Cyclohexadiene and Benzene Derivatives of $[Ru_5C(CO)_{15}]$†

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The reaction of $[Ru_5C(CO)_{15}]$ **1** with cyclohexa-1,3-diene and three equivalents of Me_3NO yielded the new compound $[Ru_5C(CO)_{11}(\eta^4\text{-}C_6H_8)_2]$ **2** and also $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **3** and $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$ **4** in approximately equal yields. The molecular structure of **2** has been established by single-crystal X-ray diffraction. The two cyclohexadiene ligands are terminally bound on opposite basal ruthenium atoms of the square-pyramidal metal framework. Compound **2** may be converted to **3** by reaction with carbon monoxide. The isomeric pair $[Ru_5C(CO)_{10}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$ **5** and $[Ru_5C(CO)_{10}(\eta^6\text{-}C_6H_6)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$ **6** may be prepared from **3** and **4**, respectively, upon reaction with cyclohexa-1,3-diene and two equivalents of Me_3NO. Clusters **5** and **6** have also been studied by single-crystal X-ray diffraction. In both molecules the cyclohexadiene ligand bridges a basal edge of the square pyramid, while the benzene fragment is in face-capping and terminal bonding mode, respectively.

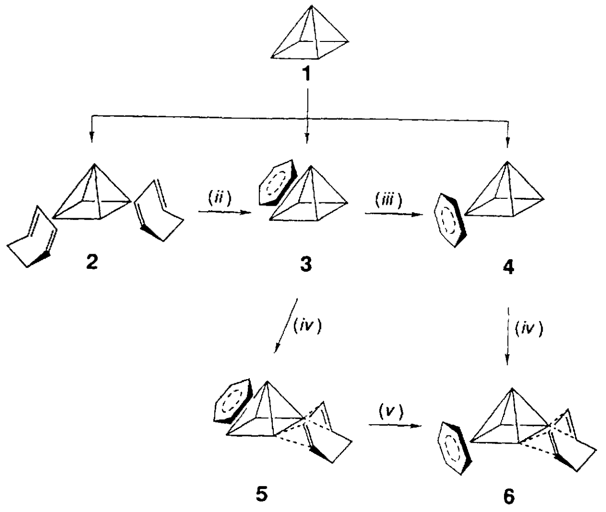
The octahedral $[Ru_6C(CO)_{17}]$ and the square-pyramidal $[Ru_5C(CO)_{15}]$ clusters have proved to be ideal starting compounds in the preparation of arene-bound clusters.[1,2] The interstitial carbido atom tends to confer stability to the cluster framework, so that the metal core remains intact during reaction.

In the case of the hexaruthenium system,[1] a wide variety of both mono- and bis-(arene) derivatives have been prepared and characterized, as well as a number of stable cyclohexadiene intermediates produced on route to these compounds.[3,4] For $[Ru_5C(CO)_{15}]$ both 1,3- and 1,4-cyclohexadiene intermediate compounds have been observed.[2,5] These may be readily converted to the appropriate benzene products. However, an additional feature of this system is the ability of the central cluster unit to undergo rearrangement by edge-cleavage to a bridged-butterfly species on reaction with certain nucleophilic reagents. Consequent removal of the nucleophilic source results in regeneration of the square-pyramidal cluster unit. This has been documented for the reaction $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)] \rightleftharpoons [Ru_5C(CO)_{13}(\eta^6\text{-}C_6H_6)]$,[5] but is also believed to be an important step in many of the mechanisms involved in this chemistry.

In this paper we report studies of the reactions of this pentaruthenium cluster with Me_3NO in the presence of cyclohexa-1,3-diene to form both cyclohexa-1,3-diene and benzene derivatives. It would appear that the formation of the benzene compounds, which occur *via* the intermediacy of a cyclohexadienyl compound, may occur *via* a rearrangement process of the type described above.

Results and Discussion

The reactions outlined herein are illustrated in Scheme 1. The dropwise addition of a solution of three molar equivalents of Me_3NO in dichloromethane to a solution of the square-pyramidal cluster $[Ru_5C(CO)_{15}]$ **1** also in dichloromethane containing a large excess of cyclohexa-1,3-diene afforded three products in approximately equal yields. Isolation was achieved by column chromatography on silica gel, eluting with dichloromethane–ethyl acetate–hexane (10:5:85, v/v). In order of elution the products have been identified as $[Ru_5C(CO)_{11}(\eta^4\text{-}C_6H_8)_2]$ **2**, $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **3** and $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$ **4**. While compounds **3** and **4** have been reported previously,[5] the bis(η^4-diene) cluster is new and has been characterized by both spectroscopic and single-crystal X-ray diffraction analyses. The mass spectrum of compound **2** is easily interpreted. A parent peak is observed at *m/z* 986 (calculated 986) followed by the strongest peak in the spectrum, *m/z ca.* 906, corresponding to the loss of one cyclohexadiene ring. Thereafter, eleven carbonyl groups are lost in succession. The ^1H NMR spectrum of compound **2** in $CDCl_3$ is somewhat more complicated. At room temperature (296 K) three broad signals are observed, centred at approximately δ 5.9, 3.5 and 2.2, with relative intensities 1:1:2, respectively. The chemical shift of the first two signals may be attributed to the olefinic protons of the diene, while the signal at δ 2.2 is consistent with the aliphatic cyclohexa-1,3-diene protons. On cooling to 212 K,



Scheme 1 (*i*) Me_3NO (3 mol equivalents) added dropwise to a CH_2Cl_2–cyclohexa-1,3-diene solution; (*ii*) CO bubbled through a CH_2Cl_2 solution; (*iii*) refluxing hexane for 4 h; (*iv*) Me_3NO (2 mol equivalents) added dropwise to a CH_2Cl_2–cyclohexa-1,3-diene solution; (*v*) refluxing toluene for 8 h

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

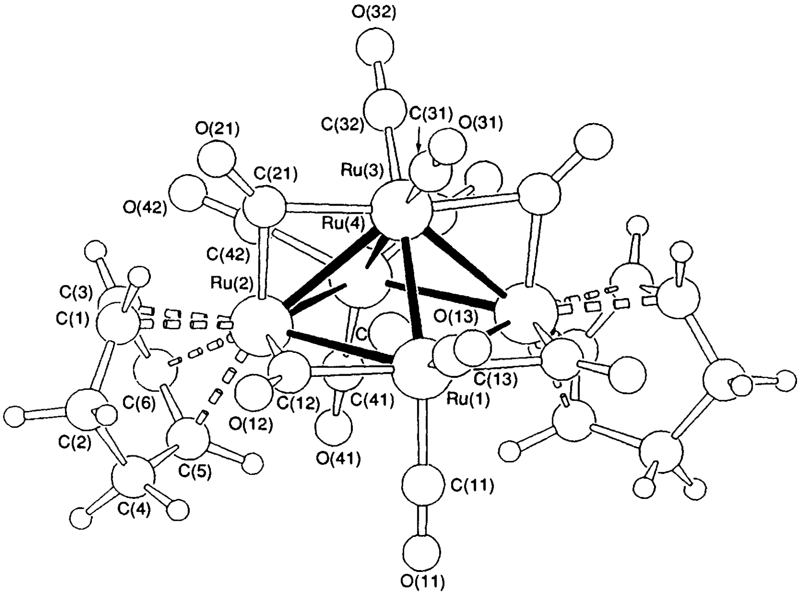


Fig. 1 Solid-state molecular structure of compound **2**

Table 1 Relevant bond distances (Å) and angles (°) for compound **2**

Ru(1)–Ru(2)	2.785(1)	Ru(4)–C	1.97(1)
Ru(1)–Ru(3)	2.844(1)	Ru(2)–C(1)	2.27(1)
Ru(2)–Ru(3)	2.785(1)	Ru(2)–C(3)	2.19(1)
Ru(2)–Ru(4)	2.897(1)	Ru(2)–C(5)	2.21(1)
Ru(3)–Ru(4)	2.760(1)	Ru(2)–C(6)	2.17(1)
Ru(1)–C(12)	2.10(1)	C(1)–C(2)	1.55(2)
Ru(2)–C(12)	2.01(1)	C(1)–C(3)	1.41(1)
Ru(2)–C(21)	2.05(1)	C(2)–C(4)	1.55(1)
Ru(3)–C–(21)	2.12(1)	C(3)–C(6)	1.42(1)
Ru(1)–C	1.99(1)	C(4)–C(5)	1.54(1)
Ru(2)–C	2.06(1)	C(5)–C(6)	1.44(1)
Ru(3)–C	2.17(1)		
Ru(1)–C(12)–Ru(2)	85.1(3)	Ru(1)–C–Ru(4)	169.2(4)
Ru(2)–C(21)–Ru(3)	83.8(3)	Ru(2)–C–Ru(4)	91.8(3)
Ru(1)–C–Ru(2)	86.7(3)		

eight signals of equal relative intensity at δ 6.41, 5.38, 4.45, 2.87, 2.79, 2.08, 1.97 and 1.55 are observed, while on warming to 329 K four multiplets (at δ 5.97, 3.72, 2.31 and 1.99), also of equal relative intensity, emerge. For both the low and high temperature spectra, the first half of the signals corresponds to olefinic protons, and the remaining signals to the aliphatic protons. Variation of the width and number of the signals with temperature suggest some fluxionality, and in this case it would appear that coalescence occurs at 296 K. While the precise fluxional processes taking place cannot be identified, the signals obtained at 212 K probably correspond to the eight chemically inequivalent protons of the dienes, while at 329 K there is a plane of symmetry bisecting each diene moiety; hence, four chemically equivalent proton pairs, illustrated by the four signals seems most likely. At 296 K rapid rotation and flipping of the cyclohexadiene ligands can be speculated.

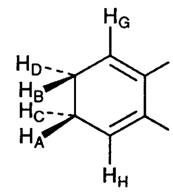
The molecular structure of compound **2** in the solid state is depicted in Fig. 1. A crystallographic mirror plane bisects the molecule passing through the apical and two opposite basal ruthenium atoms. Relevant structural parameters are listed in Table 1. In the family of benzene and cyclohexadiene derivatives of $[Ru_5C(CO)_{15}]$, compound **2** possesses some unique structural features. Although the metal framework is the familiar square pyramid of $[Ru_5C(CO)_{15}]$ bearing a C(carbido) atom almost in the middle of the square base, the ligand distribution is uncommon. First, the cyclohexadiene ligands are bound in termal fashion (η^4-bonding mode) on two opposite corners of the square base, secondly a complex pattern of CO bridges is observed. In $[Ru_5C(CO)_{15}]$ and most of its derivatives the CO ligands are usually found to adopt only terminal co-ordination. In **2**, two bridging CO ligands span two consecutive edges of the square base, while two others span two base-apex edges of the pyramid. In such a way, two ruthenium atoms bear two terminal CO and are involved in two bridging interactions, one basal ruthenium atom carries only three terminal ligands {as in $[Ru_5C(CO)_{15}]$}, while the remaining two basal ruthenium atoms involved in the interaction with the cyclohexadienes bear only two CO. This 'geometrically uneven' ligand distribution, however, achieves (at least formally) a homogeneous ligand-to-metal electron distribution with each ruthenium atom formally receiving 6 electrons from the ligands. The Ru–Ru bond lengths range from 2.760(1) to 2.897(1) Å, the CO-bridge bonds show an intermediate length [2.786(1) Å], while the shortest bond is the base-apex Ru(3)-Ru(4) distance [2.760(1) Å]. The C(carbide) atom shows longer distances from the substituted ruthenium atom [2.062(7) Å] than from the unsubstituted one [1.995(7) Å]. The CO bridges show otherwise shorter bonds from Ru(2) than from the unsubstituted atoms.

Perhaps the simplest mechanistic pathway to compound **2** may be taken to involve the systematic removal of co-ordinated CO (by oxidation to CO_2) which is then followed by addition of the diene to the vacant co-ordination sites to produce $[Ru_5C(CO)_{13}(\eta^4\text{-}C_6H_8)]$, as yet unobserved. This can then either isomerize to $[Ru_5C(CO)_{13}(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_6)]$, the precursor to **3** (and ultimately **4**), also obtained in this reaction, or react with further Me_3NO. This process must then occur again to form $[Ru_5C(CO)_{11}(\eta^4\text{-}C_6H_8)_2]$ **2**, which is transformed into **3** in good yield upon reaction with CO. In this reaction one diene must be displaced, one CO added, and 'dehydrogenation' of the remaining cyclohexa-1,3-diene to a benzene must also occur. There are two possible mechanisms by which the displacement of the η^4-C_6H_8 may occur. First, and most obviously, direct displacement; a reaction in which the η^4-bonded diene moves to an η^2-co-ordinated mode and eventually displacement by further CO. Secondly, and the mechanism we prefer, a reaction sequence of the type previously observed[5] for the reaction of $[Ru_5C(CO)_{12}(\eta^4\text{-}C_6H_6)]$ **4** with CO, in which a square-pyramidal bridged-butterfly rearrangement of the cluster core occurs. In this process, addition of CO occurs at one of the basal ruthenium atoms of the

$[Ru_5C(CO)_{11}(\eta^4-C_6H_8)_2]$ unit to generate a bridged-butterfly arrangement of metal atoms followed by reclosure to the square-pyramidal structure with the ejection of one of the η^4-C_6H_8 ligands. From here, the method by which **3** forms should parallel that described for its formation from $[Ru_5C(CO)_{13}(\mu-\eta^2:\eta^2-C_6H_8)]$ on reaction with Me_3NO.

Extending the synthetic sequence described originally for the preparation of the benzene clusters **3** and **4** from $[Ru_5C(CO)_{15}]$,[5] **3** and **4** have been treated with two molar equivalents of Me_3NO in dichloromethane in the presence of cyclohexane-1,3-diene yielding a pair of benzene–diene clusters $[Ru_5C(CO)_{10}(\mu_3-\eta^2:\eta^2:\eta^2-C_6H_6)(\mu-\eta^2:\eta^2-C_6H_8)]$ **5** and $[Ru_5C(CO)_{10}(\eta^6-C_6H_6)(\mu-\eta^2:\eta^2-C_6H_8)]$ **6**, respectively. Formulation of **5** and **6** was initially based upon mass and ^1H NMR spectra. Both clusters exhibit strong parent peaks at *m/z* 956 (calculated 956) together with the loss of ten CO groups. The ^1H NMR spectrum of **5** is simpler than that of **6** due to greater symmetry within the molecule. In **5** and **6** singlets at δ 4.14 and 5.85 can be assigned to the face-capping and η^6-terminal benzene ligands, in the respective compounds. In compound **5** the diene gives rise to four signals of relative intensity 1 : 1 : 1 : 1. The signals at δ 5.57 and 4.57 are consistent with the olefinic protons of the diene, while those at δ 2.84 and 2.03 arise from the aliphatic protons of the diene ring. The asymmetry in molecule **6** gives rise to eight signals of equal relative intensity at δ 5.33, 5.07, 4.43, 4.09, 2.60, 2.55, 1.72 and 1.69, once again four corresponding to the olefinic and four to the aliphatic protons of the diene. Selectively decoupling each signal has allowed for their unambiguous assignment. The spectra are shown in Fig. 2 together with a sketch illustrating the assignment of the protons (H_A–H_H) in the cyclohexa-1,3-diene moiety.

The solid-state molecular structures of the isomers **5** and **6** are closely related and will be discussed together. Figs. 3 and 4 show sketches of the two molecular structures and the labelling schemes. Relevant bond distances and angles are reported in Table 2 for **5** and **6**, respectively. The structures of **5** and **6** differ essentially in the mode of co-ordination of the benzene ligand. In **5** this ligand caps the square-pyramid triangular face opposite to the Ru–Ru bond carrying the μ-$\eta^2:\eta^2$-cyclohexadiene ligand, while in **6** the benzene ligand is terminally bound (η^6-co-ordination mode) to one basal ruthenium atom. These bonding modes have already been observed in the other isomeric pairs characterized so far, namely $[Ru_5C(CO)_{12}(\mu_3-\eta^2:\eta^2:\eta^2-C_6H_6)]$ and $[Ru_5C(CO)_{12}(\eta^6-C_6H_6)]$[5] and the hexanuclear octahedral clusters $[Ru_6C(CO)_{11}(\eta^6-C_6H_6)_2]$ and $[Ru_6C(CO)_{11}(\mu_3-\eta^2:\eta^2:\eta^2-C_6H_6)(\eta^6-C_6H_6)]$.[3] Unlike compound **2**, no bridging CO ligands are present in **5** and **6**, while in both molecules the cyclohexadiene ligand spans one basal edge taking the place of two radial CO ligands with respect to the



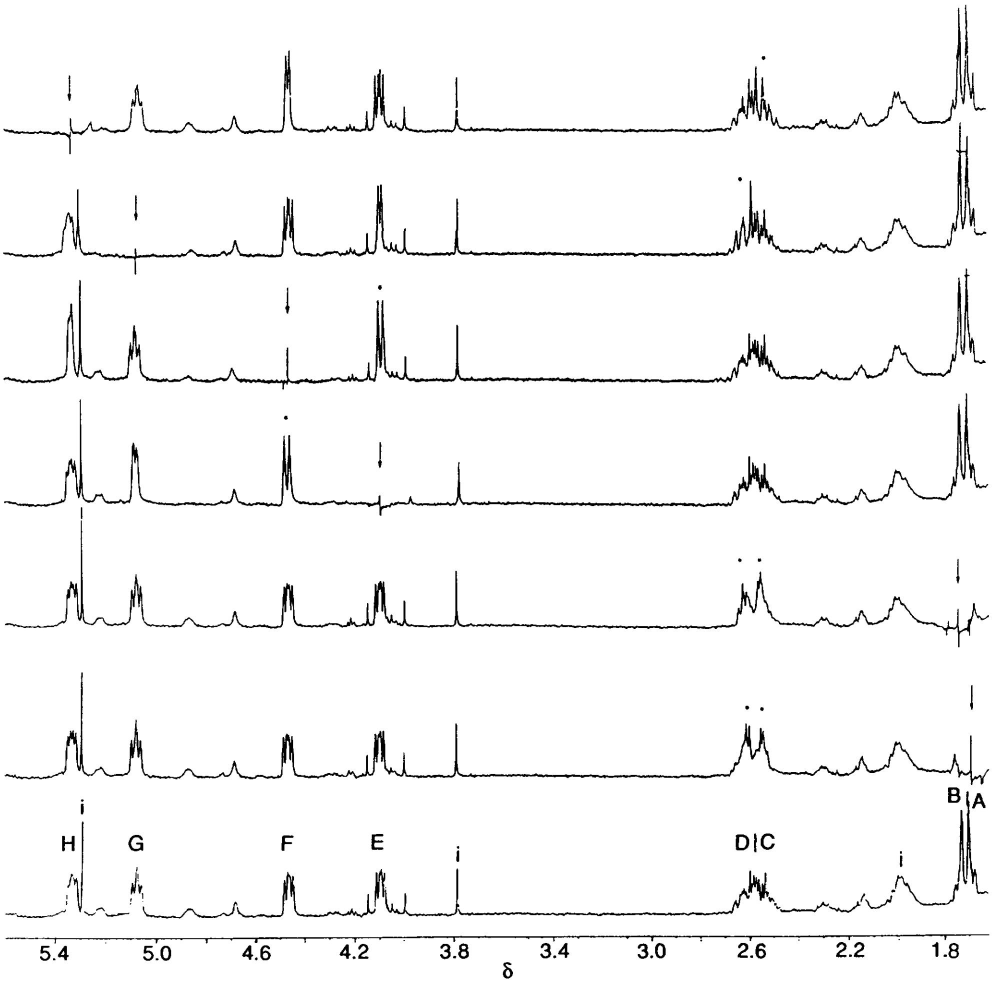


Fig. 2 The ^1H NMR decoupling spectra for compound **6** recorded at 212 K. Signals are labelled A–H and their assignment shown. The arrows indicate the sites of irradiation and the resonances marked * and i indicate affected sites and impurities, respectively

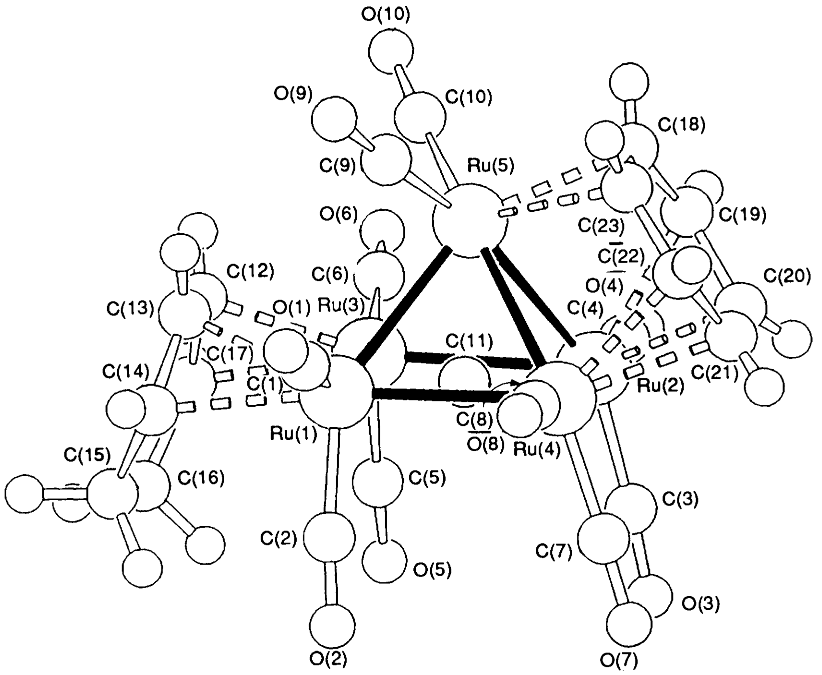


Fig. 3 Solid-state molecular structure of compound **5**

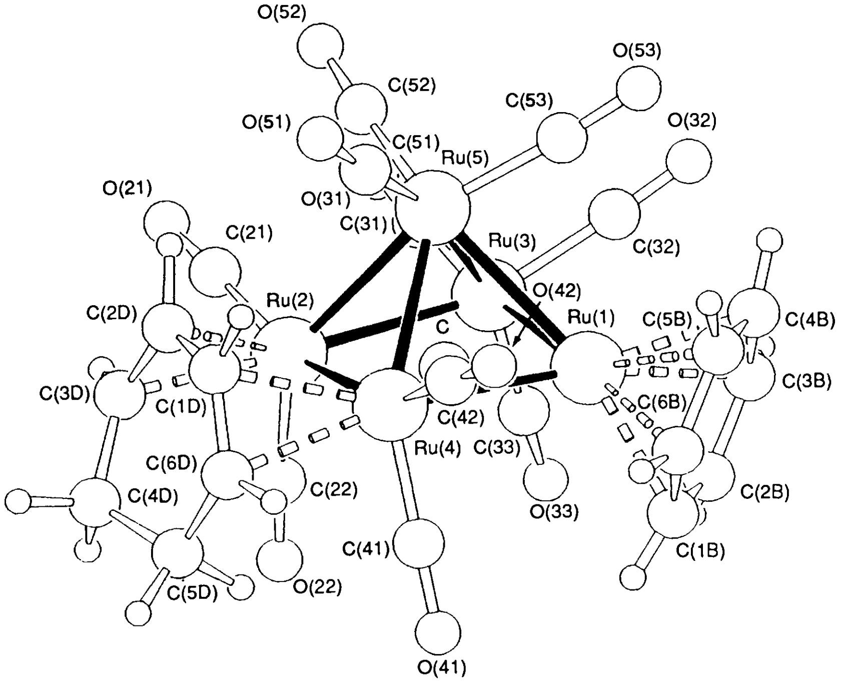


Fig. 4 Solid-state molecular structure of compound **6**

parent $[Ru_5C(CO)_{15}]$. Metal–metal bonds range from 2.804(1) to 2.881(1) in **5** and from 2.744(1) to 2.855(1) Å in **6**. The benzene ligand in **6** is disordered over two sites with site occupation factors in the ratio 7 : 3. This disorder is, very likely, dynamic in nature. It has been demonstrated in many crystalline arene complexes and clusters that a disc-like benzene ligand bound in delocalized manner to one (or more) metal centres cannot be easily locked in place by the surrounding molecules.[6] The barrier to reorientation is usually fairly small (less than 50 kJ mol^{-1}). An estimate of the reorientational barrier for jumps of the benzene atoms can be obtained by means of the atom–atom potential energy method.[6] In **6** the potential-energy profile presents the expected sinusoidal shape with minima every 60° separated by rather low potential-energy barriers (maximum *ca.* 6 kJ mol^{-1}). Intermediate minima corresponding to the alternative orientation are not detected probably because of the low sensitivity of the computational method in the presence of very low reorientational barriers. Finally, it is interesting to relate the disorder observed in crystalline **6** to the presence of two independent molecules in the asymmetric unit of $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$ **4**. In this latter case, the two molecules differ essentially in the rotameric orientation of the terminally-bound benzene ligands.[5]

In contrast to previous observations in which the facially bound benzene ring in **3** migrates to a η^6-co-ordination mode with relative ease, and nearly quantitatively, the corresponding isomerization process from **5** to **6** requires high temperatures and is accompanied by extensive decomposition. Attempts to

Table 2 Comparison of relevant bond distances (Å) for compounds **5** and **6**

	5	**6**		**5**		**6**
Ru(1)–Ru(3)	2.804(1)	2.838(1)	Ru(1)–C(13)	2.289(4)	Ru(2)–C(2D)	2.30(1)
Ru(1)–Ru(4)	2.817(1)	2.799(1)	Ru(1)–C(14)	2.317(3)	Ru(2)–C(3D)	2.30(1)
Ru(1)–Ru(5)	2.881(1)	2.827(1)	Ru(3)–C(12)	2.254(4)	Ru(4)–C(1D)	2.27(1)
Ru(2)–Ru(3)	2.829(1)	2.849(1)	Ru(3)–C(17)	2.285(4)	Ru(4)–C(6D)	2.31(1)
Ru(2)–Ru(4)	2.872(1)	2.775(1)	Ru(2)–C(19)	2.383(5)	Ru(1)–C(1B)	2.22(1)
Ru(2)–Ru(5)	2.866(1)	2.855(1)	Ru(2)–C(20)	2.216(4)	Ru(1)–C(2B)	2.21(1)
Ru(3)–Ru(5)	2.852(1)	2.744(1)	Ru(4)–C(21)	2.318(5)	Ru(1)–C(3B)	2.19(1)
Ru(4)–Ru(5)	2.837(1)	2.842(1)	Ru(4)–C(22)	2.233(5)	Ru(1)–C(4B)	2.20(1)
Ru(1)–C	1.984(3)	1.896(1)	Ru(5)–C(18)	2.210(4)	Ru(1)–C(5B)	2.22(1)
Ru(2)–C	2.004(3)	2.02(1)	Ru(5)–C(23)	2.395(5)	Ru(1)–C(6B)	2.22(1)
Ru(3)–C	2.004(3)	2.06(1)	C(12)–C(13)	1.45(1)	C(1D)–C(2D)	1.45(2)
Ru(4)–C	2.014(3)	2.00(1)	C(13)–C(14)	1.38(1)	C(2D)–C(3D)	1.40(2)
Ru(5)–C	2.083(3)	2.15(1)	C(14)–C(15)	1.49(1)	C(3D)–C(4D)	1.49(2)
C(18)–C(19)	1.46(1)		C(15)–C(16)	1.47(1)	C(4D)–C(5D)	1.54(2)
C(19)–C(20)	1.46(1)		C(16)–C(17)	1.52(1)	C(5D)–C(6D)	1.52(2)
C(20)–C(21)	1.43(1)		C(12)–C(17)	1.39(1)	C(1D)–C(6D)	1.38(2)
C(21)–C(22)	1.32(1)					
C(22)–C(23)	1.36(1)					
C(18)–C(23)	1.35(1)					

prepare bis(benzene) adducts from clusters **5** and **6** have also proved unsuccessful, with decomposition occurring and only small amounts of starting material being recovered.

Experimental

All reactions were carried out with the exclusion of air using freshly distilled solvents under a nitrogen atmosphere. Subsequent work-up of products was achieved with standard laboratory-grade solvents without precautions to exclude air. Infrared spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer in CH_2Cl_2 using NaCl cells. Positive fast-atom-bombardment mass spectra were obtained using a Kratos MS50TC spectrometer, with CsI as calibrant. Proton NMR spectra were recorded in $CDCl_3$ using a Bruker AM360 instrument, referenced to internal $SiMe_4$. Thin-layer chromatography (TLC) was carried out on plates supplied by Merck coated with a 0.25 mm layer of Kieselgel $60F_{254}$. The $[Ru_5C(CO)_{15}]$ cluster was prepared according to the literature procedure.[7] Cyclohexa-1,3-diene was purchased from Aldrich and used without further purification. Trimethylamine *N*-oxide (Me_3NO) was sublimed prior to use.

Reaction of $[Ru_5C(CO)_{15}]$ **1** *with Cyclohexa*-1,3-*diene and Trimethylamine* N-*Oxide.—Synthesis of compounds* **2**–**4**. Compound **1** (500 mg) was dissolved in dichloromethane (50 cm^3), and cyclohexa-1,3-diene (2 cm^3), and the solution cooled to −78 °C. A solution of Me_3NO (124 mg, 3.1 mol equivalent) in dichloromethane (15 cm^3) 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 on silica (60 mesh) using a solution of ethyl acetate–dichloromethane-hexane (5:10:85, v/v) as eluent. Three products were obtained and characterised spectroscopically as $[Ru_5C(CO)_{11}(\eta^4\text{-}C_6H_8)_2]$ **2** (black, 78 mg) (Found: C, 29.15; H, 1.70. Calc. for $C_{24}H_{16}O_{11}Ru_5$: C, 29.25; H, 1.60%), $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **3** (red, 84 mg) and $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$ **4** (black, 67 mg) in order of elution.

Spectroscopic data for **2**. IR (CH_2Cl_2): ν(CO) 2058w, 2039 vs, 2015s, 1981m and 1846m cm^{-1}. ^{1}H NMR ($CDCl_3$, 212 K): δ 6.41 (m, 1 H), 5.38 (m, 1 H), 4.45 (m, 1 H), 2.87 (m, 1 H), 2.79 (m, 1 H), 2.08 (m, 1 H), 1.97 (m, 1 H) and 1.55 (m, 1 H) (all signals are broad at room temperature). Mass spectrum: *m/z* 986 (M^+) (calc. 986).

Spectroscopic details for compounds **3** and **4** are in good agreement with those reported previously.

Reaction of $[Ru_5C(CO)_{11}(\eta^4\text{-}C_6H_8)_2]$ **2** *with* CO.—Compound **2** (10 mg) was dissolved in dichloromethane (20 cm^3) and CO was slowly passed through the solution for 10 min. The reaction vessel was sealed under the CO atmosphere and stored at −20 °C for 18 h. The solution changed from black to dark red during this period. Removal of the solvent *in vacuo*, followed by TLC using a solution of dichloromethane–hexane (30:70) as eluent resulted in the isolation of a major red product characterized spectroscopically as $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **3** (7 mg).

Reaction of $[Ru_5C(CO)_{12}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)]$ **3** *with Cyclohexa*-1,3-*diene.—Synthesis of compound* **5**. Compound **3** (30 mg) was dissolved in dichloromethane (20 cm^3), and cyclohexa-1,3-diene (1 cm^3), and the solution cooled to −78 °C. A solution of Me_3NO (5 mg, 2.1 mol equivalent) in dichloromethane (5 cm^3) was added dropwise over a period of 5 min. The mixture was stirred for an additional 25 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 ethyl acetate–dichloromethane–hexane (5:10:85) as eluent. The major orange band was extracted and characterized as $[Ru_5C(CO)_{10}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$ **5** (13 mg). IR (CH_2Cl_2): ν(CO) 2046w, 2020s, 1988s and 1942w cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.57 (m, 2 H), 4.57 (m, 2 H), 4.14 (s, 6 H), 2.84 (m, 2 H) and 2.03 (m, 2 H). Mass spectrum: *m/z* 956 (M^+) (calc. 956).

Reaction of $[Ru_5C(CO)_{12}(\eta^6\text{-}C_6H_6)]$ **4** *with Cyclohexa*-1,3-*diene.—Synthesis of compound* **6**. A solution of compound **4** (50 mg) in dichloromethane (25 cm^3) and cyclohexa-1,3-diene (15 cm^3) was cooled to −78 °C. A solution of Me_3NO (8 mg, 2.1 mol equivalent) in dichloromethane (5 cm^3) was added dropwise. The solution was warmed slowly to room temperature over 30 min. IR spectroscopy indicated complete consumption of the starting material. The solvent was removed *in vacuo* and the products extracted by TLC eluting with hexane–dichloromethane (70:30). The major black band was extracted and characterized as $[Ru_5C(CO)_{10}(\eta^6\text{-}C_6H_6)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$ **6** (17 mg). IR (CH_2Cl_2): ν(CO) 2052m, 1997s and 1985w(br) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 5.85 (s, 6 H), 5.33 (m, 1 H), 5.07 (m, 1 H), 4.43 (m, 1 H), 4.09 (m, 1 H), 2.60 (m, 1

Table 3 Crystal data and details of measurements for compounds **2**, **5** and **6**

	2	**5**	**6**
Formula	$C_{24}H_{16}O_{11}Ru_5$	$C_{23}H_{16}O_{10}Ru_5$	$C_{23}H_{14}O_{10}Ru_5$
M	985.7	955.7	955.7
T/K	150	293	150
Crystal size/mm	0.16 × 0.19 × 0.19	0.25 × 0.15 × 0.35	0.23 × 0.27 × 0.51
Crystal system	Orthorhombic	Triclinic	Monoclinic
Space group	*Pnma*	$P\bar{1}$	$P2_1/c$
a/Å	13.355(3)	9.687(7)	13.724(3)
b/Å	13.996(3)	16.474(4)	12.086(3)
c/Å	14.593(3)	9.036(1)	15.457(2)
α/°		92.68(2)	
β/°		116.01(3)	95.77(2)
γ/°		78.95(4)	
U/Å^3	2727(1)	1270(1)	2551(1)
Z	4	2	4
F(000)	1696	904	1808
λ(Mo-Kα)/Å	0.710 73	0.710 69	0.710 73
μ(Mo-Kα)/cm^{-1}	26.8	29.6	28.7
θ Range/°	2.5–22.5	2.5–25	2.5–22.5
Octants explored (*hkl*)	−14 to 14, 0–15, 0–15	−11 to 11, −19 to 19, 0–10	−14 to 14, 0-13, 0–16
Measured reflections	2700	4783	3532
Unique observed reflections [$I_o > 2\sigma(I_o)$]	1667	3857	2944
No. of refined parameters	202	344	224
Highest peak in final difference synthesis Å^{-3}	1.3	0.5	1.4
Goodness of fit on F^2		1.06	
R, *wR′*		0.021, 0.064	
R,[a] wR',[a,b] goodness of fit on F[a]	0.035, 0.043, 1.29		0.054, 0.057, 0.97

[a] Refinement on F_o with SHELX 76.[8b] [b] Weighting scheme: $w^{-1} = \sigma^2(F) + 0.0004 F^2$.

Table 4 Fractional atomic coordinates of compound **2** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Ru(1)	0.175 89(6)	0.25	0.051 58(5)
Ru(2)	0.267 43(4)	0.395 77(5)	−0.049 27(4)
Ru(3)	0.370 35(6)	0.25	0.037 44(6)
Ru(4)	0.356 49(6)	0.25	−0.168 65(6)
C	0.257 2(6)	0.25	−0.068 5(7)
C(11)	0.053 9(8)	0.25	−0.000 6(9)
O(11)	−0.014 2(5)	0.25	−0.038 4(8)
C(12)	0.175 6(6)	0.399 9(7)	0.063 3(6)
O(12)	0.136 0(4)	0.454 9(4)	0.117 8(4)
C(13)	0.145 2(10)	0.25	0.193 2(9)
O(13)	0.127 6(8)	0.25	0.275 8(7)
C(21)	0.380 2(6)	0.401 0(6)	0.042 2(6)
O(21)	0.428 4(5)	0.456 9(5)	0.079 0(6)
C(31)	0.370 3(8)	0.25	0.181 6(8)
O(31)	0.372 9(7)	0.25	0.265 1(6)
C(32)	0.497 8(7)	0.25	0.014 2(8)
O(32)	0.576 7(6)	0.25	−0.000 2(7)
C(41)	0.284 6(9)	0.25	−0.288 5(8)
O(41)	0.237 9(7)	0.25	−0.356 6(6)
C(42)	0.439 1(6)	0.348 8(9)	−0.206 8(6)
O(42)	0.485 4(5)	0.412 6(7)	−0.229 8(5)
C(1)	0.270 0(7)	0.556 1(7)	−0.025 0(10)
C(2)	0.171 7(7)	0.598 0(7)	−0.031 7(10)
C(3)	0.317 0(7)	0.530 0(7)	−0.113 3(7)
C(4)	0.111 7(7)	0.538 8(7)	−0.104 1(8)
C(5)	0.169 9(6)	0.461 4(6)	−0.155 6(7)

H), 1.72 (m, 1 H) and 1.69 (m, 1 H). Mass spectrum: *m*/*z* 956 (M^+) (calc. 956).

Thermolysis of $[Ru_5C(CO)_{10}(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_6H_6)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$ **5**.—Compound **5** (8 mg) in toluene (20 cm^3) was heated to reflux for 8 h. During this period the reaction mixture was monitored by IR spectroscopy, which indicated a dramatic change from the starting material. The toluene was removed *in vacuo* and the products extracted by TLC eluting with hexane–dichloromethane (70:30). A single product was isolated and

Table 5 Fractional atomic coordinates of compound **5** with e.s.d.s in parentheses

Atom	*x*	*y*	*z*
Ru(1)	0.309 81(3)	0.736 03(2)	0.069 67(3)
Ru(2)	−0.034 29(3)	0.770 79(2)	−0.377 31(3)
Ru(3)	0.218 59(3)	0.849 63(2)	−0.193 12(3)
Ru(4)	0.067 79(3)	0.650 83(2)	−0.121 86(4)
Ru(5)	0.278 97(3)	0.677 10(2)	−0.246 57(3)
C(1)	0.427 4(5)	0.643 4(3)	0.222 8(5)
O(1)	0.495 7(4)	0.588 6(2)	0.313 6(5)
C(2)	0.198 5(5)	0.779 0(3)	0.189 9(5)
O(2)	0.123 2(5)	0.803 6(3)	0.254 8(5)
C(3)	−0.205 9(5)	0.824 0(3)	−0.352 4(5)
O(3)	−0.306 8(4)	0.856 5(2)	−0.323 3(5)
C(4)	−0.101 7(5)	0.843 5(2)	−0.574 2(5)
O(4)	−0.147 2(4)	0.890 7(2)	−0.682 6(4)
C(5)	0.070 5(5)	0.938 9(3)	−0.184 3(5)
O(5)	−0.021 8(4)	0.991 8(2)	−0.179 5(5)
C(6)	0.223 4(5)	0.900 7(3)	−0.377 1(5)
O(6)	0.227 1(5)	0.932 0(2)	−0.482 9(4)
C(7)	−0.101 9(5)	0.684 8(3)	−0.070 6(6)
O(7)	−0.204 1(5)	0.706 6(3)	−0.038 8(6)
C(8)	0.147 6(5)	0.566 7(3)	0.046 3(5)
O(8)	0.190 5(5)	0.517 9(2)	0.151 5(5)
C(9)	0.469 2(5)	0.612 2(3)	−0.098 2(5)
O(9)	0.587 3(4)	0.573 1(2)	−0.011 7(4)
C(10)	0.384 7(5)	0.716 8(3)	−0.354 4(5)
O(10)	0.452 9(4)	0.736 8(2)	−0.417 6(4)
C(11)	0.137 0(4)	0.753 1(2)	−0.156 8(4)
C(12)	0.470 2(4)	0.854 7(3)	−0.024 3(5)
C(13)	0.519 4(4)	0.793 9(2)	0.108 6(5)
C(14)	0.488 9(4)	0.813 6(2)	0.242 9(4)
C(15)	0.429 5(4)	0.900 5(2)	0.269 2(4)
C(16)	0.357 9(7)	0.960 0(3)	0.127 6(6)
C(17)	0.383 0(5)	0.932 0(2)	−0.023 5(5)
C(18)	0.160 4(8)	0.601 2(5)	−0.455 9(9)
C(19)	0.012 3(11)	0.658 6(3)	−0.546 1(6)
C(20)	−0.115 8(6)	0.656 7(3)	−0.503 3(7)
C(21)	−0.085 8(7)	0.600 2(3)	−0.372 3(7)
C(22)	0.051 1(8)	0.549 8(3)	−0.299 0(6)
C(23)	0.174 7(7)	0.553 2(3)	−0.330 7(7)

Table 6 Fractional atomic coordinates of compound **6** with (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
Ru(1)	0.247 47(7)	0.128 22(8)	0.378 70(7)
Ru(2)	0.302 52(7)	−0.147 28(8)	0.260 11(7)
Ru(3)	0.391 88(7)	0.065 76(8)	0.268 93(7)
Ru(4)	0.152 22(7)	−0.075 75(8)	0.353 85(7)
Ru(5)	0.197 71(7)	0.049 61(8)	0.207 67(6)
C	0.278 1(8)	−0.007 2(10)	0.325 7(8)
C(21)	0.371 2(10)	−0.181 3(11)	0.162 6(8)
O(21)	0.411 0(7)	−0.205 1(8)	0.103 3(6)
C(22)	0.391 9(9)	−0.210 7(10)	0.346 0(6)
O(22)	0.442 5(7)	−0.244 4(9)	0.402 2(7)
C(31)	0.470 2(11)	0.030 2(12)	0.178 1(10)
O(31)	0.517 9(8)	0.009 6(9)	0.122 9(8)
C(32)	0.396 1(10)	0.219 8(12)	0.247 5(9)
O(32)	0.397 2(7)	0.312 2(7)	0.231 6(7)
C(33)	0.499 3(11)	0.049 7(12)	0.358 0(9)
O(33)	0.559 6(8)	0.040 8(9)	0.412 4(9)
C(41)	0.188 1(10)	−0.108 3(12)	0.468 6(9)
O(41)	0.214 8(8)	−0.127 9(9)	0.541 4(6)
C(42)	0.030 6(11)	−0.008 2(12)	0.370 8(9)
O(42)	−0.040 3(8)	0.038 9(10)	0.383 5(9)
C(51)	0.071 6(10)	0.001 1(12)	0.172 4(9)
O(51)	−0.007 4(7)	−0.028 4(9)	0.143 9(8)
C(52)	0.250 7(10)	0.023 3(12)	0.101 0(10)
O(52)	0.281 3(7)	0.011 1(8)	0.034 9(6)
C(53)	0.167 7(10)	0.201 3(12)	0.201 2(8)
O(53)	0.147 8(7)	0.294 6(7)	0.191 4(6)
C(1B)	0.253 7(18)	0.145 9(10)	0.522 1(7)
C(2B)	0.336 5(18)	0.195 5(10)	0.493 6(7)
C(3B)	0.326 2(18)	0.276 4(10)	0.429 0(7)
C(4B)	0.233 0(18)	0.307 6(10)	0.392 7(7)
C(5B)	0.150 2(18)	0.258 0(10)	0.421 2(7)
C(6B)	0.160 5(18)	0.177 1(10)	0.485 8(7)
C(1B′)	0.202 0(40)	0.158 3(23)	0.509 2(21)
C(2B′)	0.140 0(40)	0.223 1(23)	0.452 3(21)
C(3B′)	0.180 0(40)	0.298 8(23)	0.397 6(21)
C(4B′)	0.282 0(40)	0.309 7(23)	0.399 9(21)
C(5B′)	0.343 0(40)	0.244 9(23)	0.456 8(21)
C(6B′)	0.303 0(40)	0.169 2(23)	0.511 4(21)
C(1D)	0.091 6(10)	−0.224 1(11)	0.276 0(9)
C(2D)	0.165 0(10)	−0.250 0(12)	0.217 9(9)
C(3D)	0.240 5(10)	−0.323 7(11)	0.245 1(8)
C(4D)	0.230 1(11)	−0.393 9(12)	0.323 2(9)
C(5D)	0.181 6(10)	−0.337 7(12)	0.397 2(9)

Primed atoms are those of the minor image of the benzene ligand.

characterised spectroscopically as $[Ru_5C(CO)_{10}(\eta^6\text{-}C_6H_6)(\mu\text{-}\eta^2:\eta^2\text{-}C_6H_8)]$ **6** (> 1 mg).

Crystal Structure Determination of Compounds **2**, **5** *and* **6**.—Crystal data and details of measurements for compounds **2**, **5** and **6** are summarized in Table 3. Diffraction intensities were collected by the ω–2θ scan method, at 150 K for **2** and **6** and at room temperature for **5**, on an Enraf-Nonius CAD-4 or a Stadi-4 diffractometer equipped with Mo-Kα radiation. The structures were solved by direct methods and refined by full-matrix least squares. For all calculations the crystallographic programs SHELX 86,[8a], SHELX 76[8b] and SHELXL 92[8c] were used. Anisotropic thermal parameters were applied to all non-H atoms of **2** and **5** and to all Ru and O atoms of **6**. In this latter compound, the occupancy factor for the major image of the disordered benzene ring, upon refinement, converged to 0.69(3). In all species hydrogen atoms were added in calculated positions and refined 'riding' on the corresponding C atoms. In all compounds single isotropic parameters for the aromatic, methylenic and methylic H groups were refined. Fractional atomic coordinates of **2**, **5** and **6** are reported in Tables 4–6, respectively.

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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