Cyclohexa-1,4-diene in a bridging coordination mode: synthesis and structural characterisation of $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)$ and $Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2$

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Abstract

Reaction of the square-pyramidal cluster $[Ru_5C(CO)_{15}]$ with cyclohexa-1,4-diene and Me_3NO in CH_2Cl_2 affords the organometallic cluster $[Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)]$ (**1**). Further reaction of **1** with cyclohexa-1,4-diene and Me_3NO in CH_2Cl_2 yields $[Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$ (**2**). The molecular structures of both **1** and **2** have been established by single crystal X-ray analysis. In **1** the diene ligand occupies a radial position bridging two metal atoms on the square base of the cluster, while in **2** the second diene substitutes two axial carbonyl groups on consecutive basal ruthenium atoms. In both clusters, the 1,4-topology of the diene ligand is maintained. Studies of the variation in the ^1H NMR spectrum of **2** with temperature have revealed that as the temperature is raised the two different C_6H_8 ligands equilibrate.

Introduction

The number of arene-cluster compounds reported in recent years has increased dramatically with the advent of many new synthetic techniques. These synthetic methods may be grouped into two broad categories. First, those in which arenes are reacted directly with an appropriate cluster, and second, those using other reagents which undergo conversion to an arene at some stage during the synthesis. For example, $Co_4(CO)_9(\eta^6\text{-arene})$ may be prepared from the direct reaction of $Co_2(CO)_8$ or $Co_4(CO)_{12}$ with arene [1], whereas the synthetic approach to $[Os_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$ commences with the reaction between cyclohexa-1,3-diene and the highly reactive cluster $[H_2Os_3(CO)_{10}]$, affording the dienyl cluster $[HOs_3(CO)_9(\mu_3\text{-}\eta^1\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_7)]$ [2]. Removal of a hydride from this dienyl complex by reaction with $[Ph_3C][BF_4]$ to yield the cationic benzene species $[HOs_3(CO)_9(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]^+$ is followed by deprotonation to give the neutral benzene cluster. Recently, we have demonstrated that this same dienyl complex may be derived from an η^4-coordinated cyclohexadiene ligand [3].

Similarly, in our studies of the pentaruthenium-carbido cluster [4], we have observed the formation of stable diene intermediates which may be readily converted to arene-bound clusters. Thus, the cluster $[Ru_5C(CO)_{15}]$ reacts with cyclohexa-1,3-diene and Me_3NO in CH_2Cl_2 to afford the bridging diene complex $[Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_8)]$, which upon further reaction with Me_3NO converts to two benzene cluster isomers $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$ and $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$. The 'dehydrogenation' of the C_6H_8 ring has been proposed to occur via a C–H bond cleavage, resulting in a cyclohexadienyl-hydrido intermediate, which undergoes subsequent conversion to benzene after a second C–H bond cleavage. This second stage is almost certainly accompanied by a square pyramidal ⇔ bridged butterfly rearrangement of the cluster core; a characteristic feature of this system. Cyclohexa-1,3-diene has also been found to coordinate in an η^4-fashion in $[Ru_5C(CO)_{11}(\eta^4\text{-}C_6H_8)_2]$, which undergoes conversion to $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^2\text{-}C_6H_6)]$ when treated with carbon monoxide [5].

In this paper, we demonstrate that when cyclohexa-1,4-diene is employed in similar reactions, the 1,4-diene form persists upon coordination. This behaviour is unusual within the organometallic chemistry of cyclohexadiene. Previously, the only examples of 1,4-ligands

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to be structurally characterised by X-ray diffraction techniques have been for substituted dienes prepared indirectly from the 'hydrogenation' of coordinated arenes [6].

Results and discussion

Synthesis and chemical characterisation

Treatment of the square-pyramidal cluster $[Ru_5C(CO)_{15}]$ with two molecular equivalents of Me_3NO (trimethylamine-*N*-oxide) in dichloromethane, in the presence of cyclohexa-1,4-diene results in the formation of $[Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,4)]$ (**1**). Isolation of product **1** is achieved by thin layer chromatography eluting with dichloromethane–ethylacetate–hexane (10:5:85, vol./vol.) Formulation of compound **1** was based upon mass and ^{1}H NMR spectroscopic evidence. The mass spectrum exhibits a strong parent peak at 962 (calc. = 962) with the subsequent loss of several CO groups. ^{1}H NMR is also consistent with the proposed structure with two multiples at δ 5.08 and 4.56 ppm, consistent with the olefinic protons and a singlet at δ 2.03 ppm indicative of four chemically equivalent aliphatic protons of the diene. This spectrum is not easily interpreted, since, if all the aliphatic protons share the same chemical environment, we would expect the olefinic protons also to be equivalent.

Further treatment of compound **1** with two molecular equivalents of Me_3NO, also in dichloromethane containg excess cyclohexa-1,4-diene, followed by product extraction using TLC, eluting with dichloromethane–hexane (20:80 vol./vol.), yields, in order of elution, $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ and the novel bis-cyclohexa-1,4-diene cluster $[Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2]$ (**2**). The benzene cluster has been reported previously from the treatment of the 1,3-isomeric form of compound **1** with Me_3NO in dichloromethane only [4]. Hence, the formation of the benzene cluster is not unreasonable from this reaction. Compound **2** was characterised, initially, by spectroscopic methods. The mass spectrum of this compound contains a parent peak at 985 (calc. = 986) together with the loss of eleven CO groups. ^{1}H NMR is not simple, and deserves a detailed examination.

^{1}H NMR of compound 2

The ^{1}H NMR spectrum of compound **2** at 296 K consists of twelve signals, labelled A–L in Fig. 1(a), eight of which are of relative intensity one, and four of relative intensity two (namely signals D, F, J and L). Lowering the temperature of the sample to 223 K (Fig. 1(b)) improved the resolution of the signals such that it was possible to measure some of the larger coupling constants. This spectrum revealed that each of the signals D, F, J and L possessed a coupling constant of *c*. 7 Hz, with the remaining signals A, B, C, E, G, H, I and J each have one large coupling constant of *c*. 18 Hz. The resolution of the signals is insufficiently clear for smaller coupling constants to be

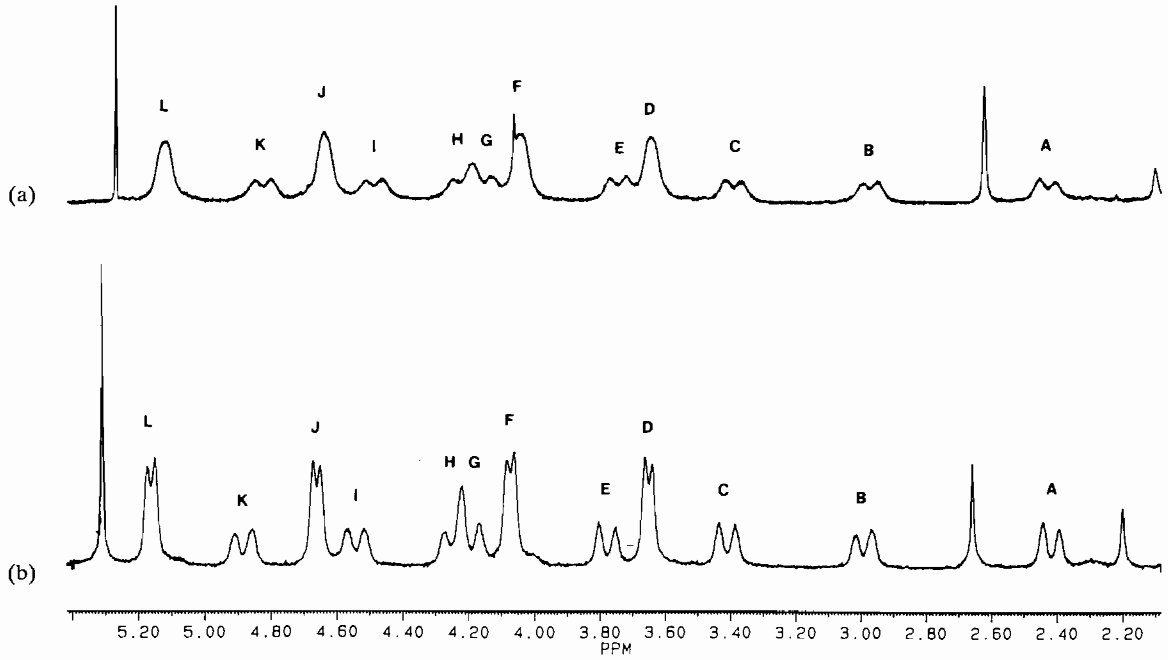


Fig. 1. 360 BMHz ^{1}H NMR spectrum of **2** obtained at 296 (a) and 223 (b) K.

established. These data are consistent with the area one signals being due to the geminal CH_2 protons, each of which would be expected to be inequivalent to its partner. A series of homonuclear decoupling/nOe experiments carried out at 223 K showed signals A, B, D, E, F and H belonged to one C_6H_8 moiety, while signals C, G, I, J, K and L are associated with the other ring. The geminals pairs found using these experiments were A/B, C/I, E/H and G/K, with signal D showing small coupling to A/B, F to E/H, J to C/I and L to G/K, suggesting the proton arrangements illustrated in Fig. 2, for the two ligands.

The observation that the spectrum of compound **2** obtained at 296 K was broader than that obtained at 223 K suggests some fluxionality. EXSY spectra, depicted in Fig. 3, carried out at 296 K, suggest that the two cyclohexadiene ligands are starting to undergo site exchange. Cross peaks are thus found between A and G, B and K, C and E, H and I, D and L, F and J.

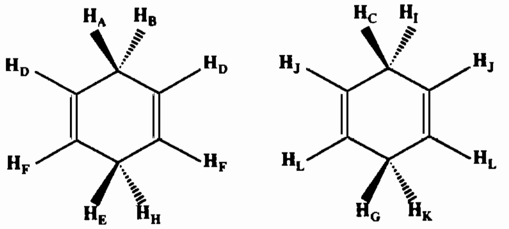


Fig. 2. Assignment of signals A–L in compound 2.

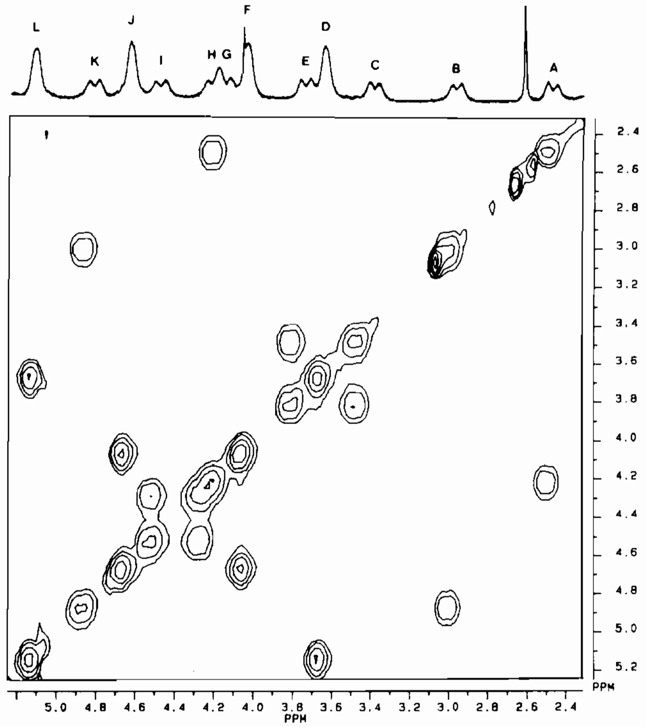


Fig. 3. The 360 BMHz ^1H 2-D EXSY spectrum of **2** with a 30 ms mixing time. The spectrum was obtained using the standard phase-sensitive NOESY sequence, 128 t_1 increments of 16 transients each were obtained, each of 512 points and 0.133 s, and a recycle delay of 2 s. A spectrum width of 1930 Hz was used in the f_2 dimension with the f_1 dimension using 965 Hz.

If therefore appears that at 296 K, the system exhibits two-site exchange. For a system exhibiting first order exchange between two sites in the same molecule, it is possible to relate cross and diagonal peak intensities derived from EXSY spectra to the exchange rate at the temperature at which the experiment was carried out. Assuming this to be the case, the rate of exchange can be evaluated by using the equation [7]:

$$k_{ex} = \frac{1}{2T_m} \times \ln \frac{1 + I_c/I_d}{1 - I_c/I_d}$$

where k_{ex} = rate of exchange, T_m = mixing time of EXSY experiment, I_c = cross peak intensity from EXSY spectrum, I_d = diagonal peak intensity from EXSY spectrum. For this work, three mixing times were used to obtain such spectra, namely 10, 20 and 30 ms, and from these k_{ex} was calculated as $31 \pm 5\ s^{-1}$.

Further elevation of the temperature caused significant broadening such that by 316 K all signals arising from diene ring protons were broadened. By 330 K there appeared to be just two broad signals forming, these gaining apparent doublet structure by 346 K. These signals are at δ values of 4.37 and 3.63 ppm. Residual underlying broadness made integration of these signals impossible, and further heating of the sample resulted in irreversible sample decomposition.

Considering all these phenomena, the NMR behaviour suggests that at 233 K, the two C_6H_8 ligands are in such slow exchange that the ^1H spectrum is essentially that of the crystallographically determined structure. At 296 K the two diene ligands appear to be undergoing site exchange, probably correlated to the rotation of the apical tricarbonyl unit (*vide infra*). This is shown in Fig. 4.

At higher temperatures (> 330 K) the situation is less clear, because the sample undergoes decomposition. However, in light of the information presently available, it would appear that in addition to the site exchange outlined above, the ligands undergo rapid rotation and flexing.

Single crystal X-ray structures of 1 and 2

The molecular structures of **1** and **2** have been determined by single crystal X-ray diffraction analysis,

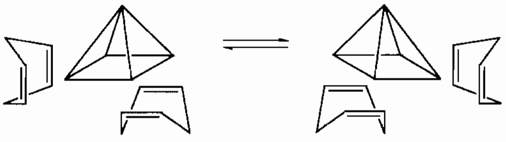


Fig. 4. Diagram showing the exchange process occurring in cluster 2.

and since they are closely related will be discussed together. Suitable crystals of compound **1** were obtained from a toluene solution stored at −25 °C for several weeks, while crystals of **2** were obtained from the slow evaporation of a dichloromethane–hexane solution. The molecular structures of compounds **1** and **2** are illustrated in Figs. 5 and 6, respectively. Relevant structural parameters for both species are compared in Table 1. Note that there are two independent ‘half’ molecules in the asymmetric unit of species **2** (see ‘Experimental’). The structural parameters relative to these two units are listed separately in Table 1. Both **1** and **2** are characterised by the presence of the square-pyramidal metal atom framework common to $Ru_5C(CO)_{15}$ [8] and other cyclohexadiene and benzene derivatives [4]. The semi-interstitial C(carbide) atom occupies roughly the centre of the square base. In **1** the 1,4-C_6H_8 ligand formally replaces two radial CO ligands belonging to two contiguous Ru atoms of the basal plane (radial μ_2-η^2:η^2 bonding mode). In **2** there are two bridging 1,4-C_6H_8 ligands, the first one is bound in a similar manner to that in **1**, while the second ligand spans the opposite Ru–Ru edge, replacing two axial COs (axial μ_2-η^2:η^2 bonding mode). Both molecules possess molecular and crystallographic $C_s - m$ symmetry with the mirror plane bisecting the C_6H_8 ligand(s) and comprising the apical Ru atom and one of its terminal ligands as well as the Central C(carbide) atom. It is interesting to observe that, in spite of the different crystal systems (see ‘Experimental’), both molecules maintain the mirror symmetry in their crystal structures. The two independent structural units in **2** are equivalent within the e.s.d.s of the structural parameters (see Table 1), thus bond distances and angles for this species will be discussed as pairs of corresponding values in the following text.

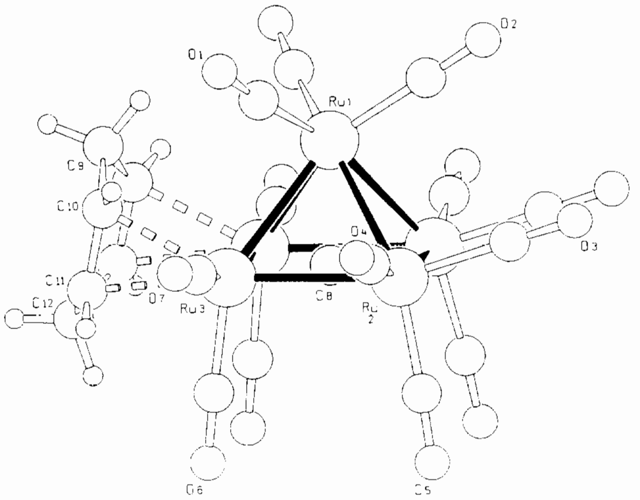


Fig. 5. The molecular structure of **1** showing the labelling of thc independent atoms. Hydrogen atoms bear the same numbering as the corresponding carbon atoms.

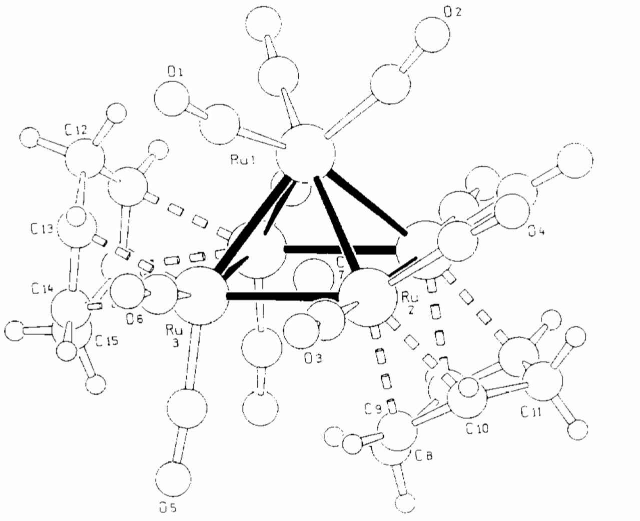


Fig. 6. The molecular structure of one of the two inuependent molecules of **2**. Hydrogen atoms bear the same numbering as the carbon atoms which they are bound to.

TABLE 1. Relevant structural parameters (Å) for **1** and the two independent molecules of **2**

	1		**2**	
			Molecule A	Molecule B
Ru(1)–Ru(2)	2.812(1)		2.807(2)	2.828(2)
Ru(1)–Ru(3)	2.859(1)		2.855(2)	2.867(2)
Ru(2)–Ru(3)	2.844(1)		2.844(2)	2.841(2)
Ru(2)–Ru(2′)	2.887(1)		2.842(2)	2.840(2)
Ru(3)–Ru(3′)	2.772(1)		2.794(2)	2.808(2)
Ru(1)–$C_{carbide}$	2.047(1)		2.10(1)	2.07(1)
Ru(2)–$C_{carbide}$	2.028(1)		2.01(1)	2.02(1)
Ru(3)–$C_{carbide}$	1.985(3)		2.00(1)	1.99(1)
C(8)–C(9)			1.51(1)	1.54(1)
C(9)–C(10)	1.497(5)		1.36(1)	1.38(1)
C(10)–C(11)	1.373(6)		1.52(1)	1.52(1)
C(11)–C(12)	1.511(6)			
C(12)–C(13)			1.52(1)	1.50(1)
C(13)–C(14)			1.37(1)	1.37(1)
C(14)–C(15)			1.51(1)	1.52(1)
Ru–C_{co}(mean)	1.91(2)		1.88(3)	1.89(1)
C_{co}–O(mean)	1.137(6)		1.14(1)	1.16(1)
Ru(3)–C(10)	2.302(4)	Ru(2)–C(9)	2.29(1)	2.26(1)
Ru(3)–C(11)	2.314(4)	Ru(2)–C(10)	2.27(1)	2.28(1)
		Ru(3)–C(13)	2.32(1)	2.32(1)
		Ru(3)–C(14)	2.30(1)	2.32(1)

Ru–Ru bond lengths range from 2.772(1) to 2.887(1) Å in **1** and from 2.794(2), 2.808(2) to 2.855(2), 2.867(2) Å in **2**, the shortest Ru–Ru bond being, in both complexes, involved in the radial 1,4-C_6H_8 bridge. The longest bond in **1** is the unbridged edge opposite to thc radially bound μ_2-η^2:η^2-C_6H_8 ligand, while in both the independent units of **2** the axially bridged bond is longer than the radially bridged one (2.842(2), 2.840(2)

Å versus 2.794(2), 2.808(2) Å). The ligands show a clear multiple bond localisation between the metal coordinated C–C systems (1.373(6) in **1**, 1.36(1), 1.38(1) and 1.37(1), 1.37(1) Å for the axial and radial ligands in **2**, respectively). The cyclohexa-1,4-diene ligands adopt regular boat conformations. Apart from the different localisation of the C=C double bonds within the unsaturated ligand, the geometry of complex **1** is strictly comparable with that shown by the analogous 1,3-C_6H_8 derivative $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,3)$ [4].

As previously pointed out [9], the reason for the radial/axial coordination of the 1,4-C_6H_8 ligands in **2** is probably due to the steric repulsions that could arise between the CO ligands attached to the apical ruthenium atom and the cyclohexadiene ligands, should both ligands occupy radial sites around the cluster basal plane.

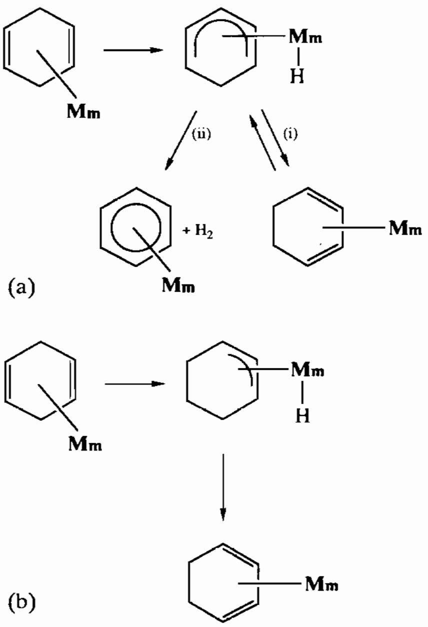
Mechanistic proposals

The use of Me_3NO is well documented as a 'chemical activator' yielding substituted derivatives of binary carbonyl complexes, and the formation of **1** from $[Ru_5C(CO)_{15}]$ can be taken to involve first the oxidative removal of two coordinated carbonyl groups (by oxidation to CO_2) creating vacant coordination sites on the central ruthenium cluster, which is possibly partially stabilised by Me_3N generated during the reaction. This is followed by addition of the diene ligand. Since the diene spans two ruthenium atoms on the square base of the cluster, replacing two equatorial CO groups, it would appear that the Me_3NO attacks these CO in preference to the others, although as an alternative, CO ligand scrambling may occur during the course of the reaction.

The formation of **2** from **1** can be envisaged as substitution of two axial CO groups, on the opposite two ruthenium atoms to which the first diene is bound, for the second diene moiety, by a mechanism paralleling that described for the formation of **1**. The reason for axial substitution, which persists in solution at the temperature at which reaction occurs (indicated by ^1H NMR) may be attributed to the steric hindrance with respect to the tricarbonyl unit on the apical ruthenium atom, described above.

The stabilisation of the 1,4-diene by the Ru_5C unit is of some considerable interest. In general, both 1,5- and 1,4-dienes undergo isomerisation to the 1,3-form in the presence of iron or ruthenium fragments. Although the stabilisation of the 1,4-diene is understandable in this case, given the appropriate and correct disposition of two metal atoms for coordination to the 1,4-double bond arrangement, it does raise some fundamental queries about the mechanism by which isomerisation to other forms or conversion to benzene takes place. Based on work carried out on a variety of other systems, e.g. Ru_6C, we have assumed that isomerisation of the 1,4-diene to the 1,3-form took place via the formation of the hexadienyl-hydrido intermediate shown in Scheme 1(a), followed by H addition as shown in step (i). However, we have established, in work on $[HOs_3(CO)_9(\mu_3\text{-}\eta^1{:}\eta^2{:}\eta^2\text{-}C_6H_7)]$ that, conversion to $[Os_3(CO)_9(\mu_3\text{-}\eta^2{:}\eta^2{:}\eta^2\text{-}C_6H_6)]$ occurs via the formal removal of H_2. This reaction is presumably driven by the demands of the central Os_3 cluster to sustain a 48-electron count.

We now believe it is unlikely that both isomerisation and conversion proceed by the same intermediate and given the need for both the precursor cluster unit and the final cluster product to sustain (in the core of Ru_6C) at 86-electron count we wish to propose that isomerisation occurs via a π-allylic intermediate of the type shown in Scheme 1(b). Throughout this process one double bond remains uncoordinated and hence the same electron count is maintained. If during this process additional ligand loss (e.g. of CO) occurs, then formation of the dienyl product and hence the benzene derivative will result. Thus, the reaction of $[Ru_6C(CO)_{17}]$ with 1,3- or 1,4-C_6H_8 to give both $Ru_6C(CO)_{15}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8)]$ and $[Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)]$ is understood.



Scheme 1.

Experimental

All reactions were carried out with the exclusion of air using solvents freshly distilled under an atmosphere of nitrogen. Subsequent work-up of products was achieved without precautions to exclude air. IR spectra were recorded on a Perkin-Elmer 1600 Series FTIR in CH_2Cl_2 using NaCl cells. Positive fast atom bombardment mass spectra were obtained using a Kratos MS50TC spectrometer, using CsI as calibrant. ^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker 360 BMHz instrument, and referenced to internal TMS. Conditions for obtaining EXSY spectra are recorded in Fig. 3. Products were separated by thin layer chromatography (TLC) on plates supplied by Merck coated with a 0.25 mm layer of Kieselgel 60 F_{254}. $Ru_5C(CO)_{15}$ was prepared by the literature procedure [8]. Cyclohexa-1,4-diene was purchased from Aldrich Chemicals and used without further purification. Trimethylamine-*N*-oxide (Me_3NO) was sublimed prior to reaction.

Preparation of $Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,4)$ (1)

$Ru_5C(CO)_{15}$ (100 mg) was dissolved in dichloromethane (20 ml) and cyclohexa-1,3-diene (1.5 ml), and the solution cooled to -78 °C. A solution of Me_3NO (16 mg, 2.1 mol. equiv.) in dichloromethane (10 ml) was added dropwise over a period of 5 min. The mixture was stirred for an additional 30 min while the solution was brought to room temperature. IR spectroscopy indicated complete consumption of the starting material. The solvent was removed *in vacuo* and the residue separated by TLC using a solution of dichloromethane/ethylacetate/hexane (10:5:85) as eluent. The major red band was extracted and characterised as $Ru_5C(CO)_{13}(\mu^2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,4)$ (**1**) (27 mg).

Spectroscopic data for **1**: IR (CH_2Cl_2): ν(CO) 2084(m), 2051(s), 2033(m, sh), 2016(vs), 1983(w, br), 1942(w, br) cm^{-1}; ^{1}H NMR ($CDCl_3$): δ 5.08 (m, 2H), 4.56 (m, 2H), 2.03 (s, 4H) ppm; MS: $M^+ = 962$ (calc. = 962) a.m.u.

Preparation of $Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2$ (2)

$Ru_5C(CO)_{13}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,4)$ (**1**) (22 mg) was dissolved in dichloromethane (20 ml) and cyclohexa-1,4-diene (1.5 ml), and the solution cooled to -78 °C. A solution of Me_3NO (6 mg, 2.1 mol. equiv.) in dichloromethane (5 ml) was added dropwise over a period of 5 min. The mixture was stirred for a further 30 min while the solution was brought to room temperature. IR spectroscopy indicated complete consumption of the starting material. The solvent was removed *in vacuo* and the residue separated by column chromatography using a solution of dichloromethane/hexane (20:80) as eluent. The major brown product was extracted and

TABLE 2. Crystal data and details of measurements for **1** and **2**

	1	**2**
Formula	$C_{20}H_8O_{13}Ru_5$	$C_{24}H_{16}O_{11}Ru_5$
Molecular weight	961.6	985.7
Crystal size (mm)	0.15 × 0.25 × 0.10	0.45 × 0.35 × 0.20
Temperature (K)	293	293
System	monoclinic	orthorhombic
Space group	$P2_1/m$	*Pbam*
a (Å)	9.785(2)	31.469(9)
b (Å)	12.098(2)	13.572(4)
c (Å)	11.273(3)	12.682(5)
α (°)		
β (°)	105.85(2)	
γ (°)		
V (Å^3)	1283.8	5416.5
Z	2	8
F(000)	904	3744
λ(Mo Kα) (Å)	0.71069	0.71069
μ (Mo Kα) (cm^{-1})	28.8	27.3
θ range (°)	3–25	3–25
ω-Scan width (°)	0.70	0.70
Requested counting $\sigma(I)/I$	0.02	0.02
Prescan rate (° min^{-1})	8	8
Prescan acceptance $\sigma(I)/I$	0.5	0.5
Maximum scan time (s)	90	90
Octants explored ($h_{min}h_{max}$, $k_{min}k_{max}$, $l_{min}l_{max}$)	−11 11, 0 14, 0 13	0 37, 0 16, 0 15
Measured reflections	2507	5750
Unique observed reflections ($I_o > 2\sigma(I_o)$)	2286	4591
No. refined parameters	184	393
R, R_w^{a}, S	0.022, 0.024, 0.62	0.052, 0.055, 1.67
K, g^{a}	1, 0.058	1, 0.1

$^aR_w = \Sigma[(F_o - F_c)w^{1/2}]/\Sigma F_o w^{1/2})$, where $w = k/[\sigma(F) + |g|F^2]$.

TABLE 3. Fractional atomic coordinates for **1**

Atom	*x*	*y*	*z*
Ru1	0.59736(4)	0.2500	0.14651(4)
Ru2	0.85010(3)	0.13069(2)	0.17051(3)
Ru3	0.72592(3)	0.13542(2)	0.37105(3)
O1	0.3937(4)	0.0589(4)	0.1460(4)
O2	0.5523(7)	0.2500	−0.1316(5)
O3	0.8879(6)	0.1244(4)	−0.0883(4)
O4	0.7671(5)	−0.1117(3)	0.1281(4)
O5	1.1582(4)	0.0875(4)	0.3076(4)
O6	0.9980(4)	0.1134(3)	0.5740(3)
O7	0.6598(5)	−0.1123(3)	0.3519(4)
C1	0.4727(5)	0.1294(4)	0.1515(4)
C2	0.5700(7)	0.2500	−0.0280(5)
C3	0.8745(6)	0.1312(4)	0.0086(5)
C4	0.7050(5)	−0.0212(4)	0.1463(4)
C5	1.0436(5)	0.1021(4)	0.2537(4)
C6	0.8933(4)	0.1182(3)	0.4969(4)
C7	0.6856(5)	−0.0208(4)	0.3559(4)
C8	0.7921(5)	0.2500	0.2735(4)
C9	0.4425(6)	0.2500	0.4109(6)
C10	0.5292(4)	0.1470(3)	0.4451(4)
C11	0.6459(5)	0.1466(4)	0.5458(4)
C12	0.6891(7)	0.2500	0.6218(5)

characterised spectroscopically to be $Ru_5C(CO)_{11}(\mu_2\text{-}\eta^2{:}\eta^2\text{-}C_6H_8\text{-}1,4)_2$ (**2**) (9 mg).

Spectroscopic data for **2**: IR (CH_2Cl_2): ν(CO) 2048(m), 2017(vs), 1984(m, br), 1935(w, br) cm^{-1}; ^1H NMR ($CDCl_3$) at 235 K: δ 5.13 (d, 2H), 4.84 (d, 1H), 4.67 (d, 2H), 4.55 (d, 1H), 4.24 (d, 2H), 4.12 (d, 2 H), 3.81 (d, 1H), 3.67 (d, 2H), 3.47 (d, 1H), 2.98 (d, 1H), 2.49 (d, 1H) ppm (all signals are broad at room temperature); MS: $M^+ = 985$ (calc. = 985) a.m.u.

Crystallographic information and details of measurements are summarized in Table 2. Diffraction intensities for both species were collected at room temperature on an Enraf-Nonius CAD-4 diffractometer. The structures were solved by direct methods and refined by full-matrix least-squares. Absorption correction was applied by the method of Walker and Stuart [10]. All non-hydrogen atoms were allowed to vibrate anisotropically. The H atoms were added in calculated positions (C–H 0.97 Å for the methylenic, 0.92 Å for the aromatic ones) and refined 'riding' on their respective C atoms. Two overall isotropic temperature factors were applied to the methylenic and aromatic hydrogen atoms of both compounds, which converged to 0.06, 0.096 and 0.08, 0.15 Å^2 for **1** and **2**, respectively. Two independent 'half molecules' are present in the asymmetric unit of **2**, each one lying on a crystallographic mirror plane. Fractional atomic coordinates for **1** and **2** are listed in Tables 3 and 4, respectively. Refinement on *F*s was carried out with SHELX-92 [11] packages of crystallographic programs.

TABLE 4. Fractional atomic coordinates for **2**

Atom	*x*	*y*	*z*
Ru1A	0.10427(2)	0.43355(5)	0.0000
Ru2A	0.16512(2)	0.32443(5)	0.11204(4)
Ru3A	0.07920(2)	0.25955(4)	0.11015(4)
O1A	0.0485(2)	0.5096(5)	0.1761(5)
O2A	0.1549(5)	0.6252(8)	0.0000
O3A	0.1608(3)	0.3428(6)	0.3512(5)
O4A	0.2295(3)	0.4879(7)	0.1206(5)
O5A	0.0935(3)	0.0485(6)	0.1685(8)
O6A	0.0663(3)	0.3184(7)	0.3412(5)
C1A	0.0691(3)	0.4753(6)	0.1126(5)
C2A	0.1393(4)	0.5498(9)	0.0000
C3A	0.1618(3)	0.3323(6)	0.2596(6)
C4A	0.2047(3)	0.4284(8)	0.1148(6)
C5A	0.0896(3)	0.1310(7)	0.1452(7)
C6A	0.0732(2)	0.2967(7)	0.2567(6)
C7A	0.1232(4)	0.2855(7)	0.0000
C8A	0.1828(5)	0.1151(9)	0.0000
C9A	0.1947(3)	0.1704(6)	0.0991(6)
C10A	0.2267(2)	0.2375(6)	0.0996(6)
C11A	0.2527(4)	0.2531(13)	0.0000
C12A	−0.0080(4)	0.3407(10)	0.0000
C13A	0.0068(2)	0.2883(6)	0.0990(5)
C14A	0.0131(3)	0.1885(6)	0.0984(7)
C15A	0.0055(6)	0.1288(10)	0.0000
Ru1B	0.09013(3)	0.89681(7)	0.5000
Ru2B	0.16785(2)	0.89585(5)	0.38802(4)
Ru3B	0.11675(2)	0.72331(5)	0.38929(4)
O1B	0.0229(4)	0.8765(11)	0.3336(8)
O2B	0.0803(8)	1.1239(11)	0.5000
O3B	0.1714(3)	0.8921(6)	0.1473(6)
O4B	0.1714(4)	1.1202(6)	0.3717(8)
O5B	0.1894(3)	0.5948(6)	0.3199(6)
O6B	0.0901(3)	0.7631(8)	0.1597(5)
C1B	0.0510(3)	0.8806(11)	0.3881(8)
C2B	0.0870(7)	1.0336(12)	0.5000
C3B	0.1686(3)	0.8928(6)	0.2379(5)
C4B	0.1683(4)	1.0342(8)	0.3823(6)
C5B	0.1620(4)	0.6426(7)	0.3422(6)
C6B	0.1006(2)	0.7523(7)	0.2453(6)
C7B	0.1433(3)	0.8068(6)	0.5000
C8B	0.2389(5)	0.7569(10)	0.5000
C9B	0.2310(2)	0.8182(6)	0.4000(5)
C10B	0.2397(3)	0.9180(7)	0.3992(6)
C11B	0.2552(6)	0.9660(11)	0.5000
C12B	0.0288(5)	0.6509(15)	0.5000
C13B	0.0541(3)	0.6337(8)	0.4016(7)
C14B	0.0869(3)	0.5670(8)	0.4011(6)
C15B	0.1000(6)	0.5120(10)	0.5000

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