Synthesis of $[M_3H(CO)_9(\mu_3\text{-}\sigma:\eta^2:\eta^2\text{-}C_6H_7)]$ (M = Ru or Os). Molecular and Crystal Structure of the Ruthenium Cluster†

Dario Braga,[*,a] **Fabrizia Grepioni,**[a] **Emilio Parisini,**[a] **Brian F. G. Johnson,**[*,b] **Caroline M. Martin,**[b] **Jacqueline G. M. Nairn,**[b] **Jack Lewis**[*,c] **and Marcia Martinelli**[c]
[a] *Dipartimento di Chimica 'G. Ciamician', Università di Bologna, Via Selmi 2, 40126 Bologna, Italy*
[b] *University of Edinburgh, Department of Chemistry, West Mains Road, Edinburgh EH9 3JJ, UK*
[c] *University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, UK*

The dienyl cluster compounds $[M_3H(CO)_9(\mu_3\text{-}\sigma:\eta^2:\eta^2\text{-}C_6H_7)]$ (M = Ru or Os) have been synthesised from $[Os_3H_2(CO)_{10}]$ or $[M_3(CO)_{10}(MeCN)_2]$ (M = Ru or Os) with cyclohexa-1,3-diene. The molecular and crystal structure of $[Ru_3H(CO)_9(C_6H_7)]$ has been established by single-crystal X-ray diffraction analysis: monoclinic, space group $P2_1$, $a = 8.487(6)$, $b = 12.031(3)$, $c = 9.073(2)$ Å, $\beta = 92.43(4)°$ and $Z = 2$. The cyclohexadienyl ligand is involved in one σ and two π interactions with the metal triangle, while the H(hydride) ligand bridges the long Ru–Ru bond [3.052(1) Å]. The other two Ru–Ru bond lengths are the same [2.837(1) Å] and comparable to those observed in $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$. The H(hydride) position afforded by the diffraction experiment has been compared with the result of potential-energy minimization procedures. The molecular organization within the lattice has been explored by means of atom–atom packing potential-energy calculations showing the presence of a network of C–H $\cdots$ O intermolecular hydrogen-bonding interactions.

An ever increasing number of structurally characterised benzene-containing cluster compounds have been found to exhibit either the terminal (η^6) or face-capping ($\mu_3\text{-}\eta^2:\eta^2:\eta^2$) bonding mode or both.[1–11] Furthermore, it has been established that the benzene ligand is able to migrate from one bonding mode to the other either as the result of isomerisation (as is the case with certain derivatives of the Ru_6C cluster units)[9a] or of chemical reaction, as observed in the formation of $[Ru_3(CO)_7(\mu\text{-}\eta^2\text{-}RC_2R'CO)(\eta^6\text{-}C_6H_6)]$ (R = R′ = H, Ph or Me; R = Ph, R′ = H) and $[Os_3(CO)_7(\mu_3\text{-}\eta^2\text{-}Me_2C_2)(\eta^6\text{-}C_6H_6)]$[12] Earlier in our studies of these systems we noted[7] that one of the products of the reaction of $[Os_3H_2(CO)_{10}]$ with cyclohexa-1,3-diene was the stable dienyl cluster $[Os_3H(CO)_9(C_6H_7)]$ with a face-capping dienyl moiety. Later, in related studies of the corresponding ruthenium systems, we made a brief report of the synthesis and full structural characterisation of the analogous ruthenium compound $[Ru_3H(CO)_9(C_6H_7)]$.[11]

As in the case of benzene, an established and well developed co-ordination chemistry is known for mononuclear systems containing the cyclohexadienyl group. In particular, the cation $[Fe(CO)_3(C_6H_7)]^+$ has proved to be especially fruitful.[13] On passing from mononuclear to cluster compounds there are alternative bonding modes, *viz.* to a single metal atom, in a bridging and in a face-capping configuration. In this paper we present a full report of the synthesis of two rare examples of face-capping dienyl clusters, *viz.* $[Ru_3H(CO)_9(C_6H_7)]$ and $[Os_3H(CO)_9(C_6H_7)]$. In addition, we discuss in some detail the molecular and crystal structure of the former derivative. We have recently been focusing our attention on the molecular organisation in the crystals of some arene clusters.[13] We have been able to show that the arene fragments tend to establish graphitic-like arene–arene intermolecular interactions upon crystal formation and that these interactions control the ease of arene reorientational motion in the solid state.[14] In order to investigate the lattice organisation in crystalline $[Ru_3H(CO)_9(C_6H_7)]$ we have applied methods based on empirical atom–atom packing potential-energy calculations. These methods were previously applied to the investigation of crystalline mono- and poly-nuclear complexes and cluster molecules and ions.[15]

Results and Discussion

On stirring a solution of the highly reactive dihydrido-cluster $[Os_3H_2(CO)_{10}]$ and an excess of cyclohexa-1,3-diene in hexane at 25 °C for 40 h a mixture of two products was obtained (see Scheme 1). After separation by TLC on silica the major yellow product was identified as the simple substituted derivative $[Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)]$ **1b** with a terminal bonded cyclohexa-1,3-diene ligand. Initial identification was based on its spectroscopic properties, particularly the ^1H NMR spectrum which is similar to that reported for $[Fe(CO)_3(C_6H_8)]$.[16] The second product of this reaction, also a yellow and air-stable solid, possessed spectroscopic properties consistent with the formulation $[Os_3H(CO)_9(C_6H_7)]$ **2b**. Again the molecular characterisation of this product rested initially on the ^1H NMR spectrum which exhibited signals at δ 5.88 (1 H, t), 5.44 (1 H, d), 4.77 (1 H, dd), 2.94 (2 H, d), 2.70 (1 H, d) and −29.3 (1 H, d). This is entirely consistent with the molecular structure established by single-crystal X-ray diffraction and with the spectrum obtained for the corresponding ruthenium compound (see Table 1) except that the resonances are shifted slightly to higher field.

When the reaction between $[Os_3H_2(CO)_{10}]$ and cyclohexa-1,3-diene was carried out in octane under reflux, all of the complex was consumed after *ca.* 5 min to give mainly the dienyl cluster **2b** and only very small amounts of **1b**. We have further observed that on heating pure samples of **1b** in octane under the same conditions no conversion into $[Os_3H_2(CO)_{10}]$ occurred. Instead only small amounts of the dienyl osmium cluster were obtained leading us to suspect, at least initially, that the reaction of this complex with cyclohexa-1,3-diene proceeded according to Scheme 2. In this we speculate that before conversion of **1b** into **2b** takes place a second isomeric form of **1b**, *viz.* **I**, in which the diene is now bonded to two metal atoms in a manner we

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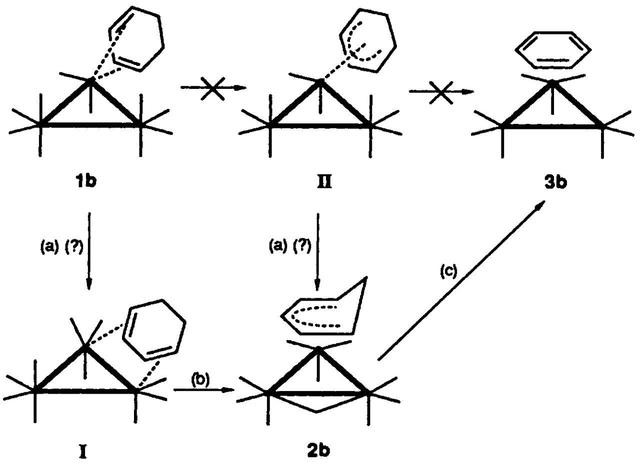
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

$$[Os_3H_2(CO)_{10}] \xrightarrow{(i)} \underset{\mathbf{1b}}{[Os_3(CO)_{10}(C_6H_8)]} + \underset{\mathbf{2b}}{[Os_3H(CO)_9(C_6H_7)]}$$

Scheme 1 (*i*) Cyclohexa-1,3-diene, hexane, 25 °C, 50 min



Scheme 2 Possible reaction sequence for the formation of complex **2b** (*a*) Isomerisation (?); (*b*) CO loss, followed by C–H bond cleavage; (*c*) C–H bond cleavage and loss of H_2

$$\underset{M\,=\,Ru\ or\ Os}{[M_3(CO)_{12}]} \xrightarrow{(i)} [M_3(CO)_{10}(MeCN)_2] \xrightarrow{(ii)}$$

$$\underset{\mathbf{1b}\ M\,=\,Os}{[M_3(CO)_{10}(C_6H_8)]} + \underset{\substack{\mathbf{2a}\ M\,=\,Ru\\ \mathbf{2b}\ M\,=\,Os}}{[M_3H(CO)_9(C_6H_7)]} + \underset{\mathbf{3a}\ M\,=\,Ru}{[M_3(CO)_9(C_6H_6)]}$$

Scheme 3 (*i*) $Me_3NO–CH_2Cl_2$ solution added dropwise to the reaction solution of CH_2Cl_2–MeCN at −78 °C; (*ii*) refluxing octane in the presence of cyclohexa-1,3-diene

have previously described for certain Ru_6C and Ru_5C cluster units,[9] must be available. However, to date no definite evidence for this second isomer has been found.

These observations, together with the fact that $[Ru_3H_2(CO)_{10}]$ is not available, led us to seek an alternative route to the required compounds **2a** and **2b**. In this the activated clusters $[M_3(CO)_{10}(MeCN)_2]$ (M = Ru or Os) were employed (see Scheme 3). These clusters have MeCN ligands bonded to two individual metal atoms and might be expected to lead to bridging diene complexes such as **I**. Basically, the same procedure was adopted for both Ru and Os; however, the product distribution was found to be different in each case. The ruthenium compound $[Ru_3(CO)_{10}(MeCN)_2]$ reacted with cyclohexa-1,3-diene to form primarily $[Ru_3(CO)_{12}]$ (*ca.* 40%) and $[Ru_3H(CO)_9(C_6H_7)]$ **2a** (*ca.* 30%) together with small amounts of $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ (*ca.* 3%). Significantly, none of the diene derivative $[Ru_3(CO)_9(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$ **1a** was observed. The required product **2a** was initially characterised on the basis of its ^1H NMR spectroscopic data which are very similar to those for the corresponding osmium derivative **2b** (see Table 1). The molecular structure of **2a** was fully established on the basis of a single-crystal X-ray diffraction analysis (see below).

In the corresponding reaction of $[Os_3(CO)_{10}(MeCN)_2]$ the products $[Os_3H(CO)_9(C_6H_7)]$ **2b** and $[Os_3(CO)_{10}(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$ **1b** were observed. In contrast to the behaviour shown by the ruthenium analogue, no evidence for the benzene cluster **3b** was found. Surprisingly in view of the structure of $[Os_3(CO)_{10}(MeCN)_2]$, the spectroscopic data for **1b** indicated that the 'terminal' isomer had again been formed.

Molecular Structure of $[Ru_3H(CO)_9(\mu_3\text{-}\sigma:\eta^2:\eta^2\text{-}C_6H_7)]$ *in the Solid State.*—The molecular structure of $[Ru_3H(CO)_9(\mu_3\text{-}\sigma:\eta^2:\eta^2\text{-}C_6H_7)]$ **2a** in the solid state has been determined by single-crystal X-ray diffraction (Fig. 1). Fractional atomic coordinates are listed in Table 2, relevant bond distances and angles in Table 3. Although the diffraction experiment was carried out at room temperature, the data were of high accuracy so as to allow confident discussion of fine structural details and direct location of the H atoms belonging to the C_6H_7 ligand of the H(hydride) atom (see below).

Table 1 Spectroscopic and analytical data for the dienyl cluster compounds $[M_3H(CO)_9(C_6H_7)]$ (M = Ru **2a** or Os **2b**)

	2a	**2b**
^1H NMR ($CDCl_3$), δ	4.93 (1 H, t)	5.88 (1 H, t)
	4.04 (2 H, d)	5.44 (1 H, d)
	3.68 (1 H, dd)	4.77 (1 H, dd)
	2.95 (2 H, d)	2.94 (2 H, d)
	2.17 (1 H, d)	2.70 (1 H, d)
	−21.16 (1 H, d)	−29.30 (1 H, d)
IR (CH_2Cl_2), ν(CO)/cm^{-1}	2083m	2080m
	2055s	2058s
	2032vs	2034vs
	2008m (br)	2021s
	1958m	1992s
		1960m
		1953m
Microanalysis (%)*	C 28.50	19.95
	(28.35)	(19.95)
	M 1.30	0.85
	(1.25)	(0.90)

* Calculated values in parentheses.

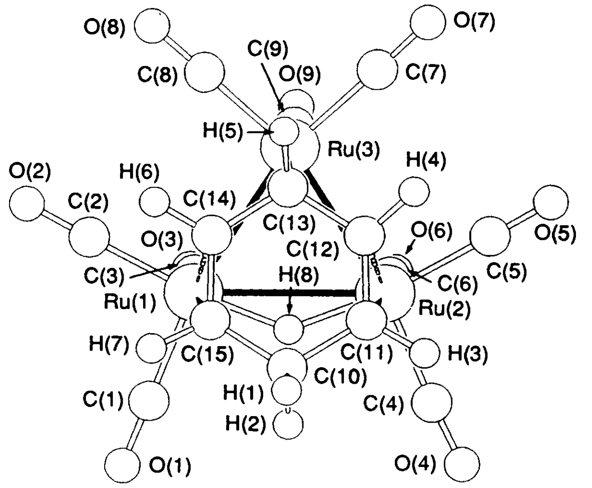


Fig. 1 Molecular structure of $[Ru_3H(CO)_9(C_6H_7)]$ **2a** showing the labelling scheme

The C_6H_7 ligand interacts with the three Ru atoms *via* one σ interaction [Ru(3)–C(13) 2.177(4) Å] and two π interactions [Ru(1)–C(14) 2.441(4), Ru(1)–C(15) 2.307(4); Ru(2)–C(11) 2.278(4), Ru(2)–C(12) 2.431(4) Å] thus formally contributing a total of five electrons to the cluster orbitals.

It is interesting to recall here that, upon dehydrogenation, the neutral species first yields the cation $[Ru_3H(CO)_9(C_6H_6)]^+$, which then evolves, in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (dbu) to the face-capped benzene cluster $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$.[11,13] The reaction, therefore, implies a change of ligand-to-metal co-ordination from a situation in which one C atom [C(13)] is eclipsed over a Ru atom (and the C=C double bonds are in 1,4 position) to the complete staggering of the C atoms with respect to the underlying metal atoms. The bond-length distribution with the C_6H_7 ligand agrees with the bonding pattern discussed above: there is delocalisation within the flat C(11)–C(12)–

Table 2 Fractional atomic coordinates for compound **2a**

Atom	x	y	z
Ru(1)	0.246 47(3)	0.608 58	0.803 11(3)
Ru(2)	0.158 29(3)	0.764 19(4)	0.547 05(3)
Ru(3)	0.245 50(3)	0.843 23(3)	0.833 66(3)
C(1)	0.244 5(6)	0.456 9(4)	0.741 7(6)
O(1)	0.238 7(7)	0.366 4(4)	0.706 3(6)
C(2)	0.322 9(5)	0.582 8(4)	0.998 9(6)
O(2)	0.371 0(6)	0.567 6(5)	1.115 7(5)
C(3)	0.035 8(5)	0.613 3(5)	0.867 0(4)
O(3)	−0.089 7(4)	0.607 2(4)	0.905 9(5)
C(4)	0.111 7(6)	0.686 0(6)	0.364 9(5)
O(4)	0.077 5(7)	0.644 4(8)	0.257 6(6)
C(5)	0.138 9(6)	0.911 4(5)	0.468 6(6)
O(5)	0.127 2(6)	0.997 6(5)	0.423 0(7)
C(6)	−0.053 9(5)	0.770 9(5)	0.604 7(5)
O(6)	−0.182 7(4)	0.771 7(5)	0.629 6(5)
C(7)	0.263 3(6)	0.999 4(4)	0.796 8(6)
O(7)	0.273 6(6)	1.091 4(4)	0.777 4(7)
C(8)	0.333 0(7)	0.853 8(5)	1.025 6(6)
O(8)	0.386 4(10)	0.860 5(6)	1.142 5(5)
C(9)	0.030 5(5)	0.853 7(5)	0.897 2(6)
O(9)	−0.090 4(5)	0.868 0(5)	0.942 1(6)
C(10)	0.477 8(5)	0.625 2(4)	0.533 0(5)
C(11)	0.414 1(4)	0.738 1(4)	0.488 7(5)
C(12)	0.429 5(4)	0.825 8(3)	0.586 5(5)
C(13)	0.474 5(4)	0.814 1(4)	0.741 3(5)
C(14)	0.501 5(4)	0.701 1(4)	0.790 2(5)
C(15)	0.488 6(5)	0.610 1(4)	0.696 9(5)
H(1)	0.576(4)	0.611(6)	0.491(6)
H(2)	0.412(6)	0.569(4)	0.488(6)
H(3)	0.406(7)	0.750(6)	0.385(2)
H(4)	0.437(7)	0.903(1)	0.568(6)
H(5)	0.539(6)	0.868(4)	0.791(6)
H(6)	0.552(6)	0.692(5)	0.885(3)
H(7)	0.537(7)	0.543(3)	0.732(6)
H(8)*	0.206(9)	0.648(3)	0.632(3)

* Calculated for M–H 1.79 Å: 0.1579, 0.6268, 0.6222.

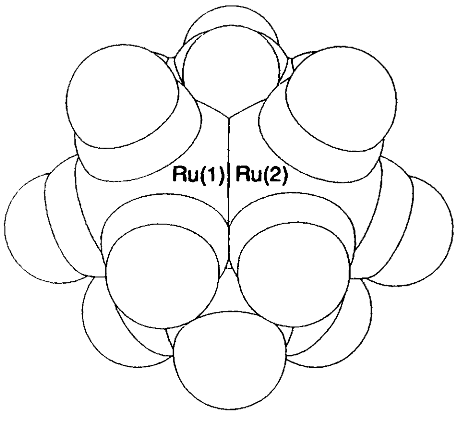


Fig. 2 Space-filling diagram of compound **2a** showing the niche in the carbonyl ligands envelope

C(13)–C(14)–C(15) moiety with two short C=C bonds for the two π interactions [C(11)–C(12) 1.38(1), C(14)–C(15) 1.39(1) Å] and two long C–C bonds involving the C atom σ bonded to the cluster [C(12)–C(13) 1.45(1), C(14)–C(13) 1.45(1) Å]. These values compare well with the 'alternating' long–short C–C bonds observed in [$Ru_3(CO)_9(\mu_3\text{-}\eta^2\!:\!\eta^2\!:\!\eta^2\text{-}C_6H_6)$] [1.45(1) *vs.* 1.40(2) Å at room temperature]. The C–C(CH_2) bond lengths are, as expected, of the σ-bond type, *i.e.* C(10)–C(11) 1.51(1), C(10)–C(15) 1.50(1) Å. As in the case of the benzene cluster there is a clear out-of-plane bending of the H atoms bound to the unsaturated C atoms and to C(13) (mean elevation from the plane 0.29 Å).

Table 3 Selected bond distances (Å) and angles (°) for [$Ru_3H(CO)_9(C_6H_7)$]

Ru(1)–Ru(2)	3.052(1)	C(1)–O(1)	1.14(1)
Ru(2)–Ru(3)	2.837(1)	C(2)–O(2)	1.13(1)
Ru(1)–Ru(3)	2.837(1)	C(4)–O(4)	1.12(1)
Ru(1)–H(8)	1.65(2)	C(5)–O(5)	1.12(1)
Ru(2)–H(8)	1.64(2)	C(7)–O(7)	1.12(1)
Ru(1)–C(1)	1.908(5)	C(8)–O(8)	1.14(1)
Ru(1)–C(2)	1.891(5)	C(3)–O(3)	1.14(1)
Ru(2)–C(4)	1.928(5)	C(6)–O(6)	1.13(1)
Ru(2)–C(5)	1.913(5)	C(9)–O(9)	1.13(1)
Ru(3)–C(7)	1.916(5)	C(10)–C(11)	1.51(1)
Ru(3)–C(8)	1.869(5)	C(11)–C(12)	1.38(1)
Ru(1)–C(3)	1.904(4)	C(12)–C(13)	1.45(1)
Ru(2)–C(6)	1.898(4)	C(13)–C(14)	1.45(1)
Ru(3)–C(9)	1.941(4)	C(14)–C(15)	1.39(1)
Ru(1)–C(14)	2.441(4)	C(10)–C(15)	1.50(1)
Ru(1)–C(15)	2.307(4)		
Ru(2)–C(11)	2.278(4)	Ru–C(CO)$_{radial}$	1.904(5) (mean)
Ru(2)–C(12)	2.431(4)	C–O$_{radial}$	1.31(1) (mean)
Ru(3)–C(13)	2.177(4)		
Ru(1)–H(8)–Ru(2)	137(2)	C(10)–C(11)–C(12)	119.5(4)
Ru(1)–C(1)–O(1)	177.9(5)	C(11)–C(12)–C(13)	124.3(4)
Ru(1)–C(2)–O(2)	179.0(5)	C(12)–C(13)–C(14)	114.9(4)
Ru(1)–C(3)–O(3)	174.6(5)	C(13)–C(14)–C(15)	123.3(4)
Ru(2)–C(4)–O(4)	176.1(7)	C(15)–C(10)–C(11)	112.3(4)
Ru(2)–C(5)–O(5)	179.8(2)	C(14)–C(15)–C(10)	120.7(4)
Ru(2)–C(6)–O(6)	175.2(5)		
Ru(3)–C(7)–O(7)	179.0(5)		
Ru(3)–C(8)–O(8)	179.8(2)		
Ru(3)–C(9)–O(9)	173.6(5)		

Altogether it would appear that the bonding between the C_6H_7 fragment and the cluster is rather strained: the entire ligand is shifted and tilted with respect to the Ru_3 triangle in order to achieve the best compromise between ligand-to-cluster bonding and steric interactions between the metal atoms and the CH_2 fragment.

The H(hydride) atom could be located directly from the Fourier maps. Its position is, however, somewhat unusual being almost coplanar with the ruthenium triangle and close to the Ru–Ru bond. Although great caution is needed in discussing H(hydride) locations from X-ray diffraction experiments, we note that the space-filling diagram shows a large niche in correspondence with the midpoint of this bond (see Fig. 2). The CO ligands lying around the site [C(1)O(1), C(2)O(2), C(4)O(4), C(5)O(5)] are 'pushed away' from the centre of the Ru(1)–Ru(2) bond, which is very long [3.052(1) Å], while the other two Ru–Ru bonds are appreciably shorter and of the same length [2.837(1) Å]. The last two bonds are strictly comparable to those observed in [$Ru_3(CO)_9(\mu_3\text{-}\eta^2\!:\!\eta^2\!:\!\eta^2\text{-}C_6H_6)$] [range 2.829(1)–2.855(1), mean 2.837(1) Å]. Altogether the molecular symmetry is C_s-*m* with the idealised mirror plane bisecting the cluster and comprising Ru(3) and the H(hydride) atom as well as the CH_2 group of the C_6H_7 ligand.

It is worth noting that the CO ligand '*trans*' to the Ru–C σ interaction discussed above shows a long Ru–C bond [Ru(3)–C(9) 1.941(4) Å] in agreement with a bonding picture involving a decreased need for back donation from the 'electron-poor' Ru(3) atom. The small differences in bond length among the remaining six CO ligands are too close to the standard deviations of each individual parameter to be trustworthy. The Ru–C and C–O distances for the radial ligands range from 1.869(5) to 1.928(5) and from 1.12(1) to 1.14(1) Å, respectively [mean 1.904(5), 1.13(1) Å], while the two other axial ligands show mean values of 1.901(4) and 1.14(1) Å.

Hydride location and crystal structure. The position of the hydride ligand afforded by the X-ray experiment (see Fig. 3) deserves a more detailed examination, if not else because its

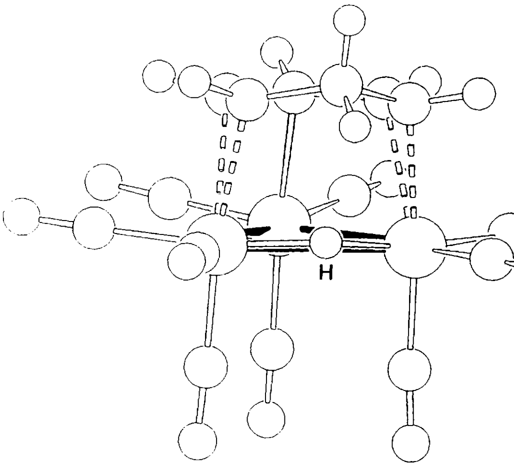


Fig. 3 Front view of compound **2a** showing the X-ray observed position of the H(hydride) atom [H(8)] which is located slightly above the plane formed by the Ru atoms

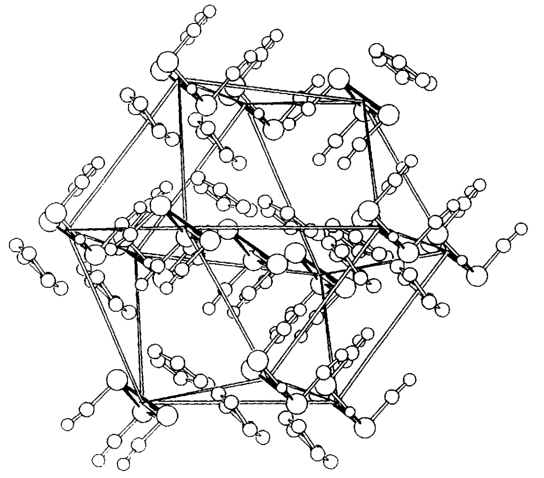


Fig. 4 Enclosure shell of $[Ru_3H(CO)_9(C_6H_7)]$ showing the A/B/C sequence of layers in the cubo-octahedral arrangement. Carbonyl groups omitted for clarity

distance relative to the metal atoms is shorter [1.65(2) Å] than one may expect on the basis of previous neutron diffraction studies conducted on analogous systems.[17] The program XHYDEX[18] was then used to calculate the site of minimum potential energy within the ligand envelope. If the experimental distance between the hydride and the connected metal atoms is chosen to constrain the hydride position, the most stable calculated position closely resembles that found by X-ray analysis, with the hydride nearly coplanar to the triangular metal core. Lengthening of the Ru–H distance to the value of 1.79 Å observed in $[Ru_3H(CO)_9(CCCMe_3)]$[19] leads to a slight bending of the hydride towards an intermediate position within the cavity shown in Fig. 2. The H-atom coordinates obtained by XHYDEX as well as those resulting from the X-ray analysis are reported in Table 2.

The packing arrangement in the crystal lattice has been investigated by means of approximate packing potential-energy (p.p.e.) calculations. The Buckingham potential function p.p.e. = $\Sigma_{ij}[A\exp(-Br_{ij}) - Cr_{ij}^{-6}]$ was used to select (within a sphere of radius of 15 Å) an 'enclosure shell' of molecules around the reference molecule.[14] This interaction energy is calculated by running the index i in the summation over all atoms of the reference molecule and j over the atoms of the neighbouring molecule generated by space-group symmetry; r_{ij} represents the distance between the pairs of atoms in turn involved in the calculation.

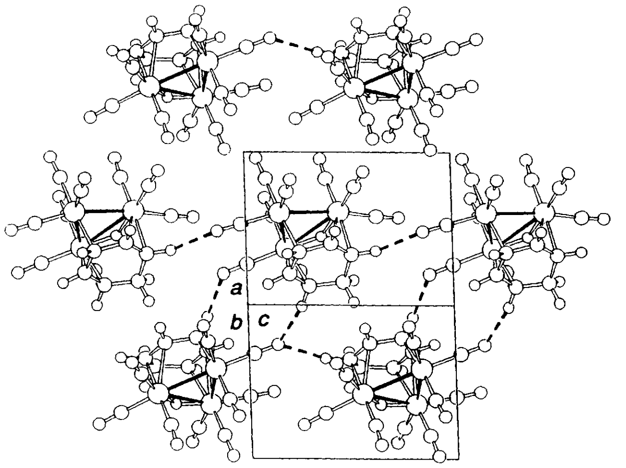


Fig. 5 View of the 110 plane in the monoclinic lattice of $[Ru_3H(CO)_9(C_6H_7)]$ showing the diffuse network of hydrogen-bonding interactions

The enclosure shell of compound **2a** is shown in Fig. 4. In the immediate surroundings of the reference molecule there are 12 molecules distributed in a cubo-octahedral fashion (A/B/C sequence of layers). These molecules contribute most of the cohesive energy in crystalline **2a**. It is worth recalling here that in a previous study[13] we found that molecules of the benzene clusters $[Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ **3a** and $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ are packed in anti- and in cubo-octahedral structures, respectively. The main difference between crystalline $[Ru_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ and **2a** arises from the relative orientation of the benzene ligands in the latter crystal with respect to that of the C_6H_7 ligand in the former. During this analysis we observed the presence of some repulsive H • • • O interactions between the H atoms belonging to the C_6H_7 ligand and the carbonyl groups. This led us to suspect the existence of a network of CH • • • O(CO) intermolecular interactions of the kind recently found in crystalline $[Ir_4(CO)_9(SCH_2)_3]$.[20] The role of this type of hydrogen-bonding interaction in contributing to crystal cohesion has recently been discussed in a comprehensive way by Desiraju.[21]

Fig. 5 shows the 110 plane of the monoclinic lattice. The set of calculated C–H • • • O distances which are below 2.6 Å [H(7) • • • O(8), H(3) • • • O(8), H(5) • • O(2) are 2.42, 2.45 and 2.53 Å respectively] gives evidence of a diffuse network of hydrogen-bonding interactions (note that the H atom positions are those preserving the experimental inclination with respect to the plane of the ring, with C–H distances of 1.08 Å). Their influence on the packing mode observed could somehow be decisive, although their importance in the crystallisation process is not understood. No short C–H • • • O interactions involving the hydride ligand have been observed.

Experimental

All reactions were carried out under an atmosphere of nitrogen, using dry, freshly distilled solvents. Subsequent work-up of products was carried out by thin-layer chromatography on Merck plates coated with a 0.25 mm layer of Kieselgel 60F-254. Trimethylamine *N*-oxide was sublimed immediately prior to use. Infrared spectra were recorded on a Perkin Elmer 1600 Series FTIR spectrometer in CH_2Cl_2, using NaCl cells (path length 0.5 mm), fast atom bombardment mass spectra on a Kratos MS5OTC using CsI as calibrant and ^1H NMR spectra in $CDCl_3$ using a Bruker WP200 instrument calibrated with $SiMe_4$.

Preparations.—$[Ru_3H(CO)_9(C_6H_7)]$ **2a**. The compound $[Ru_3(CO)_{12}]$ (64 mg, 0.1 mol equivalent) was dissolved in CH_2Cl_2 (100 cm^3), cyclohexa-1,3-diene (1 cm^3) added and the solution cooled to −78 °C. A solution of Me_3NO (38 mg, 3.2 mol equivalents) in CH_2Cl_2 (10 cm^3) was then added dropwise over 30 min. The mixture was allowed to warm to room temperature and stirred for 1 h. The solvent was evaporated *in vacuo* and the products separated by thin-layer chromatography using CH_2Cl_2 (30%)–hexane (70%) as eluent, resulting in the isolation of $[Ru_3H(CO)_9(C_6H_7)]$ **2a** (36%), $[Ru_3(CO)_9(C_6H_6)]$ **3a** (24%) and $[Ru_3H(CO)_6(C_6H_6)(C_6H_7)]$ (≈1%).

$[Os_3(CO)_{10}(MeCN)_2]$. The compound $[Os_3(CO)_{12}]$ (0.5 g) was suspended in CH_2Cl_2 (70 cm^3) and MeCN (35 cm^3) and Me_3NO (105 mg, 2.5 mol equivalents) dissolved in MeCN (50 cm^3) was added dropwise over 1 h. The resulting solution was stirred for 2 h and then filtered through a short silica column (4 cm) to remove any unreacted Me_3NO. The product was used without further purification.

$[Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)]$ **1b**. The best method of obtaining compound **1b** was the following: $[Os_3(CO)_{10}(MeCN)_2]$ (0.45 g) was dissolved in CH_2Cl_2 (100 cm^3) and cyclohexa-1,3-diene (1.5 cm^3) added. The reaction mixture was then stirred for 1 h. The solvent was removed *in vacuo* and purification by thin-layer chromatography using CH_2Cl_2 (40%)–hexane (60%) as eluent afforded $[Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)]$ **1b**, which was then crystallised from toluene (yield 90%). IR (CH_2Cl_2): ν(CO) 2110m, 2060s, 2023s, 2004m and 1975 (sh) cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.27 (2 H, m), 3.77 (2 H, m) and 1.86 (4 H, m).

$[Os_3H(CO)_9(C_6H_7)]$ **2b**, *Method A*. The compound $[Os_3(CO)_{10}(\eta^4\text{-}C_6H_8)]$ (0.40 g) was heated in octane (100 cm^3) under reflux at 125 °C. After removal of the solvent *in vacuo* the solid residue was extracted into dichloromethane (10 cm^3). After purification by thin-layer chromatography with CH_2Cl_2 (40%)–hexane (60%) as eluent the complex $[Os_3H(CO)_9(C_6H_7)]$ **2b** (≈5%) was obtained.

$[Os_3H_2(CO)_{10}]$. Hydrogen gas was passed through a solution of $[Os_3(CO)_{12}]$ (400 mg) in octane (500 cm^3) under reflux at 125 °C for 2.5–3 h. The purple solution was allowed to cool and the solvent volume reduced *in vacuo* to *ca.* 150 cm^3. After standing the supernatant liquor was decanted from any precipitated unreacted $[Os_3(CO)_{12}]$. The octane solution was used directly in the preparation of the cyclohexadienyl complex $[Os_3H(CO)_9(\mu_3\text{-}\sigma:\eta^2:\eta^2\text{-}C_6H_7)]$ **2b**. The pure product could be isolated as purple crystals by TLC separation of the crude material, eluting with CH_2Cl_2 (30%)–hexane (70%) and crystallising from CH_2Cl_2–hexane. IR (CH_2Cl_2): ν(CO) 2074s, 2060s, 2022vs, 2007m and 1980m cm^{-1}. ^1H NMR ($CDCl_3$): δ −11.48 (1 H, s).

$[Os_3H(CO)_9(C_6H_7)]$ **2b**, *Method B*. The complex was prepared by the following modification of the literature procedure. Cyclohexa-1,3-diene (1.5 cm^3) was added to an octane solution of $[Os_3H_2(CO)_{10}]$ prepared as above and the mixture heated under reflux at 125 °C for 50 min. The solvent was removed *in vacuo* and the yellow residue extracted with CH_2Cl_2 (25 cm^3). Filtration to remove any precipitated $[Os_3(CO)_{12}]$ gave a solution of $[Os_3H(CO)_9(\mu_3\text{-}\sigma:\eta^2:\eta^2\text{-}C_6H_7)]$ which was typically converted into cationic $[Os_3H(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)][BF_4]$ by reaction with $[Ph_3C][BF_4]$. The pure product could be isolated as pale yellow crystals by TLC separation of the crude material, eluting with CH_2Cl_2 (30%)–hexane (70%) and crystallising from CH_2Cl_2–hexane. IR (CH_2Cl_2): ν(CO) 2086m, 2058s, 2030vs, 2007m, 1993m and 1942w cm^{-1}. ^1H NMR ($CDCl_3$): δ 5.77 (1 H, t), 5.36 (1 H, m), 4.64 (2 H, dd), 2.82 (2 H, m), 2.60 (1 H, dt) and −19.35 (1 H, d).

Structural Characterisation of **2a**.—*Crystal data.* $C_{15}H_8O_9Ru_3$, $M = 637.3$, crystal dimensions 0.12 × 0.15 × 0.10 mm, monoclinic, space group $P2_1$, $a = 8.487(6)$, $b = 12.031(3)$, $c = 9.073(2)$ Å, $\beta = 92.43(4)°$, $U = 926$ Å^3, $Z = 2$, $D_c = 2.29$ g cm^{-3}, $F(000) = 604$, μ(Mo-Kα) = 22.31 cm^{-1}, $2.5 < \theta < 28°$, $R = 0.017$, $R'\{= \Sigma[(F_o - F_c)w^{\frac{1}{2}}]/\Sigma(F_o w^{\frac{1}{2}})\} = 0.029$ for 2228 out of 2414 independent reflections $[I > 2\sigma(I)]$.

Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer by the ω–2θ scan method using Mo-Kα radiation (λ = 0.710 69 Å). The structure was solved by direct methods and refined by full matrix least squares. For all calculations the crystallographic program SHELX 76 was used.[22] Difference maps showed weak peaks at expected H atom positions. These positions were refined with constraints on the C–H distances [C–H(CH_2) and C–H(CH) 0.95, Ru–H(hydride) 1.64 Å]. Three isotropic thermal parameters were refined for H(CH_2), H(CH) and H(hydride) atoms (0.07, 0.06 and 0.08 Å^2, respectively). All non-H atoms were allowed to vibrate anisotropically.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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