Synthesis and Characterisation of Two Clusters $[Ru_8(\mu\text{-}H)_2(\mu_6\text{-}\eta^2\text{-}CO)(CO)_{19}(\eta^6\text{-}C_{16}H_{16})]$ and $[Ru_8(\mu_6\text{-}\eta^2\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$ having an Unusual Metal Geometry and Considerable Elongation of the μ_6-C–O Bond†

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The [2.2]paracyclophane octanuclear clusters $[Ru_8(\mu\text{-}H)_2(\mu_6\text{-}\eta^2\text{-}CO)(CO)_{19}(\eta^6\text{-}C_{16}H_{16})]$ **1** and $[Ru_8(\mu_6\text{-}\eta^2\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$ **2** have been isolated as by-products from the thermal reaction between $[Ru_3(CO)_{12}]$ and [2.2]paracyclophane in heptane. Compounds **1** and **2** have been characterised in the solid-state by X-ray crystallography. Their metal cores are similar, consisting of square-based pyramidal units in which two edges have been bridged by two fused Ru atoms; this edge is also bridged by a Ru atom. In both **1** and **2** one of the carbon monoxide groups bonds to six of the Ru atoms *via* a $\mu_6\text{-}\eta^2$ interaction resulting in considerable elongation of the C–O bond. Compounds **1** and **2** are possible intermediates in the carbide-generating reaction in which $[Ru_8(\mu\text{-}H)_4(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$ undergoes quantitative conversion into $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ and $[Ru_3(CO)_{12}]$.

Investigations into arene cluster compounds were stimulated by the discovery of benzene bonded in the face-capping mode in the two complexes $[Ru_6C(CO)_{11}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ and $[Os_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$.[1] Interest was initially focused on the relevance of this bonding mode as a model for chemisorbed benzene.[2] Whilst this relationship is still under examination, a variety of other, but equally interesting phenomena have been discovered as a direct result of studies involving arene clusters. For example several bis(arene) clusters have been found to form macromolecular chains in the solid state; adjacent molecules are linked by relatively short interarene interactions, typically of the same order as those between the layers in graphite, which may result in materials with interesting properties.[3]

An aspect of cluster chemistry which has benefited from these studies is that involving carbide formation, which has relevance to the Fischer–Tropsch synthesis. This is exemplified by the preparation of $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$ from the thermolysis of $[Ru_3(CO)_{12}]$ in mesitylene–heptane.[4] Two additional compounds, $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$ and $[Ru_6H(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{13}(\mu\text{-}\eta^1:\eta^6\text{-}C_6H_3Me_2CH_2)]$ are also formed. The former complex, $[Ru_6(\mu_4\text{-}\eta^2\text{-}CO)_2(CO)_{13}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$, undergoes subsequent conversion into $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)]$, with the simultaneous evolution of CO_2, demonstrating that it is an intermediate in the formation of the octahedral carbido-cluster. The highly unusual intermediate cluster $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{16}\text{-}\mu\text{-}O)]$ has also been isolated from the thermolysis of $[Ru_3(CO)_{12}]$ with [2.2]paracyclophane in octane.[5] It contains not only a free carbide atom but also an oxo atom apparently from a cleaved CO ligand which is bonded to both the metal cluster unit and the ring moiety. This cluster also undergoes quantitative conversion into a *closo*-carbido cluster, *viz.* $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$, and CO_2 upon further heating.

In this paper we report the preparation of two new and highly unusual octaruthenium–cyclophane compounds, $[Ru_8(\mu\text{-}H)_2(\mu_6\text{-}\eta^2\text{-}CO)(CO)_{19}(\eta^6\text{-}C_{16}H_{16})]$ **1** and $[Ru_8(\mu_6\text{-}\eta^2\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$ **2** together with their detailed structural features and discuss their possible role as carbido-producing intermediates.

Results and Discussion

Previously we have described the thermolysis of $[Ru_3(CO)_{12}]$ and [2.2]paracyclophane under a number of different conditions with the isolation of a series of paracyclophane clusters with nuclearities ranging from three to eight, *viz.* $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$,[6] $[Ru_6(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{16}\text{-}\mu\text{-}O)]$,[5] $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$,[7] $[Ru_6C(CO)_{11}(\eta^6\text{-}C_{16}H_{16})(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$,[6] and $[Ru_8(\mu\text{-}H)_4(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$.[8] When the thermolysis is carried out in heptane as opposed to octane a similar range of products is obtained, but with enhanced yields of the trinuclear cluster $[Ru_3(CO)_9(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{16}H_{16})]$ and the unusual hexaruthenium species $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1:\eta^2:\eta^2\text{-}C_{16}H_{16}\text{-}\mu\text{-}O)]$. However, under these less aggressive conditions two additional by-products, not previously observed from the octane reaction, have also been isolated.[9] These two new compounds have been characterised on the basis of the customary spectroscopic techniques and also by single-crystal X-ray diffraction analysis as $[Ru_8(\mu\text{-}H)_2(\mu_6\text{-}\eta^2\text{-}CO)(CO)_{19}(\eta^6\text{-}C_{16}H_{16})]$ **1** and $[Ru_8(\mu_6\text{-}\eta^2\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$ **2**.

The solution infrared spectra of the two clusters in the CO stretching region are complicated reflecting the low molecular symmetry and both give rise to similar spectra with absorptions present in the terminal carbonyl region between 2100 and 1930 cm^{-1}. The mass spectra of **1** and **2** show distinct parent peaks at *m/z* 1580 (calc. 1579) and 1576 (calc. 1577) respectively,

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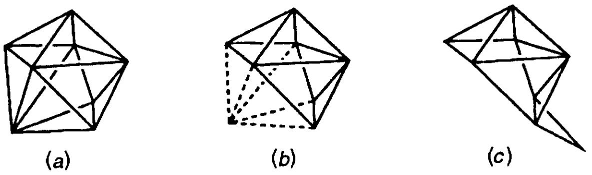
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

together with peaks corresponding to the sequential loss of several CO groups. The ^1H NMR spectrum of compound **1** contains signals at δ 6.89, 4.40, 3.38, −11.67 and −15.37 ppm, with relative intensities of 4:4:8:1:1. The first two are singlets and may be attributed to the four CH protons of the unattached and co-ordinated cyclophane rings, respectively. While the frequency of the latter resonance is low, we have found that there is an inverse relationship between cluster size and CH arene frequencies:[8] the larger the cluster the lower is the frequency of the arene CH resonance. The protons in the CH_2CH_2 linkages give rise to the signal at δ 3.38 which appears to be essentially a singlet. This is unusual since the bridge protons in related paracyclophane clusters generally give rise to two multiplet resonances (typically of AA′BB′ character) which can be attributed to the two pairs of CH_2 protons adjacent to and furthest from the co-ordinated ring. Cooling the sample to 213 K does not appear to have any effect on this signal, and while the precise mechanism by which the CH_2 group protons equilibrate has not been established it can be envisaged that the ring is undergoing not only rapid rotation about its plane but also some form of longitudinal tumbling motion. The signals at δ −11.67 and −15.37 are both singlets and correspond to the two hydride ligands.

The molecular structures of compounds **1** and **2** have been determined by single-crystal X-ray diffraction analyses. Both sets of crystals were grown from toluene solutions at 238 K. The molecular structure of **1** is shown in Fig. 1 and relevant structural parameters are listed in Table 1. The cluster consists of a highly unusual 'open' framework of eight ruthenium atoms. The geometry can be described as a square-based pyramid in which two adjacent basal edges are bridged by atoms Ru(6) and Ru(8). These two atoms are then fused and this edge is itself bridged by atom Ru(7). As far as we are aware this metal topology is the first of its type to be observed and it may be structurally compared to an edge-bridged *nido*-dodecahedron, see Scheme 1. In terms of simple electron-counting arguments, such a polyhedron should contain 116 valence-shell electrons, which is the number observed. The metal framework may also be derived from a bicapped octahedron by effectively breaking three Ru–Ru edges, and hence the addition of three electron pairs to the 110 present in the bicapped structure would result in the observed total electron count of 116, see Scheme 2.

The whole metal framework is heavily distorted with Ru–Ru distances varying considerably in the range 2.684(2)–3.019(2) Å. The cyclophane ligand is terminally bound to the only basal vertex of the square pyramid not involved in edge-bridging



Scheme 1 (*a*) Dodecahedron, (*b*) *nido*-dodecahedron and (*c*) edge-bridged *nido*-dodecahedron

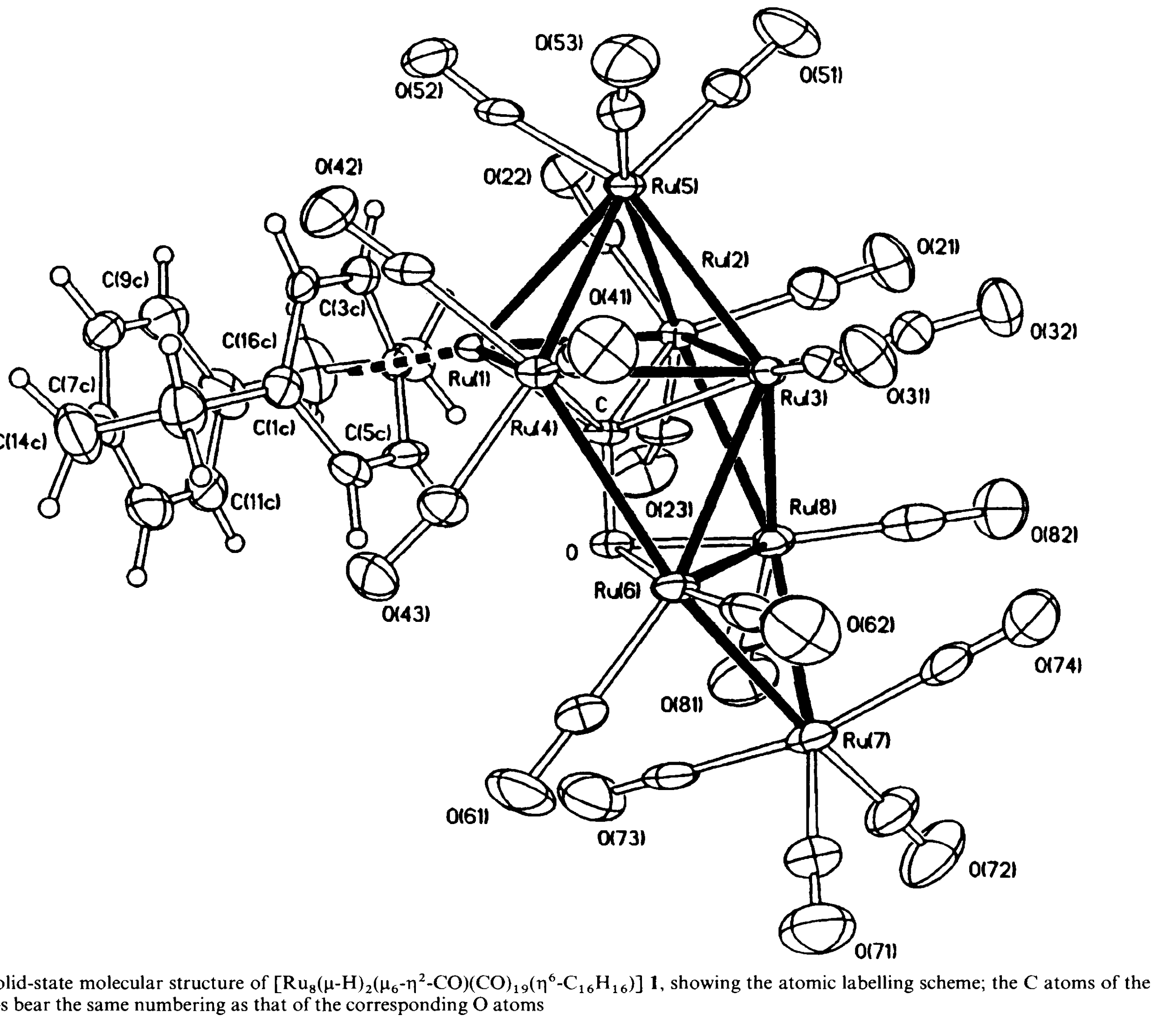
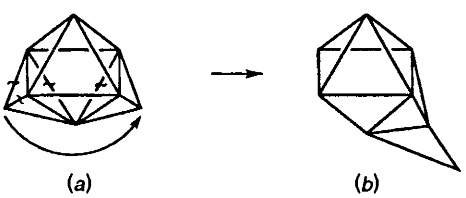


Fig. 1 Solid-state molecular structure of $[Ru_8(\mu\text{-}H)_2(\mu_6\text{-}\eta^2\text{-}CO)(CO)_{19}(\eta^6\text{-}C_{16}H_{16})]$ **1**, showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as that of the corresponding O atoms

Table 1 Selected bond distances (Å) and angles (°) for compound **1**

Ru(1)–Ru(2)	2.691(2)	Ru(1)–Ru(4)	2.684(2)	Ru(1)–Ru(5)	2.9322(14)
Ru(2)–Ru(3)	2.810(2)	Ru(2)–Ru(5)	2.828(2)	Ru(2)–Ru(8)	2.931(2)
Ru(3)–Ru(4)	2.821(2)	Ru(3)–Ru(5)	2.8618(14)	Ru(3)–Ru(6)	2.850(2)
Ru(3)–Ru(8)	2.882(2)	Ru(4)–Ru(5)	2.834(2)	Ru(4)–Ru(6)	2.983(2)
Ru(6)–Ru(7)	2.768(2)	Ru(6)–Ru(8)	3.019(2)	Ru(7)–Ru(8)	2.773(2)
Ru(1)–C	2.042(9)	Ru(2)–C	2.170(9)	Ru(3)–C	2.280(9)
Ru(4)–C	2.197(9)	Ru(6)–O	2.149(7)	Ru(8)–O	2.125(6)
C–O	1.378(11)				
mean Ru–C (CO)	1.90	mean C–O (CO)	1.14	Ru(1)–C(1c)	2.399(10)
Ru(1)–C(2c)	2.261(9)	Ru(1)–C(3c)	2.247(10)	Ru(1)–C(4c)	2.379(10)
Ru(1)–C(5c)	2.157(10)	Ru(1)–C(6c)	2.167(10)	C(1c)–C(2c)	1.410(14)
C(1c)–C(6c)	1.413(14)	C(1c)–C(13c)	1.51(2)	C(2c)–C(3c)	1.419(14)
C(3c)–C(4c)	1.411(14)	C(4c)–C(5c)	1.407(14)	C(4c)–C(15c)	1.489(14)
C(5c)–C(6c)	1.39(2)	C(7c)–C(8c)	1.39(2)	C(7c)–C(12c)	1.39(2)
C(7c)–C(14c)	1.52(2)	C(8c)–C(9c)	1.39(2)	C(9c)–C(10c)	1.40(2)
C(10c)–C(11c)	1.39(2)	C(10c)–C(16c)	1.48(2)	C(11c)–C(12c)	1.35(2)
C(13c)–C(14c)	1.56(2)	C(15c)–C(16c)	1.59(2)		
Ru(2)–C–Ru(3)	78.3(3)	Ru(1)–C–Ru(2)	79.4(3)	Ru(1)–C–Ru(4)	78.5(3)
Ru(2)–C–O	117.5(6)	Ru(3)–C–Ru(4)	78.1(3)	Ru(1)–C–O	121.2(6)
C–O–Ru(6)	95.5(5)	Ru(3)–C–O	109.8(6)	Ru(4)–C–O	117.1(6)
		C–O–Ru(8)	95.2(5)	Ru(6)–O–Ru(8)	89.9(2)



Scheme 2 Conversion of a bicapped octahedron into an edge-bridged *nido*-dodecahedron by cleavage of three Ru–Ru edges

[Ru(1)]. The cyclophane ring is not co-ordinated symmetrically over Ru(1), rather it is off-centred in such a fashion that the ring is situated towards one side, as reflected by the variation observed in the Ru–C(ring) bond distances of the non-bridgehead C atoms [Ru(1)–C(2c) 2.261(9), Ru(1)–C(3c) 2.247(10), Ru(1)–C(5c) 2.157(10) and Ru(1)–C(6c) 2.167(10) Å]. The bridgehead atoms are not in the same plane as the other four and the arene adopts a boat-shaped geometry, characteristic of paracyclophane in an η^6 bonding mode.[10] The dihapto-carbonyl ligand sits in a central cavity where it bridges six metal atoms, the carbon co-ordinating to the four square-pyramidal basal ruthenium atoms, and the oxygen to the two fused edge-bridging ruthenium atoms. The carbon atom is displaced below the plane of the four rutheniums by 0.97 Å and from the centre of the square base, being shifted slightly towards the Ru atom which carries the cyclophane ligand [Ru(1)–C 2.042(9) *vs.* an average of 2.22(1) Å]. The CO ligand acts as a six-electron donor, and it appears that compounds **1** and **2** provide the first examples of a carbonyl co-ordinated in a μ_6-η^2 fashion. The C atom bonds to four Ru atoms [Ru(1)–C 2.042(9), Ru(2)–C 2.170(9), Ru(3)–C 2.280(9), Ru(4)–C 2.197(9) Å] and the O atom interacts with two [Ru(6)–O 2.149(7), Ru(8)–O 2.125(6) Å]. The bond length of 1.378(11) Å in **1** is possibly the longest C–O distance recorded for a carbon monoxide ligand by a single-crystal X-ray diffraction analysis. The only other known example of a carbonyl ligand which donates six electrons to a cluster is found in $[Nb_3(\eta$-$C_5H_5)(CO)_7]$ (C–O 1.30 Å).[11] The remaining nineteen carbonyls are all terminal and essentially linear. They are distributed between the seven ruthenium atoms not involved in bonding to the cyclophane moiety, with two attached to Ru(3), Ru(6) and Ru(8), three to Ru(2), Ru(4) and Ru(5), and four to the unique atom Ru(7). The two hydride ligands were not located experimentally.

The solid-state structure of compound **2** is illustrated in Fig. 2, and selected bond lengths and angles are listed in Table 2. The molecular structure is very similar to that of **1**, except that the two hydrides and one terminal carbonyl ligand have been replaced by a second dihapto-CO ligand, thus maintaining the total electron count of 116. This dihapto-CO ligand donates four electrons and is situated in the butterfly site created by Ru(3), Ru(6), Ru(7) and Ru(8).

The Ru-atom topology is the same as that described for compound **1**, Ru–Ru bond lengths range from 2.693(2) to 3.126(2) Å, the longest being the edge connecting the two hinge atoms of the butterfly spanned by the μ_4-η^2-CO ligand [Ru(6)–Ru(8)]. As in **1** the cyclophane ligand is bonded, in a terminal fashion, to the only basal vertex of the square pyramid not involved in edge-bridging [Ru(1)], however, whilst the C_6 ring sits centrally over Ru(1), it is tilted in such a way that two of the four coplanar C atoms lie close to the metal [Ru(1)–C(5c) 2.158(5), Ru(1)–C(6c) 2.158(5) Å] while the other two are slightly further away [Ru(1)–C(2c) 2.249(5), Ru(1)–C(3c) 2.251(5) Å] and, due to its boat-shaped conformation, the two *para* bridgehead carbon atoms of the bound ring exhibit an even longer bonding distance from the metal centre [Ru(1)–C(1c) 2.371(5) and Ru(1)–C(4c) 2.367(5) Å]. As in **1**, the carbon atom of the μ_6-η^2 carbonyl ligand is off-centred with respect to the square base and is shifted towards the cyclophane-bound ruthenium atom [2.047(5) Å *vs.* a mean value of 2.205(5) Å]. It is also displaced beneath the basal plane by 0.97 Å, the same distance observed in **1**. The π-bonded μ_4-η^2 carbonyl ligand occupies the Ru_4 butterfly site, with the C atom interacting with the two 'hinge' [Ru(6) and Ru(8)] and 'wingtip' [Ru(3)] ruthenium atoms, and with Ru(7) *via* a C–O π interaction. Although not as long as the μ_6-η^2 C–O bond length of 1.355(6) Å, the μ_4-η^2 C–O bond length is considerably lengthened relative to the terminal CO ligands [C(1)–O(1) 1.230(7) *vs.* a mean value of 1.139(7) Å].

As far as we are aware clusters **1** and **2** provide examples of a unique and previously unobserved co-ordination mode for carbon monoxide. As already noted, when CO is co-ordinated in a 'side-on' manner the interaction with several metal atoms considerably weakens the C–O bond. Since the carbonyl group interacts with six metal atoms in this case the bond should be very weak and therefore very active to cleavage. This is evident

Table 2 Selected bond distances (Å) and angles (°) for compound **2**

Ru(1)–Ru(2)	2.695(2)	Ru(1)–Ru(4)	2.693(2)	Ru(1)–Ru(5)	2.913(2)
Ru(2)–Ru(3)	2.785(2)	Ru(2)–Ru(5)	2.815(2)	Ru(2)–Ru(8)	2.833(2)
Ru(3)–Ru(4)	2.793(2)	Ru(3)–Ru(5)	2.769(2)	Ru(3)–Ru(6)	2.788(2)
Ru(3)–Ru(8)	2.795(2)	Ru(4)–Ru(5)	2.814(2)	Ru(4)–Ru(6)	2.839(2)
Ru(6)–Ru(7)	2.758(2)	Ru(6)–Ru(8)	3.126(2)	Ru(7)–Ru(8)	2.753(2)
Ru(3)–C(1)	2.036(6)	Ru(6)–C(1)	2.242(6)	Ru(7)–C(1)	2.265(6)
Ru(7)–O(1)	2.190(4)	Ru(8)–C(1)	2.244(6)	C(1)–O(1)	1.230(7)
Ru(1)–C(2)	2.047(5)	Ru(2)–C(2)	2.199(5)	Ru(3)–C(2)	2.230(5)
Ru(4)–C(2)	2.187(5)	Ru(6)–C(2)	2.598(5)	Ru(6)–O(2)	2.148(3)
Ru(8)–O(2)	2.147(4)	C(2)–O(2)	1.355(6)	mean Ru–C (CO)	1.90
mean C–O (CO)	1.14	Ru(1)–C(1c)	2.371(5)	Ru(1)–C(2c)	2.249(5)
Ru(1)–C(3c)	2.251(5)	Ru(1)–C(4c)	2.367(5)	Ru(1)–C(5c)	2.158(5)
Ru(1)–C(6c)	2.158(5)	C(1c)–C(2c)	1.409(7)	C(1c)–C(6c)	1.414(8)
C(1c)–C(13c)	1.502(8)	C(2c)–C(3c)	1.416(8)	C(3c)–C(4c)	1.392(8)
C(4c)–C(5c)	1.412(7)	C(4c)–C(15c)	1.508(7)	C(5c)–C(6c)	1.409(7)
C(7c)–C(8c)	1.380(9)	C(7c)–C(12c)	1.400(9)	C(7c)–C(14c)	1.524(9)
C(8c)–C(9c)	1.369(9)	C(9c)–C(10c)	1.392(9)	C(10c)–C(11c)	1.393(9)
C(10c)–C(16c)	1.497(9)	C(11c)–C(12c)	1.378(9)	C(13c)–C(14c)	1.571(8)
C(15c)–C(16c)	1.571(8)				
Ru(2)–C(2)–Ru(3)	77.9(2)	Ru(1)–C(2)–Ru(2)	78.7(2)	Ru(1)–C(2)–Ru(4)	78.9(2)
Ru(2)–C(2)–O(2)	116.8(3)	Ru(3)–C(2)–Ru(4)	78.4(2)	Ru(1)–C(2)–O(2)	122.0(3)
C(2)–O(2)–Ru(6)	93.0(3)	Ru(3)–C(2)–O(2)	109.8(3)	Ru(4)–C(2)–O(2)	117.1(3)
		C(2)–O(2)–Ru(8)	93.2(3)	Ru(6)–O(2)–Ru(8)	93.38(14)

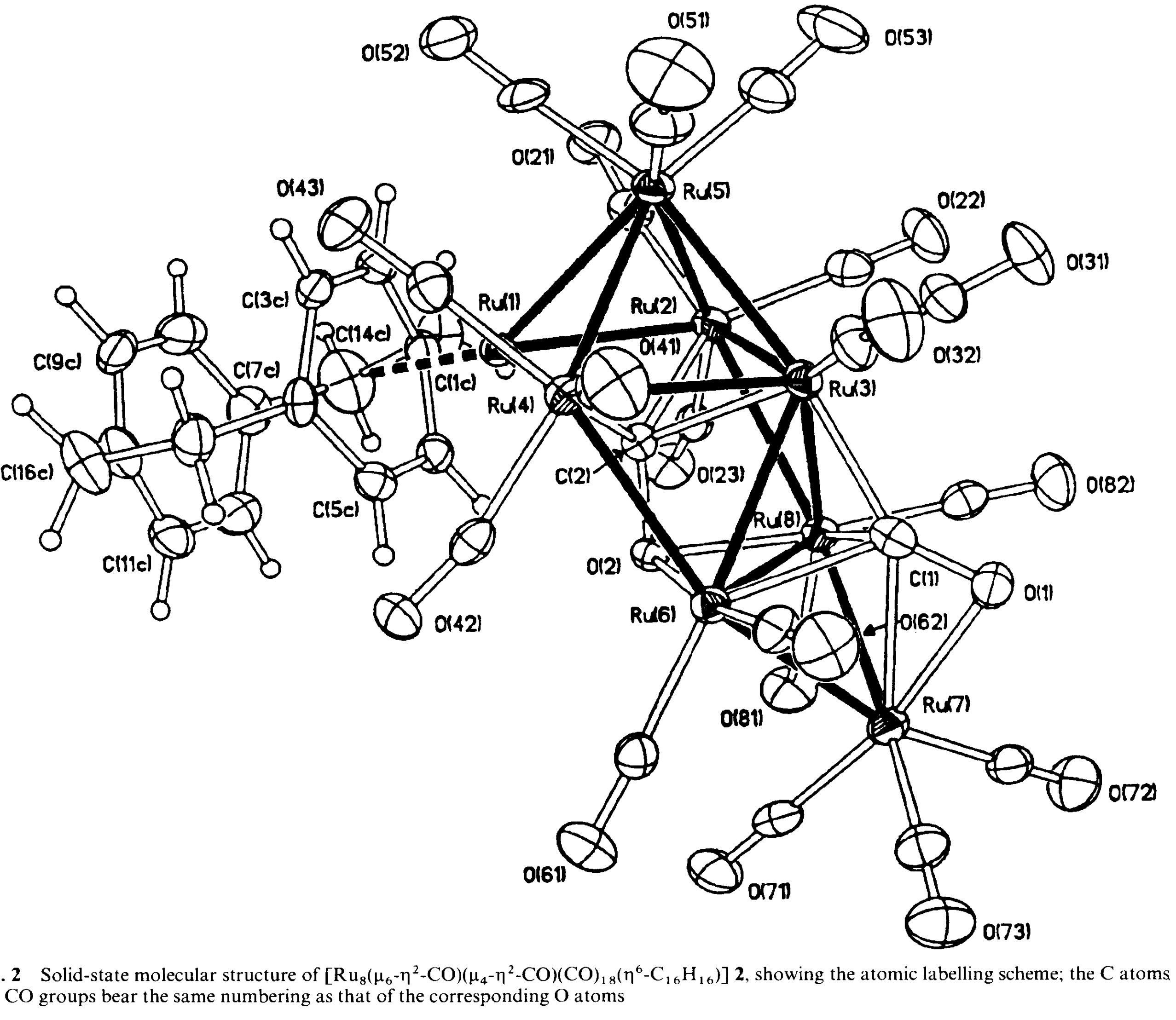


Fig. 2 Solid-state molecular structure of $[Ru_8(\mu_6\text{-}\eta^2\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$ **2**, showing the atomic labelling scheme; the C atoms of the CO groups bear the same numbering as that of the corresponding O atoms

in the C–O bond lengths observed [1.378(11) and 1.355(6) Å for **1** and **2**, respectively] and should also be apparent from the infrared stretching frequencies which are very sensitive to small changes in the C–O bond order. However the infrared spectrum of **1**, recorded in KBr, failed to show any peaks which could be attributed to the ν_{CO} mode of the μ_6-η^2-CO ligand in the region 1600–1000 cm^{-1}, probably because the vibration of a CO bonded in such a fashion would be very broad and weak. The solid-state infrared spectrum of **2** was not recorded due to insufficient amounts of material.

We have previously reported the reaction of the bicapped octahedral cluster $[Ru_8(\mu\text{-}H)_4(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$ with CO, which results in the formation of the octahedral carbido-cluster $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})]$ and $[Ru_3(CO)_{12}]$ in high yield.[8] During this reaction the metal core of the precursor compound not only undergoes a reduction in nuclearity, but must also endure a substantial polyhedral rearrangement in order to accommodate the carbido atom. Although we do not have any direct evidence, it is possible that **1**, with its unusually open metal framework and elongated dihapto-carbonyl ligand, may represent the type of intermediate produced in this process, see Scheme 3.

The multihapto co-ordination of a carbonyl ligand not only leads to a considerable elongation and weakening of the C–O bond, it also increases the nucleophilicity of the carbonyl oxygen, enabling attack at the electrophilic carbon of a terminal carbonyl necessary for the formation of CO_2. It has also been suggested that co-ordination of CO in a dihapto manner may be an essential step in any reaction sequence.[12] From an inspection of compound **1** one can speculate that cleavage of the C–O bond, by attack of the nucleophilic oxygen on an external CO molecule, would cause the resulting carbide atom to move towards the plane of the four ruthenium atoms to which it is attached so that it bonds to the apical [Ru(5)] metal atom. It should also be noted that there is a significant interaction between the carbon atom and Ru(6) [Ru(6)–C 2.447(9) Å] and hence it is possible that upon C–O bond cleavage the movement of the carbide atom towards Ru(5) results in a simultaneous movement of Ru(6) into a position such that the ruthenium atoms (1)–(6) form an octahedron. Clearly Ru(7) and Ru(8) must be cleaved, and may undergo recombination to form $[Ru_3(CO)_{12}]$, and the formation of several Ru–Ru bonds is also necessary for the generation of a *closo*-octahedron. Apart from the formation of the octahedral metal core, the cyclophane moiety must undergo migration from a terminal to a facial position, which is not entirely unexpected and similar arene slippage has been observed in related systems. It should be pointed out that neither of the open octaruthenium clusters, **1** and **2**, is observed at any stage during the transformation of $[Ru_8(\mu\text{-}H)_4(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$ to $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})]$.

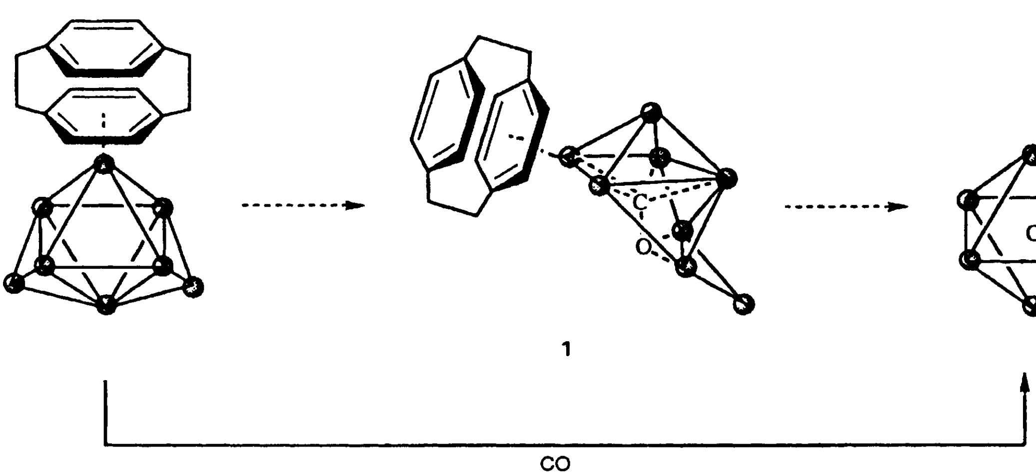
Compound **2** is more complicated by the presence of a second dihapto-carbonyl ligand within the same molecule. However, whereas the μ_6-η^2-CO is unique to these compounds, the μ_4-η^2-carbonyl, while still uncommon, has been observed in the butterfly sites of an increasing number of cluster compounds.[13,14] It is possible that compound **2** may also represent an intermediate complex in the aforementioned transformation.

Experimental

General Procedures and Materials.—Reactions were carried out under an atmosphere of nitrogen gas whilst the products were extracted without precautions to exclude air. The products were separated by column chromatography using a column equipped with nitrogen pressurisation and packed with silicagel 60 mesh. [2.2]Paracyclophane was obtained from Fluka Chemicals and used without any additional purification.

Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform instrument either in solution using NaCl cells (0.5 mm path length) or in the solid state as KBr discs, mass spectra by positive fast atom bombardment on a Kratos MS50TC spectrometer calibrated with CsI, and ^{1}H NMR spectra using a Bruker AM360 spectrometer referenced to $SiMe_4$.

Thermolysis of $[Ru_3(CO)_{12}]$ *with* [2.2]*Paracyclophane in Heptane.*—A suspension of $[Ru_3(CO)_{12}]$ (500 mg) in heptane (30 cm^3) containing an excess of [2.2]paracyclophane (200 mg) was heated to reflux for 3 h. During this period the reaction was monitored by both IR spectroscopy and spot TLC, which indicated that the majority of the starting material had been consumed and that several new materials were present. The reaction mixture was filtered and the solvent removed from the filtrate under reduced pressure. The products were separated by column chromatography, using dichloromethane–hexane (3:7, v/v) as eluent. In order of elution, the products were characterised by spectroscopy as $[Ru_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})]$ (yellow, 30%), $[Ru_8(\mu\text{-}H)_2(\mu_6\text{-}\eta^2\text{-}CO)(CO)_{19}(\eta^6\text{-}C_{16}H_{16})]$ **1** (purple, ≈1%), $[Ru_8(\mu_6\text{-}\eta^2\text{-}CO)(\mu_4\text{-}\eta^2\text{-}CO)(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$ **2** (purple, <1%), $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})]$ (red, 14%) and $[Ru_6C(CO)_{15}(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-}C_{16}H_{16}\text{-}\mu\text{-}O)]$ (purple, 10%). Spectroscopic data: **1**; IR (CH_2Cl_2) ν_{CO} 2101m, 2062s, 2034vs, 1984w and 1957w cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 6.89 (s, 4 H), 4.40 (s, 4 H), 3.38 (br s, 8 H), −11.67 (s, 1 H) and −15.37 (s, 1H); mass spectrum m/z = 1580



Scheme 3 Conversion of $[Ru_8(\mu\text{-}H)_4(CO)_{18}(\eta^6\text{-}C_{16}H_{16})]$ into $[Ru_6C(CO)_{14}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_{16}H_{16})]$ including **1** as a possible reaction intermediate

Table 3 Atomic coordinates for compound **1**

Atom	*x*	*y*	*z*
Ru(1)	0.627 57(6)	0.085 29(3)	0.717 46(5)
Ru(2)	0.432 13(6)	0.084 41(3)	0.705 80(5)
Ru(3)	0.486 90(6)	0.085 18(3)	0.872 46(5)
Ru(4)	0.688 66(6)	0.0796 4(3)	0.876 86(5)
Ru(5)	0.550 83(6)	0.000 11(3)	0.793 92(5)
Ru(6)	0.605 75(6)	0.178 53(3)	0.923 89(5)
Ru(7)	0.467 88(7)	0.260 34(3)	0.903 59(6)
Ru(8)	0.408 37(6)	0.181 99(3)	0.787 79(5)
O	0.562 2(5)	0.176 7(2)	0.796 4(4)
C	0.562 9(7)	0.122 1(4)	0.790 4(5)
O(21)	0.215 4(6)	0.054 0(4)	0.684 4(5)
O(22)	0.431 5(6)	0.012 3(3)	0.569 1(5)
O(23)	0.369 0(7)	0.172 6(4)	0.584 8(5)
O(31)	0.551 0(6)	0.058 3(3)	1.047 6(5)
O(32)	0.274 7(6)	0.059 3(3)	0.866 3(5)
O(41)	0.767 8(6)	0.049 0(3)	1.053 1(5)
O(42)	0.836 7(6)	0.003 6(3)	0.841 7(5)
O(43)	0.840 1(6)	0.168 9(3)	0.896 2(5)
O(51)	0.359 8(7)	−0.067 6(3)	0.735 6(5)
O(52)	0.641 9(6)	−0.056 3(3)	0.683 3(5)
O(53)	0.663 7(6)	−0.067 2(3)	0.938 7(5)
O(61)	0.760 6(7)	0.264 8(4)	0.956 3(5)
O(62)	0.645 7(7)	0.170 7(4)	1.099 6(5)
O(71)	0.590 1(7)	0.319 0(4)	1.055 9(6)
O(72)	0.296 5(8)	0.340 3(4)	0.838 3(6)
O(73)	0.575 9(8)	0.305 4(4)	0.793 2(6)
O(74)	0.352 1(7)	0.193 2(4)	0.988 5(6)
O(81)	0.340 6(7)	0.273 9(4)	0.675 8(6)
O(82)	0.195 5(6)	0.172 6(4)	0.787 8(6)
C(21)	0.296 4(9)	0.064 9(5)	0.695 5(6)
C(22)	0.438 7(8)	0.038 7(5)	0.622 1(7)
C(23)	0.389 2(8)	0.143 9(4)	0.636 8(7)
C(31)	0.529 7(8)	0.069 1(4)	0.981 4(7)
C(32)	0.353 9(9)	0.069 9(4)	0.866 7(6)
C(41)	0.734 3(7)	0.060 6(4)	0.986 6(7)
C(42)	0.778 2(8)	0.030 7(4)	0.851 7(6)
C(43)	0.779 9(8)	0.138 1(4)	0.893 6(6)
C(51)	0.430 6(9)	−0.042 4(4)	0.755 1(6)
C(52)	0.609 3(8)	−0.032 2(4)	0.724 1(7)
C(53)	0.624 5(8)	−0.041 7(4)	0.883 7(7)
C(61)	0.700 9(9)	0.232 3(5)	0.944 5(7)
C(62)	0.631 2(9)	0.173 5(4)	1.032 1(7)
C(71)	0.545 4(10)	0.298 4(5)	0.998 5(8)
C(72)	0.356 9(11)	0.310 8(5)	0.862 1(8)
C(73)	0.536 6(10)	0.289 1(4)	0.834 5(8)
C(74)	0.396 9(9)	0.218 2(5)	0.957 9(7)
C(81)	0.367 6(9)	0.239 0(5)	0.719 3(7)
C(82)	0.278 4(10)	0.176 7(5)	0.787 6(8)
C(1c)	0.790 6(7)	0.102 2(4)	0.707 7(6)
C(2c)	0.745 9(7)	0.055 3(4)	0.667 9(6)
C(3c)	0.652 0(8)	0.057 9(4)	0.605 3(6)
C(4c)	0.602 5(7)	0.107 1(4)	0.582 4(6)
C(5c)	0.634 3(8)	0.148 8(4)	0.638 0(6)
C(6c)	0.726 3(7)	0.146 5(4)	0.699 7(6)
C(7c)	0.885 7(9)	0.129 9(5)	0.605 9(7)
C(8c)	0.854 6(9)	0.086 8(4)	0.554 6(7)
C(9c)	0.763 2(10)	0.088 0(5)	0.493 0(8)
C(10c)	0.700 5(9)	0.132 5(5)	0.480 4(7)
C(11c)	0.744 0(10)	0.178 1(5)	0.521 5(8)
C(12c)	0.833 1(10)	0.177 1(5)	0.581 9(8)
C(13c)	0.902 7(8)	0.105 7(5)	0.749 7(7)
C(14c)	0.957 6(9)	0.122 4(6)	0.690 3(8)
C(15c)	0.531 2(8)	0.115 9(5)	0.500 3(6)
C(16c)	0.590 5(9)	0.126 9(6)	0.439 8(7)
C(1a)	1.082 5(13)	0.069 6(7)	0.963 8(10)
C(2a)	1.058 4(13)	0.112 4(7)	1.000 4(10)
C(3a)	1.006 8(11)	0.107 6(6)	1.053 0(9)
C(4a)	0.978(2)	0.149 0(8)	1.089 0(12)
C(5a)	1.007(2)	0.200 3(8)	1.072 4(13)
C(6a)	1.055(2)	0.205 2(10)	1.018 9(14)
C(7a)	1.088 2(12)	0.162 8(6)	0.986 0(10)
C(1b)	1.007(2)	0.200 3(8)	1.072 4(13)
C(2b)	1.036(2)	0.158 2(10)	1.038 4(14)
C(3b)	1.088 2(12)	0.162 8(6)	0.986 0(10)
C(4b)	1.110(2)	0.118 8(9)	0.950(2)
C(5b)	1.082 5(13)	0.069 6(7)	0.963 8(10)
C(6b)	1.030(3)	0.066 2(13)	1.015(2)
C(7b)	1.006 8(11)	0.107 6(6)	1.053 0(9)
C(8s)	1.074 0(13)	−0.044 6(7)	0.750 0(9)
C(9s)	0.996 1(11)	−0.055 1(5)	0.679 5(9)
C(10s)	0.900 9(9)	−0.067 5(5)	0.677 5(8)
C(11s)	0.828 7(14)	−0.077 7(6)	0.603 4(10)
C(12s)	0.843 9(12)	−0.074 2(7)	0.533 7(10)
C(13s)	0.942 2(12)	−0.061 5(6)	0.538 0(12)
C(14s)	1.015 5(14)	−0.051 8(6)	0.608 3(8)
C(15a)	0.263(2)	0.185 5(10)	0.231(2)
C(16a)	0.361(2)	0.196 7(8)	0.242 9(11)
C(17a)	0.424 2(12)	0.228 6(7)	0.302 7(10)
C(18a)	0.526(2)	0.239 4(9)	0.306 4(13)
C(19a)	0.556 0(13)	0.214 8(7)	0.250 3(11)
C(20a)	0.488(2)	0.187 1(13)	0.190(2)
C(21a)	0.398 4(13)	0.176 8(7)	0.186 4(10)
C(15b)	0.556 0(13)	0.214 8(7)	0.250 3(11)
C(16b)	0.463(2)	0.205 7(8)	0.245 6(12)
C(17b)	0.398 4(13)	0.176 8(7)	0.186 4(10)
C(18b)	0.300(2)	0.165 9(12)	0.174(2)
C(19b)	0.263(2)	0.185 5(10)	0.231(2)
C(20b)	0.331(2)	0.213 9(10)	0.289(2)
C(21b)	0.424 2(12)	0.228 6(7)	0.302 7(10)

(calc. 1579); **2**; IR (CH_2Cl_2) ν_{CO} 2100w, 2089m, 2060s, 2036vs, 2017s, 1983m and 1934w cm^{-1}; mass spectrum m/z = 1576 (calc. 1577).

Structural Determinations of Compounds **1** *and* **2**.—Crystals of **1** were grown from toluene at 238 K.

Crystal data. $C_{36}H_{18}O_{20}Ru_8 \cdot 3C_6H_5CH_3$, $M = 1855.47$ (including three solvated molecules of toluene, two of which exhibit 50% disorder), monoclinic, space group $P2_{1/n}$ (alternative setting no. 14), $a = 14.088(6)$, $b = 25.134(12)$, $c = 17.834(8)$ Å, $\beta = 109.54(5)°$, $U = 5951(5)$ Å^3 (by least-squares refinement of 2θ values for 36 automatically centred reflections, $\lambda = 0.710\,73$ Å), $Z = 4$, $D_c = 2.071$ g cm^{-3}, $F(000) = 3584$. Red blocks, crystal dimensions 0.38 × 0.58 × 0.85 mm, μ(Mo-Kα) = 2.047 mm^{-1}.

Data collection and processing. Stoë Stadi-4 diffractometer operating at 150 K, ω scan mode with graphite-monochromated Mo-Kα radiation. Three standard reflections were monitored every 60 min and showed a 12.1% decomposition during the data-collection period, which was corrected by applying an anisotropic decay correction. Absorption corrections were applied by the use of semiempirical ψ scans (maximum, minimum transmission coefficients 0.282, 0.253). A total of 8622 reflections were measured ($2.5 < \theta < 22.5$ °, $\pm h$, $+k$, $+l$) and averaged to yield 7740 unique reflections (merging $R_{int} = 0.0309$) of which 5946 had $F_o > 4\sigma(F_o)$. Corrections for Lorentz and polarisation effects were applied.

Structure analysis and refinement. Structure solution involved a combination of direct methods and Fourier techniques. The two metal hydrides could not be located experimentally, the remaining hydrogen atoms were placed in calculated positions and refined using a riding model. Three molecules of solvated toluene, of which two exhibited 50% disorder, were located and included in subsequent refinement cycles. Anisotropic thermal motion was assumed for all non-hydrogen atoms. Full-matrix least-squares refinement on F_o^2 for 7725 data and 720 parameters converged to $wR2 = 0.1400$ (all data), conventional $R1 = 0.0496$ (observed data), $(\Delta/\sigma)_{max} = 0.001$, goodness of

Table 4 Atomic coordinates for compound **2**

Atom	*x*	*y*	*z*
Ru(1)	0.204 68(3)	0.802 83(3)	0.214 25(3)
Ru(2)	0.405 32(3)	0.753 14(3)	0.272 70(3)
Ru(3)	0.377 37(3)	0.931 32(3)	0.340 50(3)
Ru(4)	0.173 41(3)	0.982 45(3)	0.269 61(3)
Ru(5)	0.341 58(3)	0.958 92(3)	0.157 78(3)
Ru(6)	0.215 40(3)	0.913 36(3)	0.458 90(3)
Ru(7)	0.336 70(3)	0.797 35(3)	0.609 99(3)
Ru(8)	0.400 10(3)	0.728 66(3)	0.461 18(3)
O(1)	0.431 0(3)	0.914 2(3)	0.540 6(3)
O(2)	0.241 0(3)	0.771 7(3)	0.412 4(2)
C(1)	0.388 1(4)	0.894 1(4)	0.477 7(4)
C(2)	0.265 5(4)	0.824 8(4)	0.329 0(3)
O(21)	0.419 1(3)	0.701 7(3)	0.091 5(3)
O(22)	0.642 4(3)	0.708 0(4)	0.285 9(3)
O(23)	0.390 4(3)	0.523 0(3)	0.366 0(3)
O(31)	0.610 8(3)	0.922 5(4)	0.332 7(3)
O(32)	0.365 1(4)	1.167 2(3)	0.326 1(4)
O(41)	0.130 9(3)	1.213 7(3)	0.278 3(3)
O(42)	−0.027 1(3)	0.936 8(3)	0.360 3(3)
O(43)	0.062 0(3)	1.052 5(3)	0.085 0(3)
O(51)	0.302 2(4)	1.201 4(4)	0.100 0(4)
O(52)	0.260 7(3)	0.938 7(3)	−0.020 6(3)
O(53)	0.566 3(4)	0.932 8(4)	0.107 0(4)
O(61)	0.037 7(3)	0.861 3(3)	0.578 0(3)
O(62)	0.202 1(3)	1.121 5(3)	0.505 2(3)
O(71)	0.194 0(3)	0.637 9(4)	0.665 7(3)
O(72)	0.514 9(3)	0.650 4(4)	0.733 9(3)
O(73)	0.238 3(4)	0.931 7(3)	0.733 4(3)
O(81)	0.382 8(3)	0.510 8(3)	0.579 2(3)
O(82)	0.626 5(3)	0.696 4(3)	0.511 9(3)
C(21)	0.407 0(4)	0.724 3(4)	0.157 9(4)
C(22)	0.554 7(5)	0.727 6(4)	0.282 1(4)
C(23)	0.399 0(4)	0.611 0(4)	0.340 2(4)
C(31)	0.523 8(4)	0.923 4(5)	0.334 3(4)
C(32)	0.367 2(4)	1.079 8(5)	0.330 3(4)
C(41)	0.150 7(4)	1.128 1(4)	0.275 2(4)
C(42)	0.053 0(4)	0.953 8(4)	0.335 6(4)
C(43)	0.107 3(4)	1.019 3(4)	0.153 7(4)
C(51)	0.314 4(5)	1.110 3(5)	0.123 7(4)
C(52)	0.290 3(4)	0.944 7(4)	0.047 1(4)
C(53)	0.483 1(5)	0.939 1(5)	0.127 6(4)
C(61)	0.107 1(4)	0.878 8(4)	0.534 6(4)
C(62)	0.204 9(4)	1.043 2(5)	0.486 4(4)
C(71)	0.247 1(4)	0.698 2(5)	0.644 7(4)
C(72)	0.449 1(5)	0.706 0(5)	0.689 6(4)
C(73)	0.276 3(5)	0.881 9(5)	0.688 2(4)
C(81)	0.389 1(4)	0.594 4(4)	0.536 8(4)
C(82)	0.540 5(4)	0.706 2(4)	0.491 2(4)
C(1c)	0.198 0(4)	0.637 5(4)	0.182 9(4)
C(2c)	0.172 6(4)	0.724 6(4)	0.106 2(4)
C(3c)	0.087 7(4)	0.806 8(4)	0.106 0(4)
C(4c)	0.028 0(4)	0.803 4(4)	0.181 5(4)
C(5c)	0.071 0(4)	0.732 6(4)	0.263 6(4)
C(6c)	0.155 5(4)	0.650 7(4)	0.264 7(4)
C(7c)	0.063 2(5)	0.511 8(5)	0.160 4(4)
C(8c)	0.024 5(5)	0.578 4(5)	0.078 0(4)
C(9c)	−0.057 1(5)	0.659 9(5)	0.072 8(4)
C(10c)	−0.102 8(5)	0.679 0(5)	0.150 1(4)
C(11c)	−0.079 5(5)	0.597 5(5)	0.229 5(4)
C(12c)	0.003 5(5)	0.516 2(5)	0.235 4(4)
C(13c)	0.254 2(5)	0.531 5(5)	0.175 2(4)
C(14c)	0.175 4(5)	0.454 3(5)	0.173 2(6)
C(15c)	−0.083 2(4)	0.859 9(5)	0.173 2(4)
C(16c)	−0.157 6(5)	0.788 3(5)	0.149 5(5)
C(1s)	0.106 2(6)	0.740 7(7)	0.855 6(5)
C(2s)	0.206 4(5)	0.665 4(5)	0.877 5(4)
C(3s)	0.209 7(6)	0.559 3(6)	0.882 2(4)
C(4s)	0.303 8(7)	0.487 9(7)	0.900 7(5)
C(5s)	0.391 8(6)	0.522 4(7)	0.916 5(5)
C(6s)	0.388 8(6)	0.627 8(6)	0.913 2(4)
C(7s)	0.297 5(5)	0.698 9(6)	0.894 6(4)
C(8s)	−0.130(2)	0.523(2)	0.493 6(13)
C(9s)	−0.114 6(12)	0.629 5(12)	0.494 7(10)
C(10s)	−0.014 4(12)	0.642 1(14)	0.500 7(12)
C(11s)	0.065 6(9)	0.555 1(9)	0.502 7(7)
C(12s)	0.038(2)	0.451 4(13)	0.503 4(13)

fit = 1.072. The function minimised was $\Sigma w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.0714P)^2 + 32.5109P]$ where $P = (F_o^2 + 2F_c^2)/3$ and σ was obtained from counting statistics. A final Fourier-difference electron-density synthesis revealed maximum and minimum residual peaks of 1.29 and −1.19 e Å^{-3}, which were located in close proximity to ruthenium atom positions. In the refinement process it was possible to distinguish between the oxygen and carbon atoms of the μ_6-η^2-CO ligand.

Crystals of compound **2** were grown from toluene at 238 K.

Crystal data. $C_{36}H_{16}O_{20}Ru_8 \cdot 1.5C_6H_5CH_3$, $M = 1715.25$ (including two solvated molecules of toluene, one exhibiting 50% occupancy and 50% disorder), triclinic, space group $P\bar{1}$ (no. 2), $a = 13.084(8)$, $b = 13.200(7)$, $c = 15.382(10)$ Å, $\alpha = 74.72(5)$, $\beta = 84.76(4)$, $\gamma = 80.37(4)°$, $U = 2524(3)$ Å^3 (by least-squares refinement of 2θ values for 38 automatically centred reflections, λ = 0.710 73 Å), $Z = 2$, $D_c = 2.257$ g cm^{-3}, $F(000) = 1638$. Red plate, crystal dimensions 0.08 × 0.15 × 0.47 mm, μ(Mo-Kα) = 2.402 mm^{-1}.

Data collection and processing. Details as for compound **1** except as follows: 156 K; 5.8% decomposition; maximum and minimum transmission coefficients 0.611, 0.515; 9804 reflections measured (2.6 < θ < 25.0 °, $\pm h$, $+k$, $+l$) and averaged to yield 8911 unique (merging $R_{int} = 0.0399$) of which 7509 had $F_o > 4\sigma(F_o)$.

Structure analysis and refinement. Structure solution as for compound **1**. Hydrogen atoms were placed in calculated positions and refined using a riding model. Two molecules of solvated toluene, one of which exhibited 50% occupancy and 50% disorder, were located and included in subsequent refinement. Anisotropic thermal motion was assumed for all non-hydrogen atoms, excluding the disordered toluene solvate. Full-matrix least-squares refinement on F_o^2 for 8903 data and 661 parameters converged to $wR2 = 0.0672$ (all data), conventional $R1 = 0.0310$ (observed data), $(\Delta/\sigma)_{max} = -0.226$, goodness of fit = 1.093. The function minimised was $\Sigma w(F_o^2 - F_c^2)^2$, $w = 1/[\sigma^2(F_o^2) + (0.0148P)^2 + 11.8859P]$ where $P = (F_o^2 + 2F_c^2)/3$ and σ was obtained from counting statistics. Maximum and minimum residual electron-density peaks of 1.41 and −0.61 e Å^{-3}, located in close proximity to the disordered toluene solvate.

For both structural analyses computations were performed with the SHELXTL-PC[15] package and SHELXL 93[16] program. Final atomic coordinates are given in Tables 3 and 4.

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

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