

Cluster-mediated ring contraction: synthesis and characterisation of $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ and $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_3\text{C}_3\text{H}_6)]$

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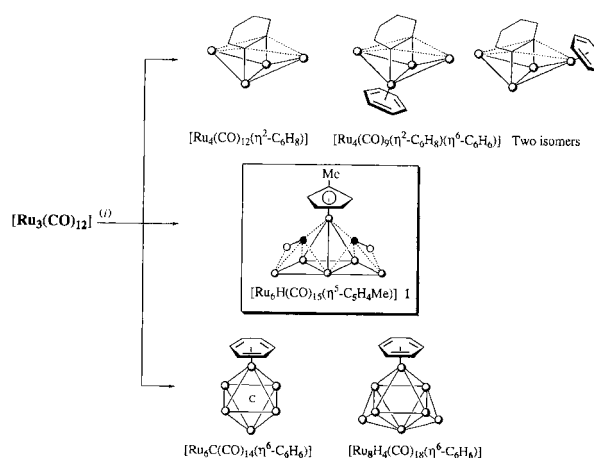
The thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with either cyclohexene or cycloocta-1,3-diene resulted in a number of cluster derivatives, including one from each reaction in which the ligand has undergone a ring contraction. Reaction with cyclohexene afforded the methylcyclopentadienyl cluster $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ **1**, whilst cycloocta-1,3-diene yielded the trihydropentalenyl cluster $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_8\text{H}_9)]$ **2**. The molecular structures of **1** and **2** have been established in the solid state by single-crystal X-ray diffraction.

The catalytic transformation of C_6 and C_8 hydrocarbons is of considerable industrial importance and it is well established that transition metals are highly effective in activating both C–H and C–C bonds.¹ Studies concerning the adsorption and subsequent reactivity of cyclic C_6 hydrocarbons such as cyclohexane, cyclohexene and cyclohexadiene on, for example, the Pt(111) surface, have revealed that their reactions are dominated by dehydrogenation to benzene.² A remarkably similar behaviour has been found to occur when such ring systems are treated with transition-metal clusters,³ and these observations suggest that small metal clusters may be used to model processes that occur on bulk metal surfaces. These studies have enhanced our understanding of the mechanisms involved on metal surfaces, since molecular reaction intermediates may be isolated and structurally characterised in solution by NMR spectroscopy and in the solid-state by X-ray crystallography.

Ring-contraction reactions involve both C–H and C–C bond activation and are known to occur at metal surfaces, molecular clusters and mononuclear metal centres.^{4,5} The contractions of C_6 and C_8 rings to cyclopentadienyl derivatives are the most common processes, although C_8 rings are also known to contract to C_6 rings. Transannular ring-closure reactions of this type, whether hydrogenative or dehydrogenative, have been observed on Pt(111) surfaces,⁶ and on supported Group VIII metals (*e.g.* Ni, Pd or Pt) and metal sulfide (*e.g.* MoS_2 , WS_2 , $\text{Co-Mo-S/Al}_2\text{O}_3$) catalysts.⁷ This paper now reports the reactions of $[\text{Ru}_3(\text{CO})_{12}]$ with cyclohexene and cycloocta-1,3-diene; in both cases the metal cluster mediates C–C bond activation resulting in a product in which ring contraction has occurred. One reaction is related to those which occur on the metal surface,⁴ whilst the other is more reminiscent of reactions observed in transition-metal complexes.⁵ Some of this work was the subject of an earlier communication.⁸

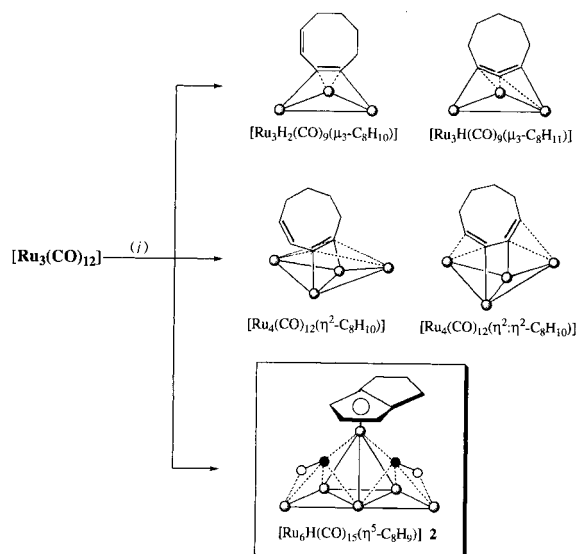
Results and Discussion

The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with cyclohexene in refluxing octane over a 6 h period produced a dark brown solution. After



Scheme 1 Thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with cyclohexene: (i) heat, octane, C_6H_{10}

removal of the solvent under reduced pressure, six products were isolated chromatographically on silica eluting with 30% dichloromethane–hexane. These compounds have been characterised as the butterfly clusters $[\text{Ru}_4(\text{CO})_9(\mu_4\text{-C}_6\text{H}_8)]$ and $[\text{Ru}_4(\text{CO})_9(\mu_4\text{-C}_6\text{H}_8)(\eta^6\text{-C}_6\text{H}_6)]$ (two isomers), the octahedral carbido cluster $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$, the *cis*-bicapped octahedral cluster $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-C}_6\text{H}_6)]$ and a new cluster in which the ligand has undergone ring closure, *viz.* $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ **1** (Scheme 1). The three clusters which are based on the Ru_4 butterfly unit have previously been isolated from the reaction between $[\text{Ru}_3(\text{CO})_{12}]$ and cyclohexa-1,3-diene.⁹ The hexaruthenium carbido cluster $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$ has been prepared by a number of different methods including the thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with cyclohexa-1,3-diene or benzene,^{9,10} the chemical activation of $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ using trimethylamine *N*-oxide in the presence of cyclohexa-1,3-diene¹¹ and by an ionic coupling route.¹² The octaruthenium cluster has only been isolated from the reaction of $[\text{Ru}_3(\text{CO})_{12}]$



Scheme 2 Thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with cycloocta-1,3-diene: (i) heat, octane, C_8H_{12}

with cyclohexene and is not observed in related reactions with benzene or cyclohexa-1,3-diene.¹³ This is in contrast to the closely related species $[\text{Ru}_8\text{H}_4(\text{CO})_{18}(\eta^6\text{-C}_{16}\text{H}_{16})]$ which has the same metal skeleton but contains a [2.2]paracyclophane moiety instead of a benzene ligand, and is isolated from the direct reaction of $[\text{Ru}_3(\text{CO})_{12}]$ and [2.2]paracyclophane.¹⁴

The hexaruthenium cluster $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ **1** was isolated from the reaction in 12% yield and differs from all the other products obtained in that the original C_6 ring has undergone contraction to form a methylcyclopentadienyl ligand. The infrared spectrum of **1** $[\nu(\text{CO})]$ contains peaks corresponding to terminal and edge-bridging carbonyls between 2093 and 1865 cm^{-1} , and at lower wavenumbers there are also two quite distinct peaks at 1431 and 1388 cm^{-1} which may be attributed to the $\mu_4\text{-}\eta^2$ carbonyl ligands found in the crystallographically determined structure. The mass spectrum contains a parent peak at m/z 1106 (calc. 1107) followed by a series of peaks corresponding to the stepwise elimination of CO ligands from the parent cluster. The ^1H NMR spectrum contains four signals at δ 5.44 (m, 2 H), 5.31 (m, 2 H), 2.10 (s, 3 H) and -17.81 (s, 1 H), which, based on the presence of a methylcyclopentadienyl ring and a hydride ligand, may be readily interpreted; the two pairs of inequivalent CH ring protons give rise to the multiplets at δ 5.44 and 5.31, the methyl group protons give rise to the singlet at δ 2.10 and the signal at δ -17.81 may be assigned to the hydride. Definitive characterisation of **1** was achieved by a single-crystal X-ray diffraction analysis (see below).

The thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ with cycloocta-1,3-diene in octane results in a dark brown solution which, upon chromatographic separation, yields five products that have been characterised as the triruthenium cluster isomers $[\text{Ru}_3\text{H}_2(\text{CO})_9(\mu_3\text{-C}_8\text{H}_{10})]$ and $[\text{Ru}_3\text{H}(\text{CO})_9(\mu_3\text{-C}_8\text{H}_{11})]$ ¹⁵ the butterfly clusters $[\text{Ru}_4(\text{CO})_{12}(\mu_4\text{-C}_8\text{H}_{10})]$ (an isomeric pair in which the C_8H_{10} ligand donates four and six electrons to the cluster cores, respectively, thus giving rise to different total electron counts of 60 and 62),¹⁶ and the new cluster $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_3\text{C}_3\text{H}_6)]$ **2** (Scheme 2). Complex **2** contains a trihydropentalenyl moiety which is produced by the dehydrogenation and transannular cyclisation of the original C_8H_{12} ligand. The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with C_8 hydrocarbons such as cyclooctene, cycloocta-1,5-diene, cyclooctatriene and cyclooctatetraene has been studied extensively, and a large number of derivatives with cluster nuclearities ranging from two to six has been prepared.^{5,17}

The infrared spectrum of compound **2** is similar to that observed for **1**, with peaks corresponding to terminal and edge-

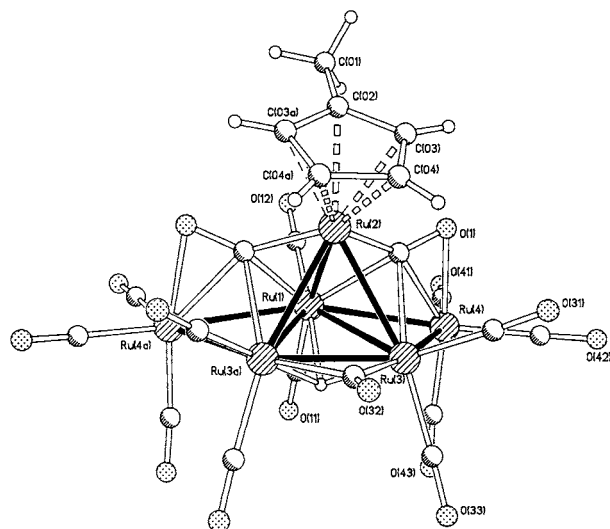


Fig. 1 Molecular structure of $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ **1** (molecule a), showing the labelling scheme; the C atoms of the CO groups bear the same numbering as the corresponding O atoms

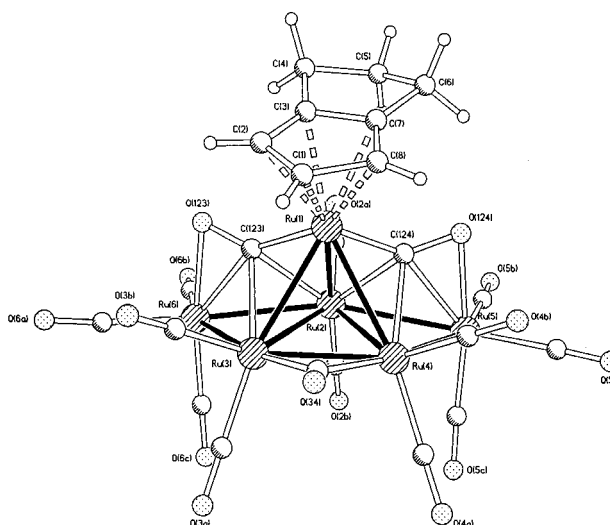


Fig. 2 Molecular structure of $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_3\text{C}_3\text{H}_6)]$ **2**. Details as in Fig. 1

bridging carbonyls between 2092 and 1859 cm^{-1} , and also at lower wavenumber, peaks at 1424 and 1384 cm^{-1} which may be attributed to the $\mu_4\text{-}\eta^2\text{-CO}$ ligands. The mass spectrum contains a strong parent peak at m/z 1133 (calc. 1132) together with peaks corresponding to the sequential loss of several CO groups. The ^1H NMR spectrum contains six signals at δ 5.13 (m, 2 H), 5.08 (m, 1 H), 2.55 (m, 4 H), 2.21 (m, 1 H), 1.46 (m, 1 H) and -24.60 (s, 1 H). The aromatic protons attached to the co-ordinated ring give rise to the signals at δ 5.13 and 5.08 while the signals between δ 2.55 and 1.46 may be assigned to the aliphatic protons. As for **1**, the signal at negative frequency may be assigned to a hydride ligand. The molecular structure of **2** was confirmed by single-crystal X-ray diffraction analysis.

Solid-state structures of compounds **1** and **2**

Single crystals of both compounds **1** and **2** were grown from toluene at $-25\text{ }^\circ\text{C}$. Compound **1** crystallises with three independent molecules in the asymmetric unit (a-c) which show no significant differences. The molecular structures of **1** (molecule a) and **2** are shown in Figs. 1 and 2, respectively, and principal bond lengths are reported in Tables 1 and 2. Since the structures of **1** and **2** are closely related they will be discussed together, however the mirror plane which bisects **1** is not present in **2**.

Table 1 Principal bond distances (Å) for the three molecules of compound **1** present in the asymmetric unit

	Molecule		
	a	b	c
Ru(1)–Ru(2)	2.759(2)	2.759(2)	2.756(2)
Ru(1)–Ru(3)	2.8440(13)	2.8436(13)	2.8556(13)
Ru(1)–Ru(4)	2.8433(10)	2.8469(10)	2.8555(10)
Ru(2)–Ru(3)	2.7798(11)	2.8061(12)	2.7933(12)
Ru(3)–Ru(3a)	2.717(2)	2.712(2)	2.2703(2)
Ru(3)–Ru(4)	2.7666(12)	2.7643(13)	2.7559(12)
Ru(1)–C(1)	2.219(9)	2.212(8)	2.225(8)
Ru(2)–C(1)	1.936(9)	1.926(8)	1.914(9)
Ru(3)–C(1)	2.267(8)	2.225(8)	2.242(8)
Ru(4)–C(1)	2.290(8)	2.294(8)	2.301(8)
Ru(4)–O(1)	2.139(5)	2.128(6)	2.136(6)
C(1)–O(1)	1.232(10)	1.246(10)	1.242(10)
Ru(3)–C(32)	2.126(10)	2.131(11)	2.124(10)
C(32)–O(32)	1.14(2)	1.14(2)	1.13(2)
Mean Ru–C (CO terminal)	1.899(13)	1.899(14)	1.895(14)
Mean C–O (CO terminal)	1.137(20)	1.132(20)	1.137(20)
Mean Ru–C (ring)	2.225(11)	2.226(14)	2.226(11)
Mean C–C (ring)	1.41(2)	1.40(2)	1.41(2)
C(01)–C(02)	1.50(2)	1.464(13)	1.51(2)
Mean Ru–H (μ_3)	1.88(5)	1.88(5)	1.88(5)

The metal geometry of compounds **1** and **2** may be described as a bis(edge-bridged) tetrahedron. The Ru–Ru bond distances range from 2.8440(13) to 2.717(2) Å in **1** and from 2.853(2) to 2.724(2) Å in **2**, the longest edges of each tetrahedron being those bridged by the two Ru atoms, and the shortest being the unique basal edge which is spanned by a symmetrical μ -carbonyl ligand. A similar metal framework has previously been observed in two η^6 -arene-containing clusters, $[\text{Ru}_6(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^6\text{-arene})]$ (arene = $\text{C}_6\text{H}_3\text{Me}_3\text{-1,3,5}$ or C_6Me_6), both of which were prepared from the direct thermal reaction between $[\text{Ru}_3(\text{CO})_{12}]$ and the appropriate arene (mesitylene¹⁸ and hexamethylbenzene,¹⁹ respectively). The mesitylene complex has been found to undergo further reaction to afford the octahedral carbido cluster $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3\text{-1,3,5})]$, and it has been suggested that the interstitial carbido-atom is obtained from the thermally induced cleavage of one of the activated $\mu_4\text{-}\eta^2\text{-CO}$ ligands in $[\text{Ru}_6(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^6\text{-C}_6\text{H}_3\text{Me}_3\text{-1,3,5})]$ with the ejection of CO_2 .¹⁸ However, neither the hexamethylbenzene cluster nor the two clusters **1** and **2** described herein has been found to undergo further reaction to form octahedral carbido clusters. All four compounds contain the 88 valence-shell electrons required to obey the effective atomic number rule with **1** and **2** both having a hydride ligand in order to achieve this valence-electron count.

The cyclopentadienyl-type ligands in compounds **1** and **2** adopt a conventional η^5 terminal co-ordination mode and are bonded to the only tetrahedron vertex not associated with the bridged edges. In **1** the ligand is in fact methylcyclopentadienyl while in **2** it is trihydropentalenyl. In both clusters a π -bonded ($\mu_4\text{-}\eta^2$) carbonyl ligand occupies each of the 'butterfly' cavities created by the bridging Ru atoms and the faces of the metal tetrahedron. The C–O bond lengths of these η^2 carbonyl ligands [1.232(10) in **1** and 1.230(12) and 1.266(12) Å in **2**] are lengthened with respect to the terminally co-ordinated ligands [mean 1.14(2) in **1** and 1.15(2) Å in **2**], which is thought to be due to an increased metal–ligand perturbation, and these carbonyl ligands are considered as four-electron donors. The triply bridging (μ_3) hydride atom has been located experimentally in **1** and is found lying beneath the basal plane, Ru(1)–Ru(3)–Ru(3a), of the central ruthenium tetrahedron. In **2** the hydride atom could not be located directly from the Fourier maps, however a close examination of the molecular space-filling diagram revealed a large niche in the ligand envelope on the Ru(2)–Ru(3)–Ru(4) face, which was accompanied by a pro-

Table 2 Principal bond distances (Å) for **2**

Ru(1)–Ru(2)	2.771(2)	Ru(1)–C(124)	1.906(11)
Ru(1)–Ru(3)	2.804(2)	Ru(2)–C(124)	2.209(11)
Ru(1)–Ru(4)	2.804(2)	Ru(4)–C(124)	2.270(11)
Ru(2)–Ru(3)	2.843(2)	Ru(5)–C(124)	2.330(11)
Ru(2)–Ru(4)	2.853(2)	Ru(5)–O(124)	2.135(8)
Ru(2)–Ru(5)	2.827(2)	C(124)–O(124)	1.266(12)
Ru(2)–Ru(6)	2.827(2)	Ru(1)–C(1)	2.242(13)
Ru(3)–Ru(4)	2.724(2)	Ru(1)–C(2)	2.209(12)
Ru(3)–Ru(6)	2.786(2)	Ru(1)–C(3)	2.214(12)
Ru(4)–Ru(5)	2.752(2)	Ru(1)–C(7)	2.257(11)
Mean Ru–C (CO terminal)	1.90(2)	Ru(1)–C(8)	2.235(12)
Mean C–O (CO terminal)	1.15(2)	C(1)–C(2)	1.39(2)
Ru(3)–C(34)	2.090(12)	C(1)–C(8)	1.44(2)
Ru(4)–C(34)	2.108(12)	C(2)–C(3)	1.39(2)
C(34)–O(34)	1.181(14)	C(3)–C(7)	1.42(2)
Ru(1)–C(123)	1.937(10)	C(3)–C(4)	1.51(2)
Ru(2)–C(123)	2.251(12)	C(4)–C(5)	1.56(2)
Ru(3)–C(123)	2.268(11)	C(5)–C(6)	1.53(2)
Ru(6)–C(123)	2.281(10)	C(6)–C(7)	1.51(2)
Ru(6)–O(123)	2.130(8)	C(7)–C(8)	1.43(2)
C(123)–O(123)	1.230(12)		

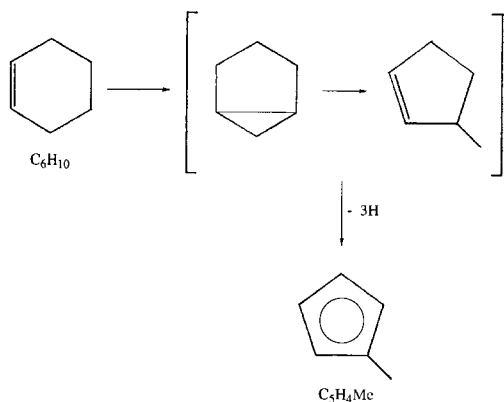
nounced distortion of the carbonyl ligands away from this face. It is therefore assumed, on the basis of the least energetic steric interactions with the surrounding ligands, that the hydride ligand is situated on this face. This is in keeping with the analogous position of the hydride in **1**.

Mechanistic inferences

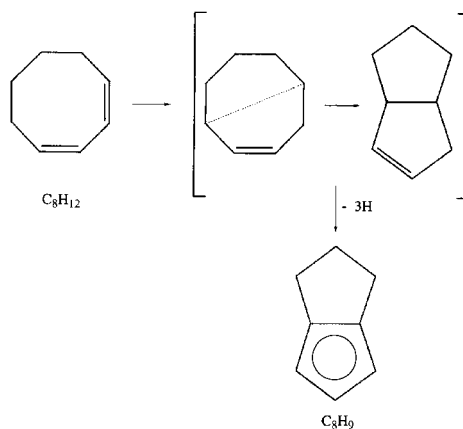
The mechanisms by which the cyclohexene and cycloocta-1,3-diene ligands undergo ring closure to form the methylcyclopentadienyl and trihydropentalenyl moieties in compounds **1** and **2** respectively, are of interest. Unfortunately, due to the complexity of the reactions, *i.e.* the change in cluster nuclearity, the CO bonding modes observed, and the number of other products isolated, it has not been possible to study the precise mechanistic pathways occurring during these reactions. However, based on related work reported in the literature, together with some observations from reactions in which these compounds are *not* isolated, some mechanistic speculations can be postulated.

It was originally postulated that a likely mechanism for the conversion of cyclohexene into the methylcyclopentadienyl ligand in compound **1** involved the initial dehydrogenation of cyclohexene (C_6H_{10}), through cyclohexadiene (C_6H_8), to form a cluster-stabilised cyclohexadienyl (C_6H_7) intermediate. Transannular addition followed by hydrogen transfer were then thought to follow producing the final $\text{C}_5\text{H}_4\text{CH}_3$ moiety.⁸ In previous work we had isolated and fully characterised several cluster derivatives bearing C_6H_9 , C_6H_8 and C_6H_7 groups and so this, at the time, seemed a reasonable suggestion. However, further work in this area has since led us to believe that this may not be the case; first, there is no sign of compound **1** when the reaction is repeated with cyclohexadiene instead of cyclohexene, and secondly, all attempts to convert the $\text{C}_6\text{H}_7\text{-}_9$ cluster compounds described above into derivatives bearing a $\text{C}_5\text{H}_4\text{Me}$ group have proved unsuccessful. An alternative view is therefore to consider that the contraction process occurs whilst the ligand is co-ordinated as cyclohexene, and that the dehydrogenation takes place afterwards thereby resulting in the methylcyclopentadienyl moiety (Scheme 3). This mechanism is also in keeping (even though reversed) with that proposed for benzene hydrogenation over, for example, a sulfided Co–Mo/ Al_2O_3 catalyst,^{4,7} where cyclohexene is considered to be a common intermediate product in hydrogenation to cyclohexane and hydroisomerisation to methylcyclopentane (Scheme 4).

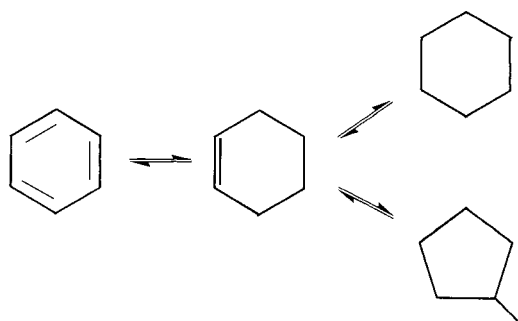
The dehydrogenative transannular cyclisation of unsaturated C_8 rings to form the trihydropentalenyl group found in com-



Scheme 3 A proposed reaction mechanism for the conversion of cyclohexene into the methylcyclopentadienyl moiety found in compound **1**



Scheme 5 A proposed reaction mechanism for the conversion of cycloocta-1,3-diene into the tetrahydropentalenyl moiety found in compound **2**



Scheme 4 The reaction network proposed for the hydrogenation of benzene on supported Group VIII metals and metal sulfide catalysts

compound **2** has previously been observed in cluster chemistry.⁵ Much work has been devoted to the synthesis of pentalene-type compounds and research was originally stimulated in this area in order to stabilise and characterise fully the polyolefin pentalene through complexation with transition metals.^{5,20} The reaction of $[\text{Ru}_3(\text{CO})_{12}]$ with cyclooctatetraene results in two such species: $[\text{Ru}_3(\text{CO})_8(\mu\text{-C}_8\text{H}_6)]$ and $[\text{Ru}_3(\text{CO})_6(\eta^5\text{-C}_8\text{H}_6)(\mu\text{-}\eta^4\text{:}\eta^3\text{-C}_8\text{H}_6)]$. The first of these products contains a pentalene unit co-ordinated over a Ru–Ru edge,²¹ whilst the second contains a trihydropentalenyl moiety co-ordinated in an η^5 manner similar to that observed in **2**.²² It has been suggested that the cyclooctatetraene must initially co-ordinate over a Ru–Ru edge before it is able to convert into the pentalene ligand, however heating μ -cyclooctatetraene complexes has not proved successful in affording pentalene complexes.

The reaction described in this paper involves cycloocta-1,3-diene and we believe that ring closure is again the first step of the reaction mechanism, with loss of three hydrogen atoms from the central bridging carbons together with concomitant C–C bond formation resulting in the observed trihydropentalenyl ligand (Scheme 5). If dehydrogenation to cyclooctatetraene were the first step then products similar to those described above should have been observed, and this is not the case. Although the precise mechanism is uncertain, it appears that the ruthenium cluster is not capable of effecting the extensive dehydrogenation required for the formation of pentalene. This reaction differs from those usually observed when C_8 rings are chemisorbed on metal surfaces as these tend to contract forming bicyclic rings which then undergo retro[2 + 2] cyclisations forming benzene and acetylene units.⁶

Although speculative mechanisms have been proposed for the ring contractions that result in the formation of compounds **1** and **2**, it is important to note that these reactions are complex and as the cluster increases in nuclearity from three to six different mechanisms may be in operation.

Conclusion

Although some similarities between the chemistry of C_6 and C_8 rings on the surface and on triangular clusters are observed, it would appear that, in general, the nature of their reactivity is different. Most importantly the formation of benzene and ethyne from C_8 systems which occurs readily on the surface does not appear to take place on metal clusters. Nonetheless, it is clear that studies of these cluster systems especially those containing apparent intermediates in the dehydrogenation and cyclisation process are leading to a better understanding of the mechanism of these metal-assisted rearrangements.

Experimental

All reactions were carried out with the exclusion of air under an atmosphere of dried nitrogen, using freshly distilled solvents. Product separation was achieved by thin-layer chromatography (TLC) using glass plates supplied by Merck, precoated with a 0.25 mm layer of Kieselgel 60F₂₅₄. Eluents were mixed from standard laboratory-grade solvents. Infrared spectra were recorded using NaCl cells (0.5 mm path length) on a Perkin-Elmer 1710 Series Fourier-transform spectrometer, calibrated with carbon dioxide, fast atom bombardment (FAB) mass spectra on a Kratos MS50TC spectrometer run in positive mode, using CsI as calibrant, and proton NMR spectra in CDCl_3 on Bruker WH200 Fourier-transform spectrometers, all chemical shifts being reported relative to internal SiMe_4 . The cluster, $[\text{Ru}_3(\text{CO})_{12}]$, was prepared according to the literature method,²³ whilst cyclohexene and cycloocta-1,3-diene were obtained from Aldrich chemicals and used without further purification.

Reactions of $[\text{Ru}_3(\text{CO})_{12}]$

With cyclohexene: synthesis of $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ **1.** The compound $[\text{Ru}_3(\text{CO})_{12}]$ (100 mg) was suspended in octane (30 cm^3). An excess of cyclohexene (2 cm^3) was added, and the reaction mixture was heated to reflux for 6 h. The solvent was removed *in vacuo* and the products separated by TLC, using dichloromethane–hexane (3:7, v/v) as eluent. Several bands were isolated and characterised, 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, **6**), $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_4\text{Me})]$ **1** (brown, **12**), $[\text{Ru}_8(\mu\text{-H})_4(\text{CO})_{18}(\eta^6\text{-C}_6\text{H}_6)]$ (brown, **10**) and $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$ (red, 14%).

Compound **1**: IR $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$ (CH_2Cl_2) 2093w, 2080m, 2066vs, 2034m, 2022m, 1965w, 1920w and 1865w (br); (KBr disc) 1431s and 1388m; ^1H NMR (CDCl_3) δ 5.44 (m, 2 H), 5.31 (m, 2 H), 2.10 (s, 3 H) and -17.81 (s, 1 H); positive-ion FAB mass spectrum m/z 1106 (M^+ , calc. m/z 1107). Spectroscopic details of the other complexes can be found in the literature.

With cycloocta-1,3-diene: synthesis of $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_3\text{C}_3\text{H}_6)]$ **2.** The compound $[\text{Ru}_3(\text{CO})_{12}]$ (100 mg) was suspended in octane (30 cm³). An excess of cycloocta-1,3-diene (1 cm³) was added, and the reaction mixture was heated to reflux for 4 h. The solvent was removed *in vacuo* and the products separated by TLC, using dichloromethane–hexane (1:4, v/v) as eluent. Several bands were isolated and characterised, in order of elution, as $[\text{Ru}_3\text{H}_2(\text{CO})_9(\mu_3\text{-C}_8\text{H}_{10})]$ (yellow, 8), $[\text{Ru}_3\text{H}(\text{CO})_9(\mu_3\text{-C}_8\text{H}_{11})]$ (yellow, 8), $[\text{Ru}_4(\text{CO})_{12}(\mu_4\text{-C}_8\text{H}_{10})]$ (brown, 6), $[\text{Ru}_4(\text{CO})_{12}(\mu_4\text{-C}_8\text{H}_{10})]$ (purple, 23) and $[\text{Ru}_6(\mu_3\text{-H})(\mu_4\text{-}\eta^2\text{-CO})_2(\text{CO})_{13}(\eta^5\text{-C}_5\text{H}_3\text{C}_3\text{H}_6)]$ **2** (brown, 10%).

Compound **2**: IR $\tilde{\nu}(\text{CO})/\text{cm}^{-1}$ (CH_2Cl_2) 2092w, 2070s, 2059w, 2033vs, 2010m, 1988w and 1859w (br); (KBr disc) 1424s and 1384m; ¹H NMR (CDCl_3) δ 5.13 (m, 2 H), 5.08 (m, 1 H), 2.55 (m, 4 H), 2.21 (m, 1 H), 1.46 (m, 1 H) and –24.60 (s, 1 H); positive-ion FAB mass spectrum m/z 1133 (M^+ , calc. m/z 1132). Spectroscopic details of the other complexes can be found in the literature.

Crystallography

Crystal data. Compound **1** crystallises with three independent molecules per asymmetric unit, $\text{C}_{21}\text{H}_8\text{O}_{15}\text{Ru}_6$, $M = 1106.69$, monoclinic, space group $P2(1)/m$, $a = 9.910(3)$, $b = 16.963(4)$, $c = 24.936(9)$ Å, $\beta = 100.26(3)^\circ$, $U = 4125(2)$ Å³, $Z = 6$, $D_c = 2.673$ g cm⁻³, red crystal $0.12 \times 0.31 \times 0.39$ mm, $\mu(\text{Mo-K}\alpha) = 3.284$ mm⁻¹, $F(000) = 3108$. Compound **2**, $\text{C}_{23}\text{H}_9\text{O}_{15}\text{Ru}_6$, $M = 1131.72$, tetragonal, space group $P4(3)2(1)2$, $a = b = 11.259(6)$, $c = 46.67(2)$ Å, $U = 5916(5)$ Å³, $Z = 8$, $D_c = 2.541$ g cm⁻³, dark red crystal $0.23 \times 0.23 \times 0.19$ mm, $\mu(\text{Mo-K}\alpha) = 3.056$ mm⁻¹, $F(000) = 4248$.

Data collection and processing. All X-ray measurements were made on a Stoe Stadi-4 four-cycle diffractometer equipped with an Oxford Cryosystems low-temperature device,²⁴ graphite-monochromated Mo-K α X-radiation (λ 0.710 73 Å), T 150(2) K, ω scans; **1**, 6287 unique data collected (θ range 2.5–25°, h –11 to 11, k –13 to 18, l 0–26), semiempirical absorption correction based on ψ scans applied,²⁵ giving 5185 unique reflections with $I > 2\sigma(I)$ for use in all calculations; **2**, 3727 unique data collected (θ range 2.5–22.5°, h 0–10, k 0–12, l 0–50), semiempirical absorption correction based on ψ scans applied, giving 3700 reflections with $I > 2\sigma(I)$ for use in all calculations.

Structure solution and refinement. The ruthenium atoms were located by automatic direct methods,²⁶ and subsequent iterative cycles of least-squares refinement and Fourier-difference synthesis located all non-H atoms.²⁷ In both compounds **1** and **2** all non-H atoms were then refined (by least squares on F^2 using SHELXL 93²⁷) with anisotropic thermal parameters. However, in **2** atoms C(123) and C(124) had a tendency to adopt non-positive definite anisotropic displacement parameters, and this was resolved by restraining these atoms to adopt approximate isotropic behaviour, while at the same time applying rigid-bond and rigid-body constraints to the carbonyl ligands of which they are part. Hydrogen-atoms on C were included at fixed, calculated positions and refined using a riding model, while thermal parameters for the H(hydride) atom in **1** were fixed at 0.08 Å².

For compound **1** at final convergence $R [I > 2\sigma(I)] = 0.0409$, $wR2 = 0.1134$ (all data), $S = 1.128$ for 620 refined parameters and the final ΔF synthesis showed no electron density above 1.20 or below –1.46 e Å⁻³. For **2** at final convergence $R [I > 2\sigma(I)] = 0.0334$, $wR2 = 0.0746$ (all data), $S = 1.103$ for 397 refined parameters and the final ΔF synthesis showed no electron density above 0.614 or below –0.594 e Å⁻³.

Atomic scattering factors were inlaid,²⁷ or taken from ref. 28. Molecular geometry calculations utilised CALC,²⁹ and Figs. 1 and 2 were produced using SHELXTL PC.³⁰

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/463.

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