{-}\sigma\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16}\text{O})]$ (purple, 5%) and $[\text{Ru}_6\text{C}(\text{CO})_{11}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16})(\eta^6\text{-C}_{16}\text{H}_{16})]$ (brown, 3%).

Spectroscopic data for **2**. IR (CH_2Cl_2): ν_{CO} 2088m, 2063s, 2028vs, 2001w (sh), 1874w cm⁻¹. ¹H NMR (CDCl_3): δ 6.78 (s, 4 H), 4.51 (s, 4 H), 3.18 (m, 4 H), 2.85 (m, 4 H), –17.80 (s, 2 H), –19.40 (s br, 2 H). Mass spectrum (*m/z*): M^+ 1524 (calc. 1525).

Reaction of $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-C}_6\text{H}_6)]$ **1 with CO in Dichloromethane.**—A steady stream of CO was bubbled through a room temperature solution of $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-C}_6\text{H}_6)]$ **1** (30 mg) in dichloromethane (20 cm³) for 5 min. The CO source was removed, the solvent removed *in vacuo* and the products isolated by TLC eluting with dichloromethane–hexane (3:7). Four products were extracted, two of which were

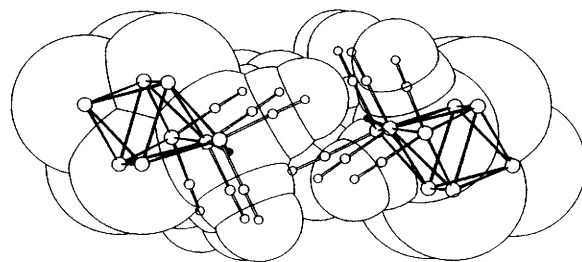


Fig. 5 Interlocking of the CO ligands bound to the long Ru(7)–Ru(1)–Ru(8) 'edges' in crystalline **1**. The two molecules are related by a crystallographic centre of inversion. The benzene ligand and the remaining CO groups are not shown for clarity

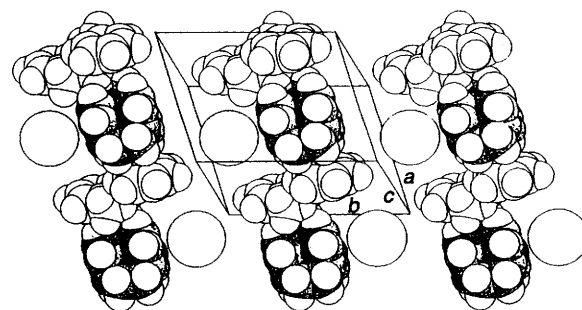


Fig. 6 Stacks of molecules extending along the *b* axis in crystalline **2**. Shaded spheres are the C($\text{C}_{16}\text{H}_{16}$) atoms, large spheres represent the centre of mass of the metal frame. Toluene solvent molecules are also shown. The CO ligands are omitted for clarity

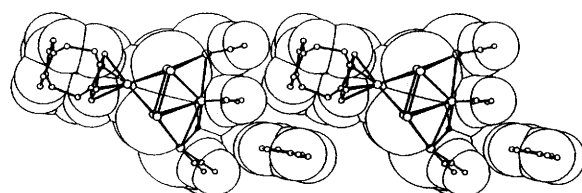


Fig. 7 Interlocking of the toluene molecule into the cavity formed by four CO ligands bound to the H(hydride) bridged Ru–Ru edge. The H($\text{C}_{16}\text{H}_{16}$) atoms and the remaining CO ligands are not shown for clarity

characterised spectroscopically as $[\text{Ru}_4\text{H}_4(\text{CO})_{12}]$ (yellow, 32%) and $[\text{Ru}_4\text{H}_2(\text{CO})_{13}]$ (orange, 40%). The other two compounds in much lower yield have not been characterised.

Reaction of $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-C}_{16}\text{H}_{16})]$ **2 with CO in Dichloromethane.**—A steady stream of CO was bubbled through a room temperature solution of $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-C}_{16}\text{H}_{16})]$ **2** (30 mg) in dichloromethane (20 cm³) for 5 min. The CO source was removed, the solvent removed *in vacuo* and the products isolated by TLC eluting with dichloromethane–hexane (3:7). Two products were extracted and characterised spectroscopically as $[\text{Ru}_3(\text{CO})_{12}]$ (yellow, 30%) and $[\text{Ru}_6\text{C}(\text{CO})_{14}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-C}_{16}\text{H}_{16})]$ (red, 62%).

Crystal Structure Determination of **1 and **2**.**—Diffraction intensities for **1** were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer equipped with a graphite monochromator (Mo-K α radiation, $\lambda = 0.71069 \text{ \AA}$). Intensity data were reduced to F_o^2 . Diffraction intensities for **2** were collected on a FAST Enraf-Nonius diffractometer. Intensity data were reduced to F_o . The structures were solved by direct methods followed by least-squares refinements. All calculations were performed using the crystallographic programs SHELX 86^{23a} and SHELXL 93.^{23b} For structure representation the molecular graphics program SCHAKAL 93²⁴ was used.

Crystal data for **1.** $\text{C}_{24}\text{H}_{10}\text{O}_{18}\text{Ru}_8$, $M = 1409.6$, monoclinic,

Table 2 Atomic coordinates ($\times 10^4$) for complex 1

| Atom | x | y | z | Atom | x | y | z |
|-------|----------|-----------|-----------|-------|-----------|-----------|-----------|
| Ru(1) | 5 212(1) | 931(1) | 6 630(1) | O(10) | 7 065(2) | 2 396(3) | 9 269(2) |
| Ru(2) | 4 812(1) | 3 222(1) | 6 555(1) | C(11) | 6 846(3) | 3 907(4) | 7 428(3) |
| Ru(3) | 3 907(1) | 1 961(1) | 7 556(1) | O(11) | 7 152(3) | 4 704(3) | 7 429(3) |
| Ru(4) | 5 501(1) | 1 299(1) | 8 415(1) | C(12) | 7 471(3) | 2 075(4) | 7 311(3) |
| Ru(5) | 5 063(1) | 3 465(1) | 8 289(1) | O(12) | 8 147(2) | 1 844(3) | 7 283(3) |
| Ru(6) | 6 377(1) | 2 600(1) | 7 431(1) | C(13) | 7 163(3) | 1 883(4) | 5 511(3) |
| Ru(7) | 6 169(1) | 2 563(1) | 5 738(1) | O(13) | 7 755(3) | 1 443(4) | 5 389(3) |
| Ru(8) | 4 302(1) | -96(1) | 7 778(1) | C(14) | 5 709(3) | 2 387(4) | 4 642(3) |
| C(1) | 4 411(3) | 454(4) | 5 809(3) | O(14) | 5 447(3) | 2 269(4) | 3 978(3) |
| O(1) | 3 918(3) | 202(3) | 5 299(2) | C(15) | 6 575(3) | 3 927(4) | 5 509(3) |
| C(2) | 5 827(3) | -320(4) | 6 639(3) | O(15) | 6 793(3) | 4 712(3) | 5 320(3) |
| O(2) | 6 204(3) | -1 054(3) | 6 622(2) | C(16) | 3 476(3) | -671(4) | 7 022(3) |
| C(3) | 4 236(3) | 3 122(4) | 5 484(3) | O(16) | 2 983(2) | -1 038(3) | 6 560(2) |
| O(3) | 3 866(3) | 3 062(4) | 4 866(2) | C(17) | 4 826(3) | -1 404(4) | 7 918(3) |
| C(4) | 5 068(4) | 4 610(4) | 6 400(4) | O(17) | 5 093(3) | -2 206(3) | 8 011(3) |
| O(4) | 5 189(4) | 5 467(3) | 6 307(4) | C(18) | 3 684(3) | -328(4) | 8 703(3) |
| C(5) | 3 706(3) | 3 545(4) | 7 083(3) | O(18) | 3 321(3) | -488(4) | 9 248(2) |
| O(5) | 3 182(2) | 4 149(3) | 7 075(2) | C(19) | 4 590(3) | 5 053(4) | 8 414(3) |
| C(6) | 2 934(3) | 1 538(4) | 6 911(4) | C(20) | 5 464(4) | 5 102(4) | 8 496(4) |
| O(6) | 2 318(3) | 1 342(4) | 6 525(3) | C(21) | 5 908(3) | 4 470(4) | 9 076(4) |
| C(7) | 3 277(4) | 1 971(4) | 8 449(4) | C(22) | 5 479(3) | 3 818(4) | 9 578(3) |
| O(7) | 2 889(3) | 1 960(3) | 8 994(3) | C(23) | 4 596(3) | 3 781(4) | 9 490(3) |
| C(8) | 6 115(3) | 55(4) | 8 645(3) | C(24) | 4 150(3) | 4 400(4) | 8 903(3) |
| O(8) | 6 497(2) | -660(3) | 8 809(2) | H(1) | 4 399(29) | 1 906(37) | 6 541(28) |
| C(9) | 5 099(3) | 1 274(4) | 9 430(3) | H(2) | 6 024(29) | 1 298(39) | 7 486(28) |
| O(9) | 4 846(3) | 1 273(3) | 10 069(2) | H(3) | 5 840(30) | 1 369(39) | 5 989(28) |
| C(10) | 6 580(3) | 2 220(5) | 8 719(3) | | | | |

Table 3 Atomic coordinates ($\times 10^4$) for complex 2

| Atom | x | y | z | Atom | x | y | z |
|-------|------------|------------|-----------|-------|------------|-----------|-----------|
| Ru(1) | 2 482(1) | 9 264(1) | 7 594(1) | C(15) | -706(15) | 8 364(13) | 6 615(11) |
| Ru(2) | 2 595(1) | 7 697(1) | 6 449(1) | O(15) | -1 317(9) | 7 954(8) | 6 377(8) |
| Ru(3) | 4 839(1) | 7 610(1) | 6 948(1) | C(16) | 5 728(14) | 9 653(12) | 7 352(11) |
| Ru(4) | 3 257(1) | 7 497(1) | 8 806(1) | O(16) | 6 324(9) | 10 173(9) | 6 944(7) |
| Ru(5) | 3 465(1) | 6 090(1) | 7 576(1) | C(17) | 4 222(12) | 9 709(11) | 9 039(10) |
| Ru(6) | 1 131(1) | 7 573(1) | 8 199(1) | O(17) | 3 920(10) | 10 224(8) | 9 595(8) |
| Ru(7) | 207(1) | 9 083(1) | 6 986(1) | C(18) | 6 231(13) | 8 031(11) | 8 533(10) |
| Ru(8) | 4 759(1) | 8 836(1) | 8 146(1) | O(18) | 7 105(10) | 7 608(9) | 8 774(7) |
| C(1) | 3 257(14) | 10 234(12) | 6 817(11) | C(19) | 3 955(12) | 4 837(11) | 6 701(10) |
| O(1) | 3 655(10) | 10 852(9) | 6 326(7) | C(20) | 2 754(14) | 4 862(12) | 7 352(11) |
| C(2) | 1 720(14) | 10 151(12) | 8 494(11) | C(21) | 2 568(12) | 4 703(11) | 8 263(10) |
| O(2) | 1 185(10) | 10 738(9) | 8 997(8) | C(22) | 3 662(12) | 4 777(11) | 8 566(11) |
| C(3) | 2 632(13) | 8 553(12) | 5 410(11) | C(23) | 4 886(12) | 4 746(11) | 7 933(10) |
| O(3) | 2 705(10) | 9 018(9) | 4 744(7) | C(24) | 5 140(13) | 4 651(11) | 7 070(10) |
| C(4) | 1 861(13) | 6 833(11) | 6 115(10) | C(25) | 6 447(13) | 4 285(11) | 6 441(11) |
| O(4) | 1 495(9) | 6 319(8) | 5 817(7) | C(26) | 6 727(14) | 3 088(12) | 6 442(11) |
| C(5) | 4 492(14) | 6 853(13) | 5 958(11) | C(27) | 5 694(13) | 2 650(12) | 7 108(11) |
| O(5) | 5 174(8) | 6 407(7) | 5 377(7) | C(28) | 4 539(14) | 2 612(12) | 6 887(12) |
| C(6) | 5 750(12) | 8 378(11) | 6 093(10) | C(29) | 3 360(14) | 2 632(12) | 7 548(11) |
| O(6) | 6 366(10) | 8 849(9) | 5 538(7) | C(30) | 3 318(13) | 2 672(12) | 8 398(11) |
| C(7) | 6 440(14) | 6 732(12) | 7 053(10) | C(31) | 4 457(13) | 2 522(11) | 8 619(11) |
| O(7) | 7 384(8) | 6 195(8) | 7 100(8) | C(32) | 5 594(14) | 2 533(12) | 7 997(11) |
| C(8) | 2 618(15) | 8 183(13) | 9 775(12) | C(33) | 1 990(13) | 3 138(11) | 9 018(11) |
| O(8) | 2 142(12) | 8 623(10) | 10 415(9) | C(34) | 1 538(13) | 4 301(11) | 8 878(10) |
| C(9) | 4 435(14) | 6 612(12) | 9 317(11) | C(35) | -1 380(15) | 6 215(14) | 4 724(12) |
| O(9) | 5 171(11) | 6 070(8) | 9 657(8) | C(36) | -628(14) | 6 498(13) | 3 796(11) |
| C(10) | 1 620(13) | 6 736(12) | 9 261(11) | C(37) | 103(11) | 5 730(11) | 3 241(9) |
| O(10) | 1 274(9) | 6 265(8) | 9 898(7) | C(38) | 773(14) | 5 977(13) | 2 373(12) |
| C(11) | 309(12) | 6 740(11) | 7 942(9) | C(39) | 791(16) | 6 957(15) | 2 103(14) |
| O(11) | -288(9) | 6 247(8) | 7 849(7) | C(40) | 80(15) | 7 640(15) | 2 683(13) |
| C(12) | -407(14) | 8 313(11) | 8 950(10) | C(41) | -601(16) | 7 466(15) | 3 500(13) |
| O(12) | -1 377(9) | 8 711(8) | 9 433(8) | H(1) | 3 339 | 8 575 | 6 600 |
| C(13) | -1 311(15) | 9 825(14) | 7 680(12) | H(2) | 1 955 | 8 369 | 8 436 |
| O(13) | -2 250(9) | 10 356(9) | 8 145(8) | H(3) | 1 239 | 10 048 | 7 200 |
| C(14) | 182(14) | 10 104(13) | 6 041(11) | H(4) | 4 286 | 6 823 | 7 889 |
| O(14) | 113(11) | 10 753(9) | 5 508(8) | | | | |

space group $P2_1/n$, $a = 15.930(7)$, $b = 12.909(5)$, $c = 16.43(2)$ Å, $\beta = 95.51(6)^\circ$, $U = 3363.1$ Å³, $Z = 4$, $D_c = 2.78$ g cm⁻³, $F(000) = 2600$, $\mu(\text{Mo-K}\alpha) = 32.81$ cm⁻¹, $3.0 < \theta < 25^\circ$, final

wR_2 (on F^2 , all data) = $[\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{\frac{1}{2}} = 0.0658$, final R_1 [on F , for 4687 unique reflections with $I > 2\sigma(I)$] = 0.0222, 6401 collected reflections, 5869 unique reflections used

in the refinement, goodness of fit (on F^2) = 1.04. All non-H atoms allowed to vibrate anisotropically. The H(benzene) atoms were added in calculated positions (C–H 0.93 Å) and refined riding on the respective C atoms. The H(benzene) atoms were refined isotropically, while thermal parameters for the three refined H(hydride) atoms were fixed to 0.05 Å².

Crystal data for 2. C₄₁H₂₈O₁₈Ru₈, $M = 1617.2$, triclinic, space group $P\bar{1}$, $a = 11.087(7)$, $b = 14.047(7)$, $c = 16.090(9)$ Å, $\alpha = 80.68(6)$, $\beta = 72.11(7)$, $\gamma = 72.91(4)^\circ$, $U = 2272$ Å³, $Z = 2$, $D_c = 2.36$ g cm⁻³, $F(000) = 1540$, $\mu(\text{Mo-K}\alpha) = 26.58$ cm⁻¹, $2.0 < \theta < 27^\circ$, final wR_2 (on F , all data) = 0.1169, final R_1 [on F , for 2266 unique reflections with $I > 2\sigma(I)$] = 0.0455, 10 726 collected reflections, 7506 unique reflections used in the refinement, goodness of fit (on F^2) = 1.42. The Ru and O atoms were allowed to vibrate anisotropically. The H(C₁₆H₁₆) atoms were added in calculated positions [C_(sp³)–H 0.93, C_(sp³)–H 0.96 Å] and refined riding on the respective C atoms. The C and H(C₁₆H₁₆) atoms were refined isotropically, while thermal parameters for the H(hydride) atoms were fixed to 0.05 Å².

Fractional atomic coordinates of **1** and **2** are reported in Tables 2 and 3, respectively.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We thank Professor Michael B. Hursthouse and Dr. Alexander Karaulov (Cardiff) for collecting the X-ray data (FAST Enraf-Nonius diffractometer) for compound **2**. Financial support from the SERC (to C. M. M.) and the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (to D. B., F. G.) is acknowledged. D. B., F. G. and B. F. G. J. thank NATO for a travel grant.

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Received 14th September 1994; Paper 4/05598E