Thermolytic reaction of 1,4-diisopropenylbenzene with $[Ru_3(CO)_{12}]$: an arene ligand as a template for cluster formation

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The reaction of $[Ru_3(CO)_{12}]$ with 1,4-diisopropenylbenzene in refluxing octane led to the isolation of a series of clusters with nuclearities from 2 to 7: $[Ru_4(CO)_{10}(C_{12}H_{14})]$ **1**, $[Ru_3(CO)_8(C_{12}H_{12})]$ **2**, $[Ru_6H(CO)_{15}(C_{12}H_{11})]$ **3**, $[Ru_6H(CO)_{15}(C_{12}H_{13})]$ **4**, $[Ru_2(CO)_6(C_{12}H_{12})]$ **5**, $[Ru_7C(CO)_{16}(C_{12}H_{12})]$ **6**, $[Ru_3H(CO)_9(C_{12}H_{11})]$ **7**, $[Ru_5H(CO)_{14}(C_{12}H_{11})]$ **8** and $[Ru_6C(CO)_{15}(C_{11}H_{10})]$ **9**. The molecular structures of **1** and the three metallacycle compounds **2**–**4** have been determined by X-ray crystallography. The hexaruthenium species **3** and **4** represent a new category of arene cluster. The six ruthenium atoms describe an edge-bridged tetrahedron with a ruthenium spike bound to the edge-bridging atom. The arene ligand acts as an eleven-electron donor *via* both σ and π bonds. The pathway of the reaction has been established and provides evidence for ligand-moderated modular cluster build-up in which the ligand acts as a template.

Arene cluster chemistry has emerged as an important area of modern organometallic cluster chemistry. Studies have revealed a number of different co-ordination modes of the carbocycle to more than one metal centre.[1] Structural analysis of these cluster derivatives has provided valuable insight into the surface chemistry of such chemisorbed organic molecules.[2] One area of interest that has recently emerged is the chemistry of clusters in which the arenes carry unsaturated side chains such as isopropenyl groups.[3–5]

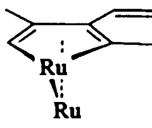
α-Methylstyrene has been shown to bond to ruthenium carbonyl clusters in several different modes. It is remarkable in that it forms π-bonded complexes involving all four unsaturated C=C bonds, from both the ring and the exocyclic arm.[4,6] Other complexes involving both σ and π bonds from the ring and also the isopropenyl group have been isolated.[3,5] In addition to these compounds, clusters have been isolated which contain interactions with either the ring or the isopropenyl group independently.[7] 1,3-Diisopropenylbenzene shows a similarly extensive chemistry with the added dimension that the second isopropenyl has also been observed to co-ordinate to give a ten-electron, face-capping, donor ligand. We have now extended these studies to the interactions of 1,4-diisopropenylbenzene with ruthenium clusters and here report some compounds obtained from the reaction of $[Ru_3(CO)_{12}]$. This organic compound has two unsaturated side arms and as a consequence several co-ordination possibilities.

Results and Discussion

Thermolysis of $[Ru_3(CO)_{12}]$, with 1,4-diisopropenylbenzene in octane for 2 h results in the formation of several products as evidenced by IR spectroscopy and spot TLC. After removal of the solvent these products were separated by TLC. The following compounds, most in relatively low yields, were isolated and characterised by IR, FAB mass and ^1H NMR spectroscopy: $[Ru_4(CO)_{10}(C_{12}H_{14})]$ **1** (1.8%), $[Ru_3(CO)_8(C_{12}H_{12})]/[Ru_3(CO)_8(C_{12}H_{14})]$ **2/2a** (2.6%), $[Ru_6H(CO)_{15}(C_{12}H_{11})]/[Ru_6H(CO)_{15}(C_{12}H_{13})]$ **3/4** (2.9%), $[Ru_2(CO)_6(C_{12}H_{12})]/[Ru_2(CO)_6(C_{12}H_{14})]$ **5/5a** (3.1%), $[Ru_7C(CO)_{16}(C_{12}H_{12})]$ **6** (2.9%), $[Ru_3H(CO)_9(C_{12}H_{11})]$ **7** (4%), $[Ru_5H(CO)_{14}(C_{12}H_{11})]$ **8** (2.2%) and $[Ru_6C(CO)_{15}(C_{11}H_{10})]$ **9** (0.7%). Comprehensive spectroscopic data for them are given in the Experimental section.

Structures were assigned for compounds **1**, **2** and **5**–**9** on the basis of the similarity of their spectroscopic data with their analogues in the related reaction with α-methylstyrene. The NMR spectra of **2** and **5** provide evidence for the presence of similar complexes **2a** and **5a** respectively where the non-bonded isopropylene substituent has been hydrogenated to an isopropyl group. Separation of these species has not been possible. A similar situation is observed for **3** however the hydrogenated analogue **4** was also characterised in an X-ray crystallographic analysis. The structures proposed for **1** and **2** have been confirmed by X-ray crystallographic analysis.

In contrast to the reactions with α-methylstyrene and 1,3-diisopropenylbenzene, the 1,4-diisopropenylbenzene face-capping analogues[4] were formed in much lower yield. The complex $[Ru_3(CO)_8(\mu_3\text{-}\eta^2:\eta^2:\eta^2\text{-}C_{12}H_{14})]$ **A** was not isolated and $[Ru_4(CO)_{10}(\mu_3\text{-}\eta^2:\eta^2:\eta^2:\eta^2\text{-}C_{12}H_{14})]$ **1** was obtained only as a minor product. The molecular structure of **1** has been determined and is shown in Fig. 1. Selected bond lengths and angles are given in Table 1. As predicted only one of the two exocyclic double bonds is co-ordinated to the cluster. The four ruthenium atoms describe a tetrahedron with one face capped by the aromatic ring and one isopropylene substituent of the ligand bonded in an $\eta^2:\eta^2:\eta^2:\eta^2$ arrangement. The ring is distorted from planarity (mean deviation from the plane 0.0314 Å) such that C(4) lies above and C(5) lies below the best plane through the ring. The ligand may alternatively be described in terms of two diene units: one, C(5)–C(6)–C(7)–C(8), is η^4-co-ordinated to Ru(2) and other, C(1)–C(2)–C(3)–C(4), is co-ordinated $\eta^2:\eta^2$ to Ru(3) and Ru(4). The dihedral angle between the best planes through the two diene units is 14.5°. The ring does not span the Ru_3 face symmetrically but is displaced away from Ru(2) presumably to permit co-ordination of the η^2-alkene as shown in Fig. 2. This is similar to $[Ru_4(CO)_{10}(C_9H_8)]$[4] but the displacement is more marked in this example. For the diisopropenylbenzene ligand two conformations X (cisoid) and Y (transoid) are possible (Fig. 3). It is only possible for the ligand to donate all ten π electrons to



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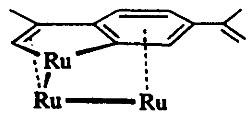

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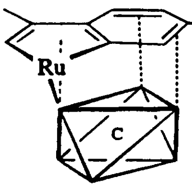

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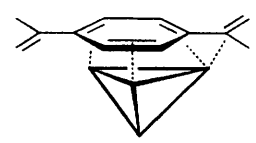

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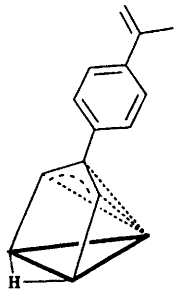

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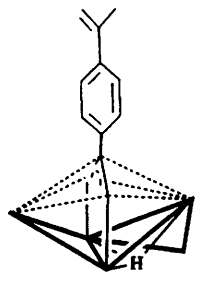

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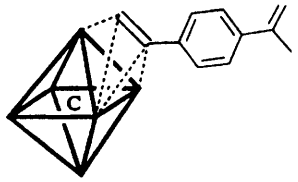

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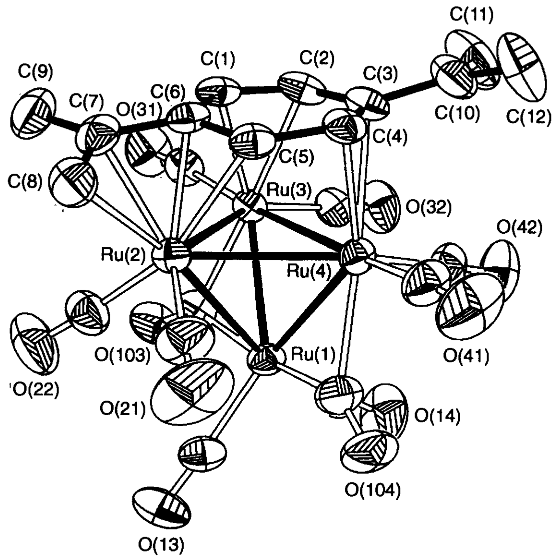


Fig. 1 Molecular structure of complex **1** in the solid state. The C atoms of the CO ligands bear the same numbering as that of the corresponding O atoms

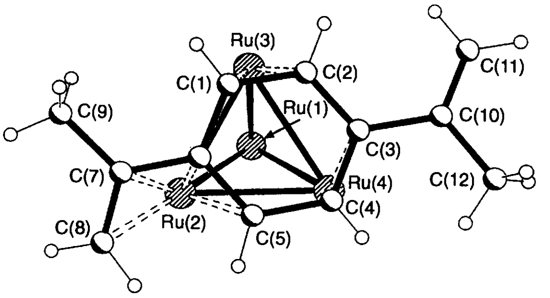


Fig. 2 Plan view of complex **1**; CO groups are omitted for clarity

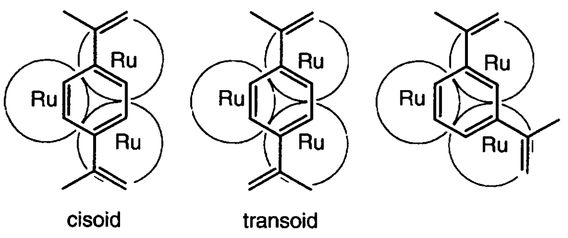


Fig. 3 Comparative projection of the ligands interacting with a ruthenium triangle

the metal cluster when it takes up the cisoid conformation. Two *cis*-butadiene units and one alkene in the ring can then overlap effectively with the orbitals of the metal. This conformation was observed for the 1,3-diisopropenylbenzene ligand in $[Ru_4(CO)_{10}(\mu_3\text{-}\eta^2:\eta^2:\eta^2:\eta^2\text{-}C_{12}H_{14})]$ which is a very stable cluster and can be obtained in relatively high yields. In **1** the ligand takes up a transoid configuration of the free with respect to the co-ordinated isopropylene. This is consistent with its behaviour as an eight-electron donor. The C(10) atom of the non-co-ordinated isopropylene unit is displaced away from the ruthenium face and lies above the plane of the appropriate diene grouping by 0.38 Å. Similarly, the directly located positions of the hydrogen atoms bonded to the ring are displaced by an average of 0.35 Å in the same direction. This bending back of the substituents away from the ring is greater than is observed for η^6 co-ordination and is not unexpected in view of the $\eta^2:\eta^2:\eta^2$ bonding mode.[8]

The four ruthenium atoms describe a distorted tetrahedron with each co-ordinated to two terminal carbonyls. The remaining two carbonyls bridge Ru(1)–Ru(4) [Ru(1)–C(104) 1.995 and Ru(4)–C(104) 2.225 Å] and Ru(1)–Ru(3) [Ru(1)–C(103) 2.048 and Ru(3)–C(103) 2.139 Å] respectively. These two edges [Ru(1)–Ru(4) 2.6864 and Ru(1)–Ru(3) 2.6924 Å] are shorter than the other Ru–Ru bonds which lie in the range 2.8609–2.9177 Å. The presence of bridging carbonyls is consistent with the high π-donor ability of the eight-electron-donor organic ligand.

The molecular structure of $[Ru_3(CO)_8(C_{12}H_{12})]$ **2** is shown in Fig. 4 and is consistent with the expected geometry. Selected bond lengths and angles are given in Table 2(*a*). The three ruthenium atoms describe a bent chain with the Ru(1)–Ru(2) distance (2.951 Å) significantly longer than that of Ru(2)–Ru(3) (2.781 Å) and the angle Ru(1)–Ru(2)–Ru(3) 84.8°. The ligand acts as a $\eta^2:\eta^6$ π donor with two σ bonds to Ru(3) [Ru(3)–C(5) 2.106, Ru(3)–C(8) 2.052 Å] to form a five-membered metallacycle fused to the six-membered carbon ring. One isopropylene unit co-ordinates η^2 to Ru(2) [Ru(2)–C(7) 2.280, Ru(2)–C(8) 2.252 Å] and the benzene ring co-ordinates η^6 to Ru(1) with Ru–C distances 2.261–2.342 Å. The ring is approximately planar with a mean deviation from the best plane of 0.012 Å; C(5) and C(6) have the longest bonds to Ru(1) such that the ring is slightly distorted at C(6). The non-bonded isopropylene is twisted out of the plane of the co-ordinated ring

Table 1 Selected bond lengths (Å) and angles (°) for $[Ru_4(CO)_{10}(C_{12}H_{14})]$ **1**

Ru(1)-Ru(4)	2.6864(6)	Ru(1)-Ru(3)	2.6924(5)
Ru(1)-Ru(2)	2.8660(6)	Ru(2)-Ru(3)	2.8609(5)
Ru(2)-Ru(4)	2.8990(6)	Ru(3)-Ru(4)	2.9177(5)
Ru(3)-C(1)	2.254(4)	Ru(3)-C(2)	2.294(4)
Ru(4)-C(3)	2.500(4)	Ru(4)-C(4)	2.201(4)
Ru(2)-C(5)	2.343(4)	Ru(2)-C(6)	2.192(3)
Ru(2)-C(7)	2.210(4)	Ru(2)-C(8)	2.251(5)
C(1)-C(2)	1.399(6)	C(2)-C(3)	1.431(6)
C(3)-C(4)	1.401(6)	C(4)-C(5)	1.442(6)
C(5)-C(6)	1.437(5)	C(1)-C(6)	1.453(5)
C(6)-C(7)	1.432(6)	C(7)-C(8)	1.411(7)
C(7)-C(9)	1.507(7)	C(3)-C(10)	1.490(6)
C(10)-C(11)	1.319(7)	C(10)-C(12)	1.496(8)
Ru(1)-C(103)	2.048(4)	Ru(3)-C(103)	2.139(4)
Ru(1)-C(104)	1.995(5)	Ru(4)-C(104)	2.225(4)
C(103)-O(103)	1.166(5)	C(104)-O(104)	1.161(5)
Ru(4)-Ru(1)-Ru(3)	65.701(14)	Ru(4)-Ru(1)-Ru(2)	62.85(2)
Ru(3)-Ru(1)-Ru(2)	61.861(14)	Ru(3)-Ru(2)-Ru(4)	60.866(14)
Ru(1)-Ru(2)-Ru(4)	55.545(14)	Ru(1)-Ru(3)-Ru(2)	62.05(2)
Ru(1)-Ru(3)-Ru(4)	57.051(14)	Ru(2)-Ru(3)-Ru(4)	60.213(14)
Ru(1)-Ru(4)-Ru(2)	61.60(2)	Ru(1)-Ru(4)-Ru(3)	57.247(14)
Ru(2)-Ru(4)-Ru(3)	58.921(14)		
C(2)-C(1)-C(6)	120.6(4)	C(1)-C(2)-C(3)	121.6(4)
C(4)-C(3)-C(2)	118.2(4)	C(3)-C(4)-C(5)	121.7(4)
C(6)-C(5)-C(4)	119.2(4)	C(5)-C(6)-C(1)	117.9(4)
C(7)-C(6)-C(5)	119.0(4)	C(7)-C(6)-C(1)	122.5(4)
C(8)-C(7)-C(6)	116.8(4)	C(8)-C(7)-C(9)	121.0(5)
C(6)-C(7)-C(9)	122.0(4)	C(4)-C(3)-C(10)	120.2(4)
C(2)-C(3)-C(10)	119.8(4)	C(11)-C(10)-C(3)	121.2(5)
C(11)-C(10)-C(12)	120.5(5)	C(3)-C(10)-C(12)	118.3(5)
O(103)-C(103)-Ru(1)	143.2(3)	O(103)-C(103)-Ru(3)	136.8(3)
Ru(1)-C(103)-Ru(3)	79.99(14)	O(104)-C(104)-Ru(1)	148.3(4)
O(104)-C(104)-Ru(4)	132.7(4)	Ru(1)-C(104)-Ru(4)	78.8(2)
Terminal carbonyls			
Ru-C	1.857(5)-1.909(5)	Ru-C-O	174.5(4)-178.4(4)
C-O	1.129(5)-1.143(5)		

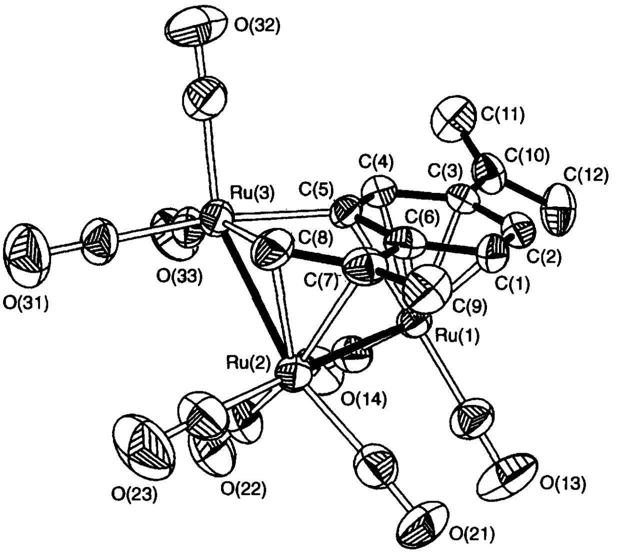


Fig. 4 Molecular structure of complex **2** in the solid state. The C atoms of the CO ligands bear the same numbering as that of the corresponding O atoms

by 30.9°. This structure is similar to known examples with the same ligand co-ordination.[3,9]

Analogues of the hexaruthenium species $[Ru_6H(CO)_{15}(C_{12}H_{11})]$ **3** and $[Ru_6H(CO)_{15}(C_{12}H_{13})]$ **4** have not previously been structurally characterised. The infrared spectrum shows a bridging carbonyl at 1838 cm^{-1} and the ^1H NMR spectrum exhibits peaks which can be assigned to an unco-ordinated isopropylene and an isopropyl group. However, it has not been possible to separate the two compounds. Crystals were obtained from a solution containing both these species and an X-ray crystallographic analysis undertaken. This revealed that both **3** and **4** are randomly distributed in the crystal in approximately equal proportions and differ only with respect to the non-co-ordinated group which is retained as an isopropylene group in **3** whereas in **4** it has been hydrogenated to an isopropyl substituent. The molecular structures are shown in Fig. 5(*a*) and 5(*b*) respectively. The ruthenium framework consists of a distorted tetrahedron with one edge bridged by a fifth ruthenium. This edge-bridging atom Ru(2) is further co-ordinated to Ru(1) which may be described as a spike. The framework may also be viewed as derived from the bent triruthenium chain of **2** with a ruthenium triangle Ru(4)-Ru(5)-Ru(6) bonded to Ru(2)-Ru(3). The co-ordination of the organic ligand is very similar to that in **2**, differing only in the formation of two σ bonds to the additional ruthenium triangle and the transfer of a hydrogen from the ligand at C(8) to the metal framework, where it adopts a bridging position along Ru(3)-Ru(6). A comparison of all relevant bond lengths and angles and other selected lengths and angles is given in Table 2. The ligand is π-bonded η^6 through the arene ring to the spike Ru(1) and through one isopropylene unit η^2 to the edge-bridging atom Ru(2). The ligand is also σ bonded *via* C(5) and C(8). Carbon atom C(8) forms three shorter bonds to Ru(3), Ru(4) and Ru(5) (2.077-2.087 Å) and one longer bond to Ru(2) (2.311 Å) as part of the π bond to Ru(2). It may therefore be regarded as a μ_4-three-electron donor and overall has a distorted trigonal-pyramidal environment of four ruthenium atoms and one carbon atom, an unusual co-ordination mode. Overall the ligand is therefore an eleven-electron donor and the co-ordination mode is unique. In **3** the second isopropylene unit is not co-ordinated. The plane of the isopropylene is twisted from the plane of the ring by 41.8° and takes up a transoid configuration with respect to the co-ordinated isopropylene unit. In **4** the second isopropylene has been hydrogenated to an isopropyl group. Hydrogenation of similar ligands has been observed previously in related reactions[7] and is also observed in the formation of compounds **2a** and **5a**. The hydrogen required is believed to be formed in the initial σ co-ordination of the ligand to give **2** which occurs with loss of two hydrogen atoms. One carbonyl group bridges one edge of the edge-bridge Ru(2)–Ru(5) [Ru(2)–C(205) 2.056, Ru(5)–C(205) 2.049 Å]. The hydride was located directly and bridges the longest tetrahedral edge Ru(3)–Ru(6) (3.015 Å) [Ru(3)–H(306) 1.926, Ru(6)–H(306) 1.869 Å] and is semi-face bridging between Ru(3)–Ru(6) and Ru(5) [Ru(5)–H(306) 2.503 Å].

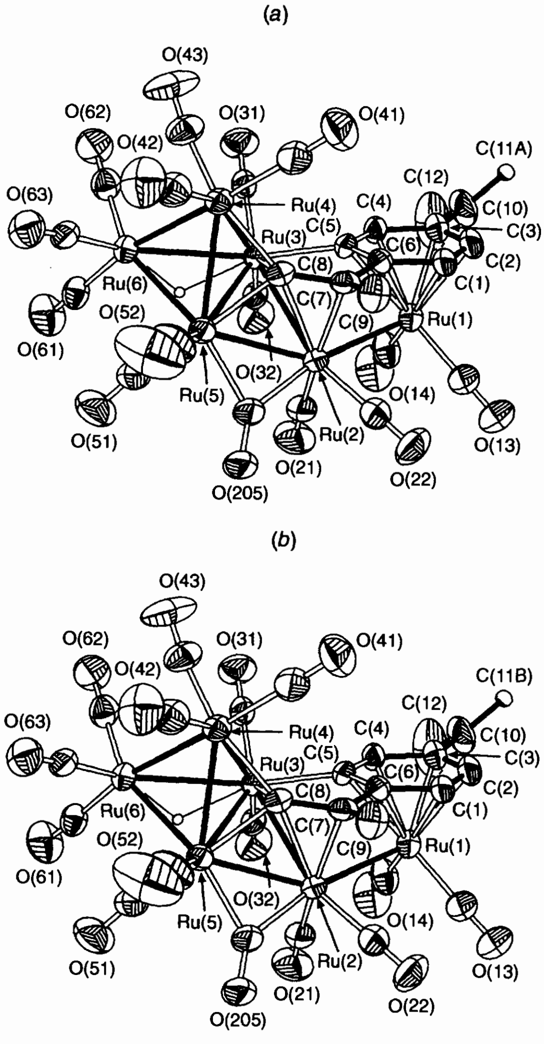


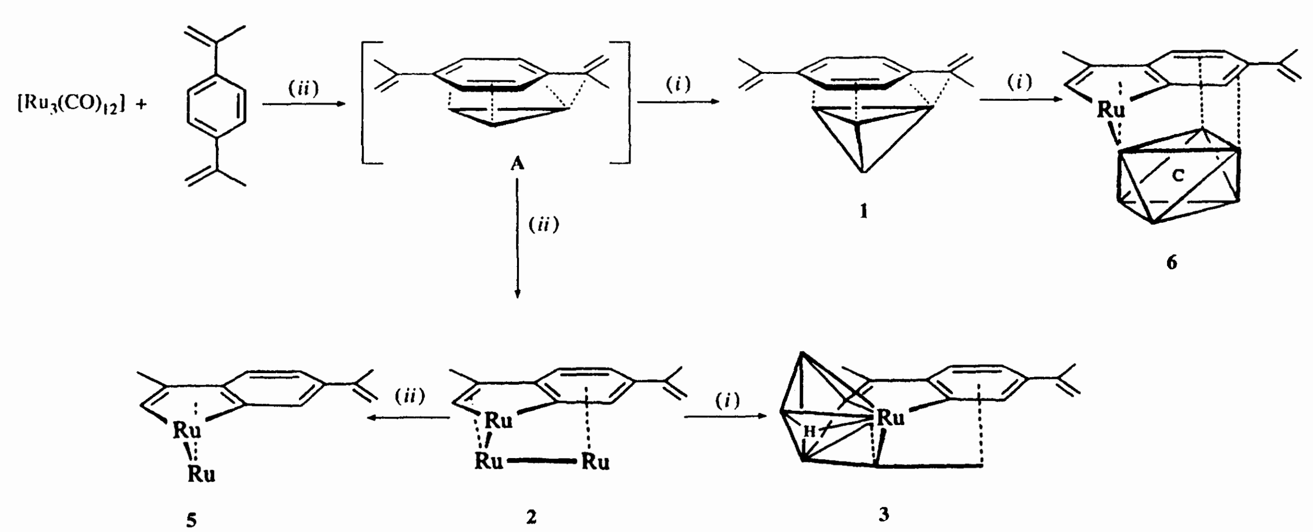
Fig. 5 Molecular structure of complexes **3** (*a*) and **4** (*b*) in the solid state. The C atoms of the CO ligands bear the same numbering as that of the corresponding O atoms

The ruthenium framework of complexes **3** and **4** has not been previously reported and may be viewed as described above or as a face-capped *arachno* octahedron with the remaining vertex having a spike ruthenium. Both descriptions are consistent with the observed electron count of 90. Alternatively the structure may be viewed as derived from the trinuclear ruthenium metallacycle **2**. Comparison of the structures [Figs. 4 and 5(*a*)] and bond lengths and angles of **2** and **3** [Table 2(*a*)] clearly shows the presence of a fragment derived from **2** consisting of Ru(1), Ru(2), Ru(3) and the diisopropylenebenzene ligand. The hexanuclear cluster **3** may then be considered to be the addition product of the reaction of **2** with $[Ru_3(CO)_{12}]$, equation (1).

$$[Ru_3(CO)_8(C_{12}H_{12})] + [Ru_3(CO)_{12}] \longrightarrow [Ru_6H(CO)_{15}(C_{12}H_{11})] + 5CO \quad (1)$$

This is supported by the observation that in a separate reaction when **2** was heated with $[Ru_3(CO)_{12}]$ in octane for 1 h **3** was detected by IR spectroscopy and spot TLC in the reaction mixture. On heating alone **2** undergoes fragmentation to give **5**.[8] The addition reaction involves oxidative addition of the terminal C–H of the η^2 unit of **2** to $[Ru_3(CO)_{12}]$ with associated loss of one CO. The formation of four Ru–Ru bonds involves a further loss of four CO; each of the ruthenium atoms of $[Ru_3(CO)_{12}]$ forms one bond to Ru(3) and Ru(4) forms an additional bond to Ru(2). The observed location of the hydride implies migration has occurred after initial addition. Significantly this provides further evidence for $[Ru_3(CO)_8(C_{12}H_{12})]$ as a template for cluster build-up.

The presence of the metallacycle products $[Ru_3(CO)_8(C_{12}H_{12})]$ **2**, $[Ru_6H(CO)_{15}(C_{12}H_{11})]$ **3**, $[Ru_2(CO)_6(C_{12}H_{12})]$ **5** and $[Ru_7C(CO)_{16}(C_{12}H_{12})]$ **6** indicates the formation of the compounds **A** and **1** as intermediates. We have previously established that **A** is the precursor to **2**.[3] This process demands the fission of one Ru–Ru bond and the C–H activation and cleavage of an *ortho*-H bond and the *cis*-H bond of the ethyl unit. The formation of the heptanuclear cluster **6** is observed when **1** is heated with $[Ru_3(CO)_{12}]$ in octane. These reactions are summarised in Scheme 1. These observations show that these ligands show considerable utility as a template in cluster build-up.



Scheme 1 (*i*) Heating with $[Ru_3(CO)_{12}]$, (*ii*) heating in octane

Table 2 Selected bond lengths (Å) and angles (°) for $[Ru_3(CO)_8(C_{12}H_{12})]$ **2** and $[Ru_6H(CO)_{15}(C_{12}H_{11})]$ **3**/$[Ru_6H(CO)_{15}(C_{12}H_{13})]$ **4**

(*a*) Comparison between **2** and **3/4**

	2	**3/4**		**2**	**3/4**
Ru(1)–Ru(2)	2.951(1)	2.913(1)	Ru(1)···Ru(3)	3.867(1)	3.922(1)
Ru(2)–Ru(3)	2.781(1)	2.865(1)			
Ru(1)–C(1)	2.285(5)	2.269(7)	C(2)–C(3)	1.408(8)	1.414(11)
Ru(1)–C(2)	2.277(6)	2.269(7)	C(3)–C(4)	1.438(8)	1.444(10)
Ru(1)–C(3)	2.299(6)	2.286(8)	C(4)–C(5)	1.412(8)	1.416(10)
Ru(1)–C(4)	2.261(6)	2.284(7)	C(5)–C(6)	1.449(7)	1.441(9)
Ru(1)–C(5)	2.316(5)	2.342(7)	C(1)–C(6)	1.414(8)	1.418(9)
Ru(1)–C(6)	2.342(6)	2.362(7)	C(6)–C(7)	1.478(9)	1.429(10)
Ru(2)–C(7)	2.280(6)	2.241(7)	C(7)–C(8)	1.394(8)	1.419(9)
Ru(2)–C(8)	2.252(6)	2.311(7)	C(7)–C(9)	1.513(8)	1.517(10)
Ru(3)–C(5)	2.106(6)	2.089(6)	C(3)–C(10)	1.492(9)	1.512(12)
Ru(3)–C(8)	2.052(6)	2.077(7)	C(10)–C(11)	1.316(9)	1.357*
C(1)–C(2)	1.400(9)	1.401(11)	C(10)–C(12)	1.497(10)	1.502(16)
Ru(3)–Ru(2)–Ru(1)	84.8(1)	85.5(1)	C(1)–C(6)–C(7)	125.5(5)	125.6(6)
C(5)–Ru(3)–C(8)	78.4(2)	76.4(3)	C(5)–C(6)–C(7)	115.1(5)	115.1(6)
C(6)–C(5)–Ru(3)	113.6(4)	116.1(5)	C(6)–C(7)–C(8)	112.6(5)	112.0(6)
C(7)–C(8)–Ru(3)	118.9(4)	118.5(5)	C(6)–C(7)–C(9)	120.4(5)	122.3(6)
C(4)–C(5)–Ru(3)	128.6(4)	125.3(5)	C(9)–C(7)–C(8)	125.7(6)	122.9(6)
C(2)–C(1)–C(6)	121.6(5)	121.6(7)	C(10)–C(3)–C(2)	121.9(5)	121.9(7)
C(1)–C(2)–C(3)	121.1(5)	120.9(7)	C(10)–C(3)–C(4)	120.8(5)	120.4(7)
C(2)–C(3)–C(4)	117.2(5)	117.6(7)	C(11)–C(10)–C(3)	119.7(6)	116.3*
C(3)–C(4)–C(5)	123.3(5)	122.2(6)	C(11)–C(10)–C(12)	122.2(6)	126.2*
C(4)–C(5)–C(6)	117.4(5)	118.5(6)	C(12)–C(10)–C(3)	117.9(5)	116.1(8)
C(1)–C(6)–C(5)	119.3(5)	119.0(6)			

Terminal carbonyls

Ru–C	1.864(8)–1.938(7)	1.791(10)–1.912(8)	Ru–C–O	175.9(6)–179.1(7)	172.8(7)–179.4(7)
C–O	1.128(9)–1.147(10)	1.119(10)–1.149(12)			

(*b*) Additional values for **3/4**

Ru(2)–Ru(5)	2.799(1)	Ru(3)–Ru(4)	2.805(1)	Ru(5)–C(8)	2.087(6)	Ru(4)–C(8)	2.085(7)
Ru(3)–Ru(5)	2.876(1)	Ru(3)–Ru(6)	3.015(1)	C(10)–C(11B)	1.514	C(11A)···C(11B)	0.955
Ru(4)–Ru(5)	2.835(1)	Ru(4)–Ru(6)	2.788(1)	Ru(2)–C(205)	2.056(8)	Ru(5)–C(205)	2.049(9)
Ru(5)–Ru(6)	2.738(1)			C(205)–O(205)	1.166(11)		
Ru(5)–Ru(2)–Ru(1)	145.3(1)	Ru(5)–Ru(2)–Ru(3)	61.0(1)	Ru(6)–Ru(5)–Ru(4)	60.0(1)	Ru(4)–Ru(6)–Ru(3)	57.7(1)
Ru(4)–Ru(3)–Ru(2)	99.4(1)	Ru(5)–Ru(3)–Ru(2)	58.3(1)	Ru(5)–Ru(6)–Ru(3)	59.8(1)	Ru(5)–Ru(6)–Ru(4)	61.7(1)
Ru(5)–Ru(3)–Ru(4)	59.9(1)	Ru(6)–Ru(3)–Ru(2)	112.3(1)	Ru(3)–C(8)–Ru(2)	81.3(2)	Ru(4)–C(8)–Ru(2)	159.6(3)
Ru(6)–Ru(3)–Ru(4)	57.1(1)	Ru(6)–Ru(3)–Ru(5)	55.3(1)	Ru(4)–C(8)–Ru(3)	84.8(2)	Ru(5)–C(8)–Ru(2)	78.9(2)
Ru(5)–Ru(4)–Ru(3)	61.3(1)	Ru(6)–Ru(4)–Ru(3)	65.2(1)	Ru(5)–C(8)–Ru(3)	87.4(2)	Ru(5)–C(8)–Ru(4)	85.6(2)
Ru(6)–Ru(4)–Ru(5)	58.3(1)	Ru(3)–Ru(5)–Ru(2)	60.6(1)	C(7)–C(8)–Ru(2)	69.2(4)	C(7)–C(8)–Ru(3)	118.5(5)
Ru(4)–Ru(5)–Ru(2)	100.3(1)	Ru(4)–Ru(5)–Ru(3)	58.8(1)	C(7)–C(8)–Ru(4)	131.1(5)	C(7)–C(8)–Ru(5)	133.8(5)
Ru(6)–Ru(5)–Ru(2)	123.8(1)	Ru(6)–Ru(5)–Ru(3)	64.9(1)				

* For C(11A) instead of C(11).

Conclusion

This work emphasises the wide range of activity introduced into unsaturated carbocyclic organic molecules by co-ordination to the triruthenium unit, and is clearly dominated by C–H bond cleavage and formation reactions. Of particular interest is the ability of the organo-unit to serve as a template for systematic cluster synthesis. A feature of special note is the unusual formation of a crystalline solid containing approximately equal amounts of both the precursor and product molecules of the hydrogenation of $[Ru_6H(CO)_{15}(C_{12}H_{11})]$ **3**. It is clear that this crystalline lattice is moderately insensitive to the nature of the eno-cyclic ring in these compounds.

Experimental

General procedures and materials

All reactions were carried out using octane from Aldrich Chemicals, and under a nitrogen atmosphere. The work-up of the products was carried out using standard laboratory-grade solvents. Infrared spectra were recorded on a Perkin-Elmer 1710 Fourier-transform spectrometer, mass spectra by positive fast atom bombardment on a Kratos MS50TC calibrated with CsI and ^1H NMR spectra using a Bruker AM200 spectrometer referenced to internal $SiMe_4$. The cluster $[Ru_3(CO)_{12}]$ was prepared using a standard procedure. 1,4-Diisopropenylbenzene was prepared from 1,4-diacetylbenzene with methyltriphenylphosphonium bromide and LiBu *via* a Wittig reaction in tetrahydrofuran.

Thermolysis of $[Ru_3(CO)_{12}]$ with 1,4-diisopropenylbenzene in octane: preparation of complexes 1–9

The complex $[Ru_3(CO)_{12}]$ (350 mg) was heated to reflux in octane with 1,4-diisopropenylbenzene (100 mg) for 2 h. 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 solvent was removed *in vacuo* and the reaction mixture separated by TLC using hexane–dichloromethane (7:3) as the mobile phase. In order of elution the following compounds were obtained: 13.4 mg (3.1%) $[Ru_2(CO)_6(C_{12}H_{12})]$/$[Ru_2(CO)_6(C_{12}H_{14})]$ **5/5a**, 15.3 mg (4%) $[Ru_3H(CO)_9(C_{12}H_{11})]$ **7**, 2.3 mg (0.7%) $[Ru_6C(CO)_{15}(C_{11}H_{10})]$ **9**, 13.4 mg (3.1%) $[Ru_3(CO)_8(C_{12}H_{12})]$/$[Ru_3(CO)_8(C_{12}H_{14})]$ **2/2a**, 7.6 mg (2.2%) $[Ru_5H(CO)_{14}(C_{12}H_{11})]$ **8**, 4.8 mg (1.5%)

Table 3 Crystal data and structure refinement for complexes **1**–**4**

	1	**2**	**3/4**
Empirical formula	$C_{22}H_{14}O_{10}Ru_4$	$C_{20}H_{12}O_8Ru_3$	$C_{27}H_{12}O_{15}Ru_6/C_{27}H_{14}O_{15}Ru_6$
M	842.61	651.35	1182.45/1184.47
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2_1/n$
a/Å	8.9566(11)	8.446(1)	8.910(1)
b/Å	8.9606(10)	10.340(2)	16.291(3)
c/Å	17.567(2)	25.346(4)	23.267(4)
α/°	102.771(10)		
β/°	93.220(14)	99.44(2)	97.06(2)
γ/°	112.191(9)		
U/Å³	1257.8(2)	2183.5	3351.7
Z	2	4	4
D_c/g cm⁻³	2.225	2.079	2.148
μ(Mo-Kα)/cm⁻¹	2.408	1.92	2.08
F(000)	804	1312	2064
10² Crystal size/mm	44 × 42 × 18	8 × 15 × 35	20 × 16 × 24
Crystal colour	Red	Yellow	Black
θ Range/°	2.5–30	3–25	3–25
hkl Ranges	−1 to 10, −11 to 11, −24 to 24	−10 to 9, 0–12, 0–30	−10 to 10, 0–19, 0–27
Reflections collected	5687	4168	6282
R_{int}	0.0175	0.0444	0.0407
No. independent observed data	4305	2962	4397
No. parameters	328	284	428
R	0.0235 [$I > 2\sigma(I)$]	0.0338 [$I > 3\sigma(I)$]	0.0346 [$I > 3\sigma(I)$]

$[Ru_6H(CO)_{15}(C_{12}H_{11})]/[Ru_6H(CO)_{15}(C_{12}H_{13})]$ **3/4**, 12.7 mg (2.9%) $[Ru_7C(CO)_{16}(C_{12}H_{12})]$ **6** and 8.3 mg (1.8%) $[Ru_4(CO)_{10}(C_{12}H_{14})]$ **1**. Further separation of **2/2a**, **3/4** and **5/5a** was not possible. The relative proportions in solution were determined from ¹H NMR spectra to be **2**:**2a** 50:50, **3**:**4** 45:55 and **5**:**5a** 35:65. The unsubstituted hexanuclear cluster $[Ru_6C(CO)_{17}]$ was also observed as a major product but was not isolated. Some decomposition was evidenced by a heavy baseline. Crystals of **1**, **2** and **3/4** were each grown by slow cooling of a dichloromethane–hexane solution to 248 K.

Reactions with $[Ru_3(CO)_{12}]$

A solution of complex **2** (*ca.* 2 mg) and $[Ru_3(CO)_{12}]$ (5 mg) was heated in refluxing octane (2 cm³) for 1 h. The progress of the reaction was monitored by IR spectroscopy and spot TLC. Similarly for a solution of **1** (*ca.* 3 mg) and $[Ru_3(CO)_{12}]$ (5 mg).

Spectroscopic data

$[Ru_4(CO)_{10}(C_{12}H_{14})]$ 1. ¹H NMR (CDCl₃): δ −0.62 (m, H^5), 1.14 (d, *J* 2.3, H^{8a}), 1.61 (s, 3 H, H^9), 2.06 (s, 3 H, H^{12}), 3.15 (d, *J* 2.3 Hz, H^{8b}), 4.63 (m, H^1), 5.19 (m, H^2), 5.20 (m, H^{11a}) and 5.38 (m, H^4, H^{11b}). Mass spectrum (FAB): *m/z* = 843 (M^+). IR (CH_2Cl_2): ṽ/cm⁻¹ = 2059s, 2020vs, 2007vs, 1986s, 1969w, 1805m and 1806m.

$[Ru_3(CO)_8(C_{12}H_{12})]$ 2. ¹H NMR (CDCl₃): δ 2.17 (s, 3 H, H^9), 2.20 (br s, 3 H, H^{12}), 4.37 (d, ^3J 7, H^1) 5.21 (d, ^4J = 1.7, H^4), 5.30 (m, H^{11a}), 5.54 (m, H^{11b}), 6.18 (dd, ^3J 7, ^4J 1.7 Hz, H^2) and 8.80 (s, H^8).

$[Ru_3(CO)_8(C_{12}H_{14})]$ 2a. ¹H NMR (CDCl₃): δ 1.40 (d, 6 H, ^3J 7, H^{11}), 2.16 (s, 3 H, H^9), 2.83 (spt, ^3J 7, H^{10}), 4.30 (d, ^4J = 7, H^1), 5.05 (d, ^4J 1.7, H^4), 6.00 (dd, ^3J 7, ^4J 1.7, H^2) and 8.78 (s, H^8). Mass spectrum (FAB): *m/z* 687 (M^+). IR (CH_2Cl_2): ṽ/cm⁻¹ = 2071s, 2039vs, 2008vs, 1994s (br), 1966m (br) and 1948w (br).

$[Ru_6H(CO)_{15}(C_{12}H_{11})]$ 3. ¹H NMR (CDCl₃): δ −16.26 (s, hydride), 1.90 (s, 3 H, H^9), 2.21 (br s, 3 H, H^{12}), 4.35 (d, ^3J 7, H^1), 5.39 (m, H^{11a}), 5.55 (d, ^4J 1.7, H^4), 5.70 (m, H^{11b}) and 6.07 (dd, ^3J 7, ^4J 1.7 Hz, H^2).

$[Ru_6H(CO)_{15}(C_{12}H_{13})]$ 4. ¹H NMR (CDCl₃): δ −16.24 (s, hydride), 1.44 (d, 6 H, ^3J 7, H^{11}), 1.89 (s, 3 H, H^9), 2.82 (spt, ^3J 7, H^{10}), 4.29 (d, ^3J 7, H^1), 5.55 (d, ^4J 1.7, H^4) and 6.04 (dd, ^3J 7, ^4J 1.7 Hz, H^2). Mass spectrum (FAB): *m/z* 1185 (M^+). IR (CH_2Cl_2): ṽ/cm⁻¹ = 2084m, 2075w, 2045vs, 2024s, 1992m, 1967w and 1838w.

$[Ru_2(CO)_6(C_{12}H_{12})]$ 5. ¹H NMR (CDCl₃): δ 2.10 (q, 3 H, ^4J 0.6, H^{12}), 2.69 (s, 3 H, H^9), 5.16 (qnt, *J* 0.6 Hz, H^{11a}), 5.39 (br s, H^{11b}), 6.82 (s, H^8), 7.47 (m, H^2), 7.77 (m, H^1) and 7.80 (m, H^4).

$[Ru_2(CO)_6(C_{12}H_{14})]$ 5a. ¹H NMR (CDCl₃): δ 1.18 (d, 6 H, ^3J 6.8, H^{11}), 2.68 (s, 3 H, H^9), 2.80 (spt, ^3J 6.8 Hz, H^{10}), 6.65 (s, H^8), 7.20 (m, H^2), 7.60 (m, H^4) and 7.77 (m, H^1). Mass spectrum (FAB): *m/z* 529 (M^+). IR (CH_2Cl_2): ṽ/cm⁻¹ = 2077s, 2045vs, 2006vs (br), 1982 (sh), 1972m (sh) and 1913vw.

$[Ru_7C(CO)_{16}(C_{12}H_{12})]$ 6. ¹H NMR (CDCl₃): δ 1.00 (s, 3 H, H^9), 2.12 (s, 3 H, H^{12}), 5.29 (m, H^1), 5.31 (m, H^4), 5.37 (m, H^{11a}), 5.39 (m, H^{11b}), 5.59 (m, H^2) and 7.00 (s, H^8). Mass spectrum (FAB): *m/z* 1326 (M^+). IR (CH_2Cl_2): ṽ/cm⁻¹ = 2088m, 2060s, 2032vs, 2007m, 1970w, 1930w (br) and 1835w (br).

$[Ru_3H(CO)_9(C_{12}H_{11})]$ 7. ¹H NMR [$(CD_3)_2CO$]: δ −20.64 (s, hydride), 2.16 (m, 3 H, H^{12}), 5.13 (qnt, *J* 1.5 Hz, H^{11a}), 5.46 (m, H^{11b}), 7.53 (s, 4 H, H^{5-9}) and 9.03 (s, $H^{1/3}$). Mass spectrum (FAB): *m/z* 713 (M^+). IR (CH_2Cl_2): ṽ/cm⁻¹ = 2100m, 2074vs, 2045vs, 2028s, 2013s and 1995 (sh).

$[Ru_5H(CO)_{14}(C_{12}H_{11})]$ 8. ¹H NMR (CDCl₃): δ −19.40 (s, hydride), 2.18 (s, 3 H, H^{12}), 5.16 (m, H^{11a}), 5.47 (m, H^{11b}), 6.33 (d, ^2J 2.4, H^1), 7.53 (m, 2 H, $H^{5/9}$), 7.69 (m, 2 H, $H^{6/8}$) and 8.02 (d, ^4J 2.4 Hz, H^3). Mass spectrum (FAB): *m/z* 998 ([*M* − 2 CO]⁺). IR (CH_2Cl_2): ṽ/cm⁻¹ = 2108m, 2083s, 2072m, 2038vs (br), 2027 (sh), 2009m, 1994m, 1951w and 1883vw.

$[Ru_6C(CO)_{15}(C_{11}H_{10})]$ 9. ¹H NMR (CDCl₃): δ 2.44 (s, 3 H, H^{12}), 5.02 (m, H^{11a}), 5.33 (m, H^{11b}), 7.53 (d, 2 H, ^3J 8.4, $H^{5/7}$), 7.80 (d, 2 H, ^3J 8.4 Hz, $H^{4/8}$) and 10.23 (s, H^1). Mass spectrum

(FAB): *m*/*z* 1181 (M^+). IR (CH_2Cl_2): $\tilde{\nu}$/cm^{-1} = 2095w, 2089w, 2064s, 2054s, 2044vs, 2016m, 1988m, 1966m and 1949w.

X-Ray crystallography

The crystal data for compounds **1**–**4** are summarised in Table 3.

(*i*) **Data collection.** Data for complex **1** were collected with a Siemens P4 diffractometer and for **2** and **3** with a Phillips PW1100 diffractometer both using graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å) with scan type ω–2θ. A variable scan speed was used for **1** and a scan width of 0.90° for both **2** and **3**/**4**. All data were collected at room temperature. Absorption corrections were applied to the data for **1** using 50 ψ scans (maximum, minimum transmission 0.887, 0.553), empirical corrections[9] for **2** and **3**/**4**.

(*ii*) **Structure solution and refinement.**[10] For each structure the positions of the ruthenium atoms were located by a Patterson synthesis and the remaining non-hydrogen atoms in a series of Fourier-difference syntheses. Difference syntheses using low-angle data ($\sin \theta < 0.35$) were used to locate suitable positions for as many hydrogen atoms as possible. The remaining hydrogen atoms were placed in calculated positions (C–H 0.96 Å) with fixed thermal parameters of 0.08 Å^2 and included in the structure-factor calculations but were not refined unless otherwise indicated. Refinement was by full-matrix least squares on F_o^2 for **1** and on F_o for **2** and **3**/**4**.

[$Ru_4(CO)_{10}(C_{12}H_{14})$] **1.** Suitable positions were found for all hydrogen atoms attached to those carbon atoms bonded to ruthenium and for one additional hydrogen atom. These were assigned a common thermal parameter and included in the structure-factor calculations with fixed positions. Anisotropic thermal parameters were assigned to all non-hydrogen atoms in the final cycles of refinement which converged at $R1 = 0.0235$ [$I > 2\sigma(I)$] and $wR2$ 0.0557 (all data) with a goodness of fit of 1.098. Reflections were weighted as $1/[\sigma^2F_o^2 + (0.0322P)^2 + 1.23P]$ where $P = [(\max F_o^2, 0) + 2F_c^2]/3$.

[$Ru_3(CO)_8(C_{12}H_{12})$] **2.** After refinement with isotropic thermal parameters for all atoms, an empirical absorption correction[11] was applied (maximum 1.0389, minimum 0.9822). Eleven hydrogen atoms were located and the remainder placed in calculated positions. Individual weights of $1/\sigma^2(F)$ were assigned to each reflection and in the final cycles of refinement all non-hydrogen atoms were given anisotropic thermal parameters; refinement converged at $R = 0.0338$, $R' = 0.0339$ [$I > 3\sigma(I)$].

[$Ru_6H(CO)_{15}(C_{12}H_{11})$] **3** *and* [$Ru_6H(CO)_{15}(C_{12}H_{13})$] **4.** After location of all non-hydrogen atoms and refinement with isotropic thermal parameters, a large isotropic thermal parameter for C(11) indicated the presence of disorder. A Fourier-difference synthesis calculated without this atom revealed two local maxima which were assigned as C(11A) and C(11B). These peaks had bond lengths and angles consistent with a methylene and methyl group respectively. Refinement of their site occupancy factor, with fixed thermal parameters and coordinates gave relative populations of 0.48 and 0.52 respectively. The most satisfactory refinement was then obtained by assigning these populations and allowing only the thermal parameters to refine in subsequent refinements. The structure therefore consists of two compounds **3** and **4** present in approximately equimolar ratio, which differ only in the unsaturation of the non-co-ordinated group. A high anisotropic thermal parameter for C(12) in one direction is consistent with the expected disorder at this atom for this model. A Fourier-difference synthesis using low-angle data ($\sin \theta < 0.35$) enabled the three hydrogens attached to carbons bonded to ruthenium to be located. The highest peak was found to lie symmetrically between Ru(3)–Ru(6) and leaning over towards Ru(5) and was therefore assigned as the hydride in a semi-face-bridging bonding mode. This was supported by a potential-energy-minimisation calculation[12] which gave two minima, one along the Ru(3)–Ru(6) bond and the other on the Ru(3)–Ru(5)–Ru(6) face with the lowest over the face. Location of the hydride along the Ru(3)–Ru(6) bond is further supported by the rather long Ru(3)–Ru(6) (3.015 Å) distance compared with Ru(3)–Ru(5) (2.876 Å) and Ru(5)–Ru(6) (2.738 Å). The located position was therefore retained. Attempts to locate the remaining hydrogen atoms were unsuccessful. Individual weights of $1/\sigma^2(F)$ were assigned to each reflection and an empirical absorption correction was applied (maximum 1.0255, minimum 0.9687). In the final cycles of refinement anisotropic thermal parameters were assigned to all non-hydrogen atoms except C(11A) and C(11B). Refinement converged at $R = 0.0346$, $R' = 0.0399$ [$I > 3\sigma(I)$].

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.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/233.

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References

1 D. Braga, P. Dyson, F. Grepioni and B. F. G. Johnson, *Chem. Rev.*, 1994, **94**, 1585.
2 B. F. G. Johnson, M. Gallop and V. Y. Roberts, *J. Mol. Catal.*, 1994, **86**, 51.
3 P. Dyson, P. Escarpa, B. F. G. Johnson and A. Blake, *Inorg. Chim. Acta*, 1996, **241**, 11.
4 P. Dyson, P. Escarpa, B. F. G. Johnson, A. Blake, J. J. Byrne, F. Grepioni, E. Parisini and D. Reed, *Organometallics*, 1995, **14**, 4892.
5 P. Dyson, P. Escarpa, B. F. G. Johnson, A. Blake, D. Braga and E. Parisini, *J. Chem. Soc., Dalton Trans.*, 1995, 3431.
6 D. Braga, E. Parisini, P. Dyson, S. L. Ingham, B. F. G. Johnson and A. Blake, *J. Chem. Soc., Chem. Commun.*, 1995, 537.
7 P. Escarpa, B. F. G. Johnson, A. Blake, P. Dyson and S. Parson, *J. Chem. Soc., Dalton Trans.*, in the press.
8 M. A. Gallop, M. P. Gomez-Sal, C. E. Housecroft, B. F. G. Johnson, J. Lewis, S. M. Owen, P. R. Raithby and A. H. Wright, *J. Am. Chem. Soc.*, 1992, **114**, 2502.
9 A. J. Arce, Y. De Sanctis, A. Karam and A. J. Deeming, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1381.
10 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.
11 G. M. Sheldrick, SHELX 76, University of Cambridge, 1976; SHELXS 86, University of Göttingen, 1986; SHELXTL-PC, version 5.03, Siemens Analytical X-Ray Instruments, Madison, WI, 1994.
12 A. G. Orpen, *J. Chem. Soc., Dalton Trans.*, 1980, 2509.

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