

Reactions of $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ with ethyne: molecular structures of some prototypical cluster complexes

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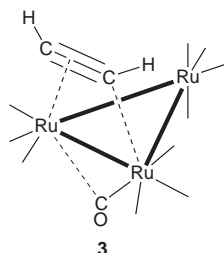
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Formation of Ru_4 , Ru_5 and Ru_6 complexes accompanies the synthesis of the previously described of $\text{Ru}_3(\mu_3\text{-C}_2\text{H}_2)(\mu\text{-CO})(\text{CO})_9$ **1** [from $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ and C_2H_2] and its conversion to $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_2\text{H})(\text{CO})_9$ **2**. In $\text{Ru}_4(\mu_4\text{-C}_2\text{H}_2)(\text{CO})_{12}$ **4**, the ethyne forms part of the pseudo-octahedral C_2Ru_4 . In contrast, $\mu_4\text{-}\eta^2\text{-CCH}_2$ ligands are found in $\text{Ru}_5(\mu_4\text{-CCH}_2)(\text{CO})_{15}$ **5** and $\text{Ru}_6(\mu_4\text{-CCH}_2)_2(\text{CO})_{16}$ **7**; in the former, the Ru_5 core is an edge-bridged tetrahedron, while in **7**, two butterflies share an $\text{Ru}=\text{Ru}$ double bond [2.686(1) Å]. Other minor products are $\text{Ru}_5(\mu\text{-CHCHCCH}_2)(\text{CO})_{15}$ **6** and $\text{Ru}_6(\mu\text{-H})(\mu_4\text{-C})(\mu\text{-CCMe})(\mu\text{-CO})(\text{CO})_{16}$ **8**. Crystal structures of **1**, **2**, **4**, **5** and **7**· CH_2Cl_2 are reported.

Introduction

Reactions of $\text{Ru}_3(\text{CO})_{12}$ with alkynes have been the source of many different types of complex.^{1,2} The commonly accepted route to these complexes is *via* initial formation of an η^2 -alkyne complex which subsequently interacts with the other metal atoms of the cluster, in the process becoming attached to all three Ru atoms. Subsequently, a cluster-bound 1-alkyne may undergo a facile H-shift from carbon to the cluster to give a hydrido-alkynyl complex. Other reactions involving coupling with further molecules of alkyne and fragmentation/reassembly of the metal cluster are known.

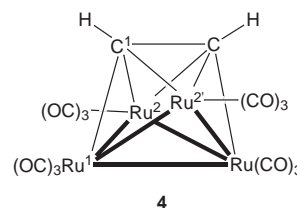
The chemistry of the simplest alkyne, ethyne, with $\text{Ru}_3(\text{CO})_{12}$ has a long history. In the 1960s, the cluster carbonyl was used as a catalyst for the conversion of mixtures of ethyne, hydrogen and CO to hydroquinone.^{3–6} Other reports describe either cluster degradation or oligomerisation reactions. The reaction between $\text{Ru}_3(\text{CO})_{12}$ and ethyne, carried out in thf, afforded only binuclear complexes.⁷ Although methods for the activation of $\text{Ru}_3(\text{CO})_{12}$ have been available for many years, few studies of its reactions with ethyne have been described and no structural studies have been reported. To our knowledge, the earliest report of products containing monomeric ethyne or its derivatives obtained from the reactions between $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ and ethyne dates from 1991 and describes the formation of $\text{Ru}_3(\mu_3\text{-C}_2\text{H}_2)(\mu\text{-CO})(\text{CO})_9$ **1** and $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_2\text{H})(\text{CO})_9$ **2**.⁸ Use of $\text{Ru}_3(\text{CO})_9(\text{NCMe})_3$ as precursor gave **2** in 70% yield.⁹ Of interest in the present context is the more recently described facile reaction that occurs (at 183 K) between $\text{Ru}_3\text{H}(\mu\text{-H})(\text{CO})_{11}$ and ethyne which leads to $\text{Ru}_3(\text{CO})_{11}(\eta\text{-C}_2\text{H}_2)$ **3**, the cluster-bound hydrogens being removed as ethene.¹⁰ On warming to room temperature, decarbonylation and conversion to $\text{Ru}_3(\mu_3\text{-C}_2\text{H}_2)(\mu\text{-CO})(\text{CO})_9$ occurs. On NMR evidence, a structure for **3** containing partially bridging CO and C_2H_2 ligands was proposed.



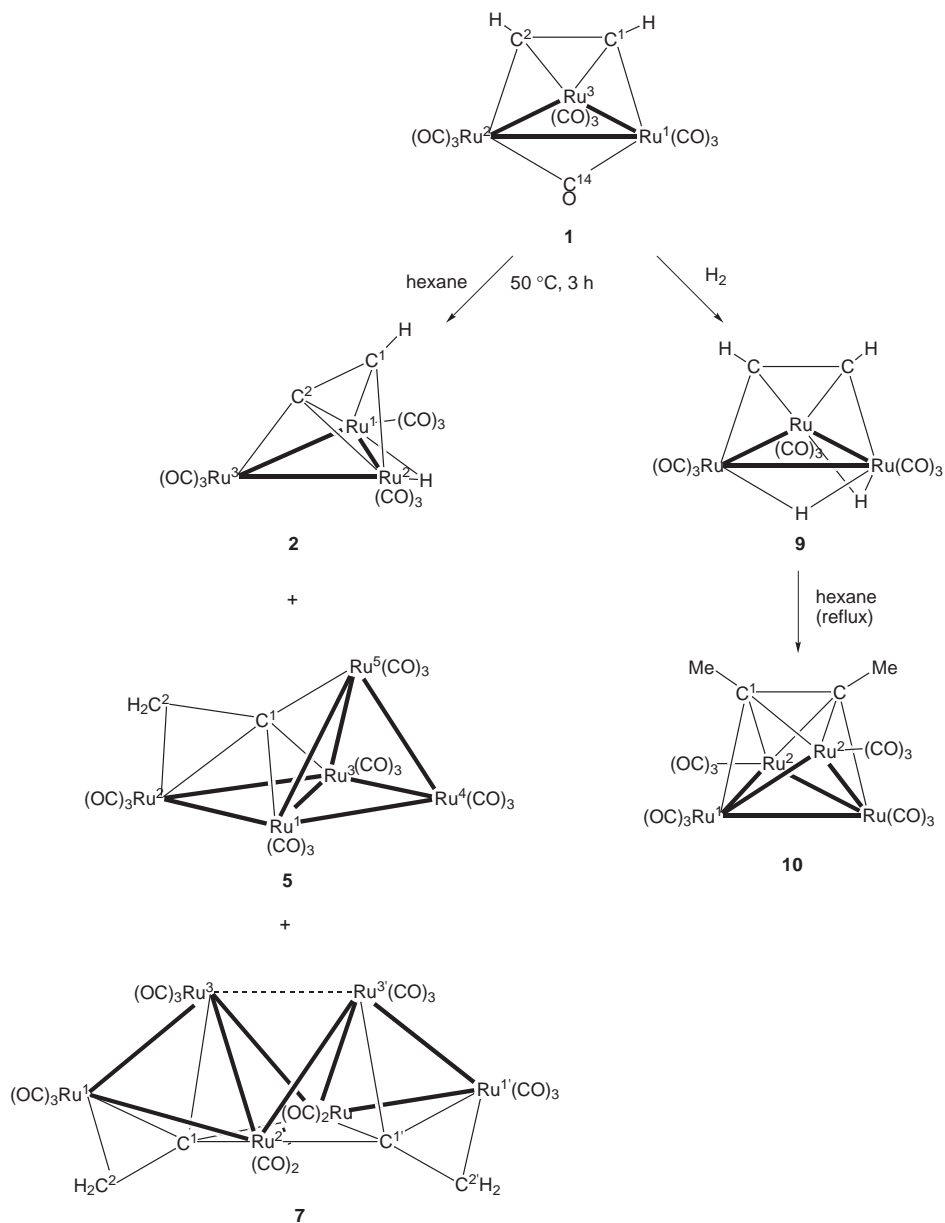
In connection with our studies of cluster complexes containing all-carbon ligands,^{11,12} we considered deriving the C_2 ligand from ethyne and have studied some related chemistry. This paper contains an account of the molecular structures of **1** and **2**, together with those of three clusters of higher nuclearity isolated from thermolytic reactions of **1** and **2**.

Results and discussion

As described earlier by Aime and co-workers,⁸ the reactions of acetonitrile derivatives of $\text{Ru}_3(\text{CO})_{12}$ with ethyne proceed readily at room temperature. We did not isolate the complex $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$, but used the solution obtained from $\text{Ru}_3(\text{CO})_{12}$ and Me_3NO in CH_2Cl_2 containing acetonitrile after filtering through alumina. However, in our hands, three complexes were obtained by separation of the reaction products by preparative TLC on silica gel. Complex **1** was obtained in 41% yield and identified by comparison of its IR $\nu(\text{CO})$ and ^1H NMR spectra with the literature values. The molecular structure was established by a single-crystal X-ray study. Among the products, dark red crystals of $\text{Ru}_4(\mu_4\text{-C}_2\text{H}_2)(\text{CO})_{12}$ **4** were obtained in 7% yield. The IR $\nu(\text{CO})$ spectrum of **4** contained eight bands between 2098 and 1977 cm^{-1} and is similar to that of other complexes of this type, such as $\text{Ru}_4(\mu_4\text{-C}_2\text{Me}_2)(\text{CO})_{12}$.¹³ The ^1H NMR spectrum contained a singlet δ 10.01 for the C_2H_2 protons: no high field signals for metal-bound protons were found. Interestingly, the FAB mass spectrum contains no M^+ ion, but only ions corresponding to $[\text{Ru}_4\text{C}_2(\text{CO})_n]^+$ ($n = 5\text{--}12$); the strongest peak is found for $n = 1$. The molecular structure of **4** was also determined as being the simplest cluster of its type.



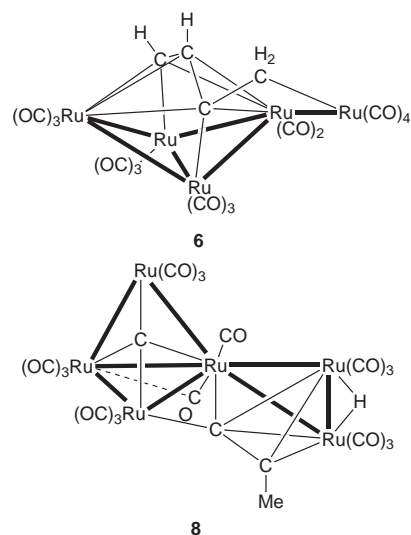
Of unusual interest was the isolation of a pentanuclear complex, $\text{Ru}_5(\mu_4\text{-CCH}_2)(\text{CO})_{15}$ **5** as red crystals in 1.5% yield which decompose rapidly in solution. The molecular structure of this complex was determined from a single-crystal X-ray study. This



Scheme 1

complex has a complex IR $\nu(\text{CO})$ spectrum with seven bands between 2098 and 1975 cm^{-1} . The ^1H NMR spectrum contained a singlet resonance for the two equivalent H atoms at δ 4.23. The FAB mass spectrum contained M^+ at m/z 952, which fragmented by loss of up to five CO groups; apparent loss of O from $[\text{M} - 5\text{CO}]^+$ is then followed by loss of a further seven CO groups. Presumably formation of a carbido cluster ion $[\text{Ru}_5\text{C}(\text{CO})_9]^+$ has occurred by fragmentation of a CO ligand.

In an effort to determine the origins of the higher nuclearity clusters, we heated a hexane solution of **1** at 50 °C until only thermolysis products were present (3 h) (Scheme 1). Preparative TLC enabled the separation of six complexes from the reaction mixture, which were characterised as $\text{Ru}_3(\text{CO})_{12}$ (**2**) (51%), **5** (2.4%), $\text{Ru}_5(\mu_5\text{-CHCHCCH}_2)(\text{CO})_{15}$ **6** (6.2%), $\text{Ru}_6(\mu_4\text{-CCH}_2)(\text{CO})_{16}$ (**7**) (1%), and $\text{Ru}_6(\mu\text{-H})(\mu_4\text{-C})(\mu_4\text{-CCMe})(\mu\text{-CO})(\text{CO})_{16}$ **8** (8%). With the exception of $\text{Ru}_3(\text{CO})_{12}$, the structures of these complexes were determined crystallographically. The molecular structures of **6** and **8** have been described elsewhere.¹⁴ Complex **2** was also identified by comparison of its spectral properties with those of related complexes; as indicated in the Experimental section, our IR $\nu(\text{CO})$ spectra differ from those reported by Aime and co-workers.⁸ The ^1H NMR spectra



are similar, however, and the molecular structure determination confirms the nature of our product; we have no explanation for this discrepancy.

Table 1 Selected bond lengths (Å), bond angles (°) and dihedral angles (°) for complexes **1**, **2**, **4**, and **10**

	1	2 (molecules 1, 2)	4	10
Ru(1)–Ru(1')			2.7946(8)	2.878(2)
Ru(1)–Ru(2)	2.843(1)	2.792(1), 2.790(1)	2.769(3)	2.724(2)
Ru(1)–Ru(2')			2.725(3)	2.709(2)
Ru(1)–Ru(3)	2.755(1)	2.803(1), 2.815(1)		
Ru(2)–Ru(3)	2.721(1)	2.810(1), 2.803(1)		
Ru(1)–C(1)	2.122(7)	2.232(7), 2.229(7)	2.118(7)	2.13(1)
Ru(1)–C(2)		2.213(6), 2.221(6)		
Ru(2)–C(1)		2.235(7), 2.228(7)		
Ru(2)–C(2)	2.048(7)	2.230(7), 2.216(6)	2.188(7)	2.21(1)
Ru(2')–C(1)			2.176(4)	2.27(1)
Ru(3)–C(1)	2.213(7)			
Ru(3)–C(2)	2.246(7)	1.942(8), 1.935(8)		
C(1)–C(2)	1.41(1)	1.28(1), 1.31(1)	1.472(9)	1.43(1)
Ru(1)–C(11)	1.91(1)	1.905(8), 1.889(8)	1.926(7)	1.88(2)
Ru(1)–C(12)	1.916(9)	1.916(9), 1.95(1)	1.91(1)	1.92(1)
Ru(1)–C(13)	1.962(8)	1.913(8), 1.902(9)	1.895(6)	1.88(2)
Ru(1)–C(14)	2.021(8)			
Ru(2)–C(14)	2.380(9)			
Ru(2)–C(21)	1.92(1)	1.934(9), 1.913(9)	1.907(7)	1.89(2)
Ru(2)–C(22)	1.89(1)	1.906(8), 1.911(8)	1.906(7)	1.89(1)
Ru(2)–C(23)	1.955(8)	1.923(8), 1.906(8)	1.889(8)	1.92(1)
Ru(3)–C(31)	1.885(9)	1.887(8), 1.898(8)		
Ru(3)–C(32)	1.920(9)	1.918(9), 1.902(8)		
Ru(3)–C(3)	1.925(8)	1.897(8), 1.918(8)		
C–O	1.12(1)–1.15(1)	1.11(1)–1.15(1)	1.13(1)–1.14(1)	
average	1.13	1.13	1.13 ₅	
Ru(1)–C(1)–C(2)	107.6(5)		108.2(4) ^b	
Ru(2)–C(2)–C(1)	112.6(5)			
Ru(3)–C(2)–C(1)		151.9(5), 151.7(5)		
Ru(1)–C(14)–O(14)	149.2(7)			
Ru(2)–C(14)–O(14)	130.7(6)			
Ru–C–O	175.3(8)–178.4(8) ^a	176.0(7)–179.3(7)	173.5(7)–178.7(7)	
average	177.2	177.7	177.2	
Ru(1,2,3)/Ru(1,2)C(14)	21.2(3)			
Ru(1,2,3)/Ru(1,2)C(1,2)	89.24(3)			
Ru(1,1',2)/Ru(1,1',2')			69.5(2)	
Ru(2)C(1,1')/Ru(2')C(1,1')			37.7(2)	
Ru(1,1',2)/Ru(1,1',2')				63.11(4)
Ru(2)C(1,1')/Ru(2')C(1,1')				45.69(5)

^a Ru(1)–C(11)–O(11) 168.1(9). ^b For C(2), read C(1') here and above.

Hydrogenation of **1** (hexane, r.t., 24 h) affords Ru₃(μ-H)₂(μ₃-C₂H₂)(CO), **9** in 58% yield.⁸ Further pyrolysis of **9** in refluxing hexane overnight resulted mainly in decomposition, but small amounts of Ru₃(CO)₁₂ (4%) and Ru₄(μ₄-C₂Me₂)(CO)₁₂ **10** (5%) were isolated by preparative TLC. Complex **10** was identified by a single-crystal X-ray structure determination and has been reported as one of the products obtained from Ru₃(CO)₁₂ and ethene (30 bar, 150 °C).¹³ The formation of **10** can be seen to occur by transfer of the cluster-bound H atoms to the coordinated ethyne in **9** with concomitant addition of an Ru(CO)₃ group (Scheme 1).

Molecular structures of complexes **1**, **2**, **4**, **5** and **7**

Plots of the various molecules are given in Figs. 1–5, while significant bond parameters are collected in Tables 1 and 2. The structures of **1**, **2** and **4** hold no surprises and are closely related to those determined for several other similar complexes. However, they are of particular interest as being the prototypical compounds of their type.

Ru₃(μ₃-C₂H₂)(μ-CO)(CO), **1.** The three Ru atoms form an approximate isosceles triangle [Ru–Ru, 2.721(1), 2.755(1), 2.843(1) Å], the longest bond being that bridged by the C₂H₂ ligand and by CO(14). These values are considerably shorter than the average Ru–Ru separation in Ru₃(CO)₁₂ (2.854 Å).¹⁵ The ethyne ligand is attached by two σ bonds to Ru(1) and Ru(2) [Ru(1)–C(1) 2.122(7), Ru(2)–C(2) 2.054(7) Å] and a π-

type interaction of the C₂ unit with Ru(3) [Ru(3)–C(1,2) 2.213(7), 2.246(7) Å]. The C(1)–C(2) separation is 1.41(1) Å, being lengthened by coordination to the cluster, and the hydrogens are directed away from the metal cluster. The C(1)–C(2) and Ru(1)–Ru(2) vectors are only quasi-parallel, with a deviation of 3.9°, presumably conforming with the more general molecular distortion (see below).

The Ru(1)–Ru(2) vector is asymmetrically bridged by CO(14) [Ru(1,2)–C(14) 2.021(8), 2.380(9) Å; Ru(1,2)–C(14)–O(14) 149.2(7), 130.7(6)°]. The Ru(1,2)–CO(ax) bonds [1.962(8), 1.955(8) Å] are longer than the corresponding Ru(1,2)–CO(eq) bonds [1.89(1)–1.92(1) Å], while the three CO groups on Ru(3) are between 1.885(9) and 1.925(8) Å away from the metal. The Ru–C–O moieties are approximately linear [175.3(8)–178.4(9)°] with the exception of Ru(1)–C(11)–O(11) [168.1(9)°]; the reason for this anomaly is not clear.

Interestingly, the molecule is not symmetrical, the asymmetry in the attachment of CO(14) to Ru(1) and Ru(2) being reflected in the Ru(1,2)–Ru(3) separations and in the interaction of the C₂H₂ ligand with the cluster. More back bonding from Ru(1) to C(14) results in a weaker bond from this ruthenium atom to C(1); there is a smaller effect on the Ru(3)–C(1,2) separations. Similar structural features have been observed in a number of analogous triosmium cluster complexes¹⁶ and may be the result of the solid state structure being the lowest energy conformation (perhaps also including intermolecular interactions) of a fluxional complex in which the alkyne is rapidly rotating, with

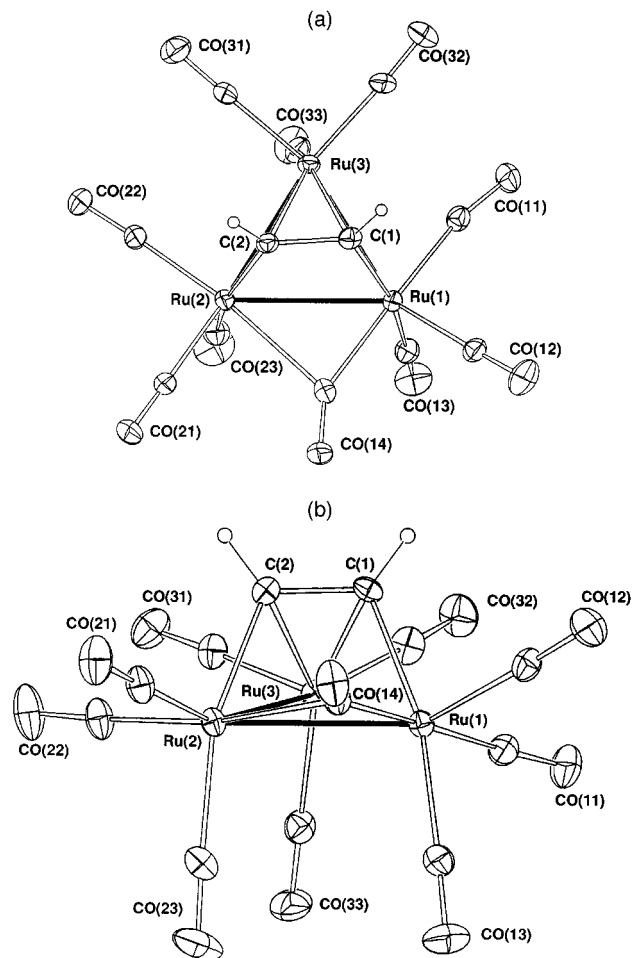


Fig. 1 Projections of $\text{Ru}_3(\mu_3\text{-C}_2\text{H}_2)(\mu\text{-CO})(\text{CO})_9$ **1**, (a) normal to, and (b) 'through' the Ru_3 plane, showing atom numbering scheme. In this and subsequent Figs., 20% thermal ellipsoids are shown for the non-hydrogen atoms, hydrogen atoms having arbitrary radii of 0.1 Å.

concomitant exchange of terminal and bridging CO ligands around the Ru_3 triangle.^{8,17} Alternatively, the observed asymmetry may result from superpositioning of the alkyne ligand on the more general distortion found for substituted $\text{Ru}_3(\text{CO})_{12}$ systems.

$\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_2\text{H})(\text{CO})_9$ **2.** Two pseudo-symmetrically related molecules comprise the asymmetric unit of this structure. Values for the two independent molecules are given. Conversion of **1** to **2** results in a 90° rotation of the C(1)–C(2) vectors with respect to the Ru(1)–Ru(2) bonds, with which they are now perpendicular ($89.5, 89.9^\circ$). These bonds are also bridged by the H atoms and are 2.792, 2.790(1) Å, some 0.013–0.025 Å shorter than the other two Ru–Ru separations. The average Ru–Ru separation increases from 2.773 Å in **1** to 2.803 Å in **2**, consistent with the change from a 4-e donor (alkyne) to a 6-e donor (alkynyl + H) and with loss of one (more strongly π acidic) CO ligand. All CO ligands are terminal, with angles subtended at each Ru atom by the three CO groups attached to it ranging between 91.7 and 101.8° (average 95.2°).

The ethynyl ligands are attached by pairs of π -type interactions with Ru(1) and Ru(2) [Ru(1,2)–C(1,2) 2.213(6)–2.235(7) Å] and by short σ bonds from C(2) to Ru(3) [1.942(8), 1.935(8) Å]. The C(1)–C(2) separations are 1.28(1), 1.31(1) Å and the angles Ru(3)–C(2)–C(1) and C(2)–C(1)–H(1) are $151.9(5), 151.7(5)$ and $142(4), 151(4)^\circ$, respectively. Both Ru_3 clusters are electron-precise 48-e systems. The asymmetry found in each structure relative to those found in **1** is minor.

$\text{Ru}_4(\mu_4\text{-C}_2\text{H}_2)(\text{CO})_{12}$ **4.** The molecule has a two-fold axis

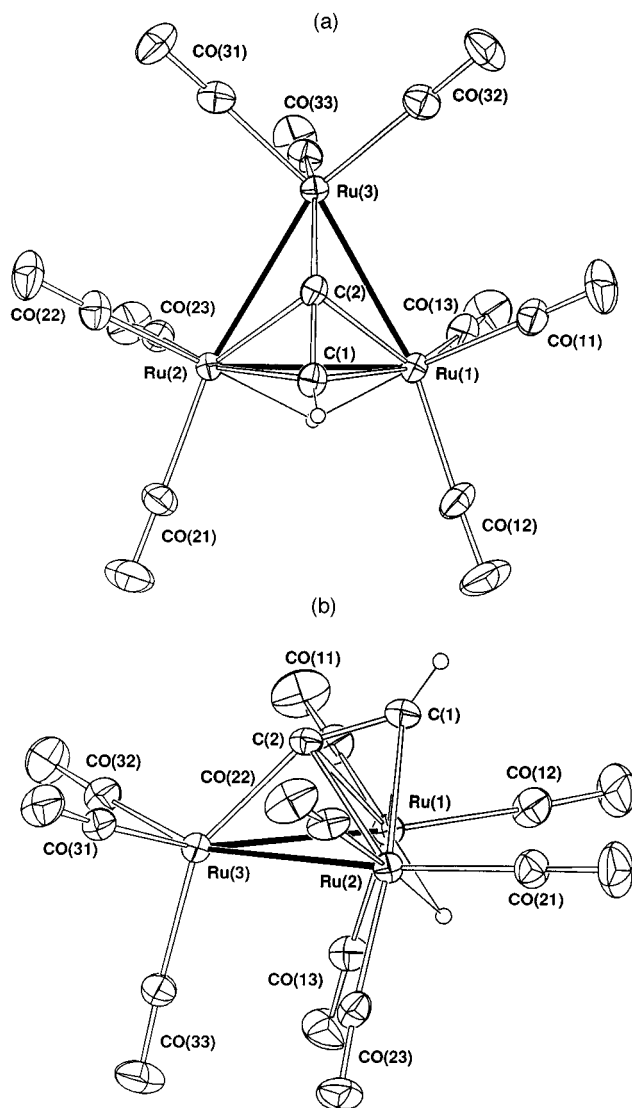


Fig. 2 Projections of $\text{Ru}_3(\mu\text{-H})(\mu_3\text{-C}_2\text{H})(\text{CO})_9$ **2** (molecule **1**), (a) normal to, and (b) 'through' the Ru_3 plane, showing atom numbering scheme.

within the distorted C_2Ru_4 octahedron as found for previous examples of complexes of this type.^{1,2} Some comparative data for the dimethyl complex **10**¹³ are given in Table 1. The four Ru atoms form a butterfly with the hinge bond [2.7946(8) Å] being significantly longer than the other four Ru–Ru bonds [Ru–Ru 2.725–2.769(3) Å]. The C_2H_2 ligand fills the cleft formed by the butterfly wings, the Ru–C bonds falling into two types, those involving the wing-tip Ru atoms [2.176(5)–2.188(7) Å] and the shorter bonds to the hinge Ru atoms [2.118(7) Å]. The internal dihedral between the two Ru_3 faces is $69.5(2)^\circ$ and that between the two C_2Ru faces is $37.7(2)^\circ$. The C(1)–C(2) separation is 1.472(9) Å, the considerable lengthening being the result of incorporation of all π electrons of the alkyne within the cluster framework.

The CO ligands (three to each Ru atom) are disposed so that the wing-tip Ru(2)(CO)₃ groups are quasi-staggered. A similar feature is found for the Ru(1)(CO)₃ moieties. The average Ru–CO separation is 1.905 Å [range 1.889(8)–1.926(7) Å]. The cluster has 60 cluster valence electrons (c.v.e.) and is best considered as a *closo*- C_2Ru_4 octahedron, rather than as an Ru_4 butterfly containing a 6-e alkyne ligand, for which a c.v.e. count of 62 is expected.

Comparison with the structure of **10**, previously described¹³ shows that the Ru–Ru bonds are considerably lengthened in **10**, the hinge bond being 2.878(2) Å and the other Ru–Ru separations being 2.709, 2.724(2) Å. The Ru(1,2)–C(1) distances are

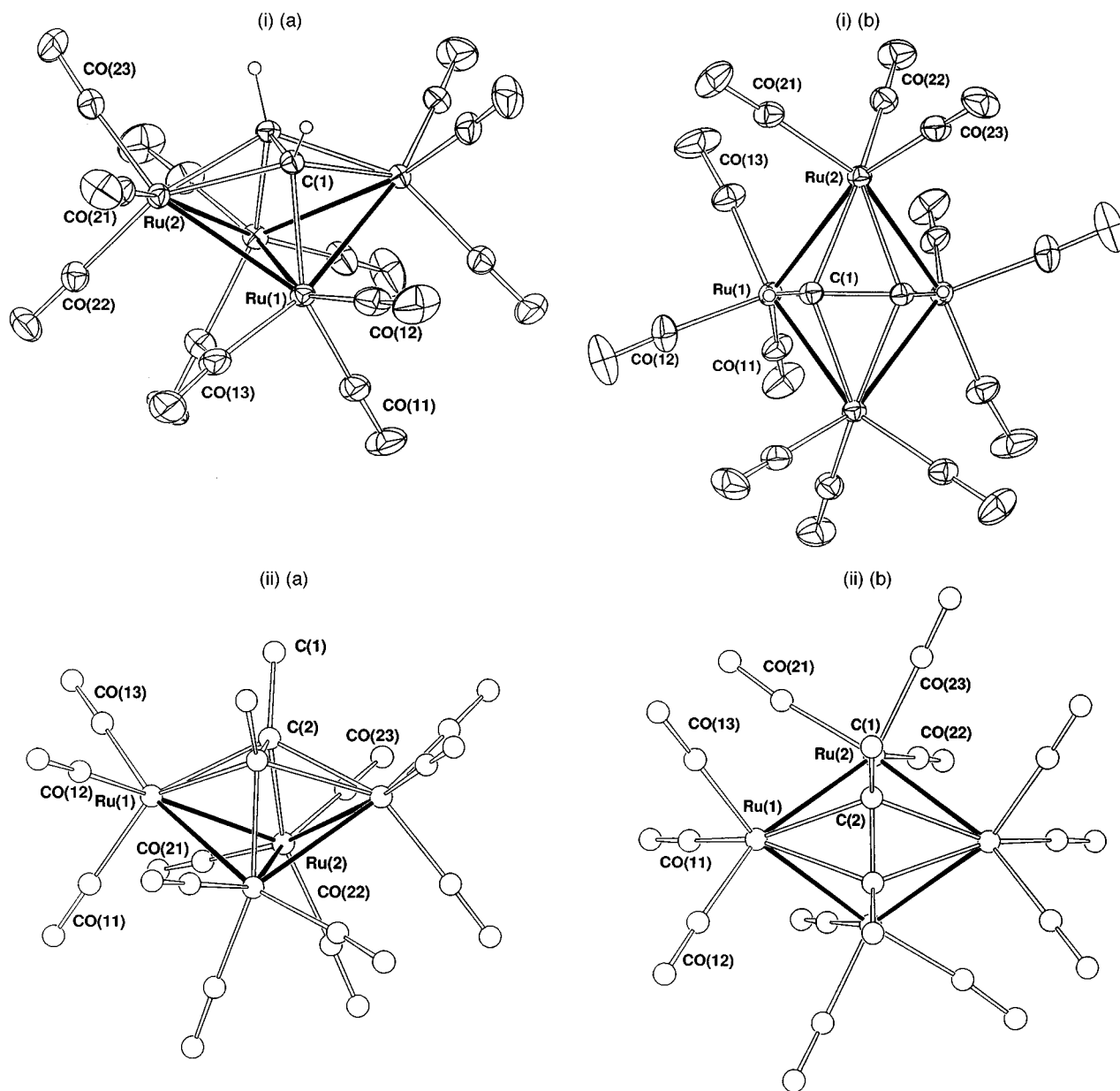


Fig. 3 Projections of (i) $\text{Ru}_4(\mu_4\text{-C}_2\text{H}_2)(\text{CO})_{12}$ **4** and (ii) $\text{Ru}_4(\mu_4\text{-C}_2\text{Me}_2)(\text{CO})_{12}$ **10** (from ref. 13), (a) normal to the C(1)–Ru(1) vector, and (b) normal to the C(1)–C(1') vector, showing atom numbering scheme.

2.13(1), 2.21(1) Å and the C(1)–C(2) separation is 1.43(1) Å. These changes are consistent with the more strongly electron-donating character of the methyl groups as substituents on the C_2Ru_4 cluster.

$\text{Ru}_5(\mu_4\text{-CCH}_2)(\text{CO})_{15}$ **5.** The Ru_5 core in **5** is an edge-bridged tetrahedron, the butterfly portion holding a vinylidene ligand which is attached to four of the five rutheniums by both carbons. The bridging Ru atom is 2.273(1) Å below the Ru_3 plane, with the Ru(1,2,3)/Ru(1,3,4) dihedral angle being 12.89(4)°. The Ru–Ru bonds range from 2.753(1) to 2.8321(9) Å, the shortest being the Ru-bridged edge of the tetrahedron. We note that Ru(4) is unique, not being attached to the CCH_2 ligand; the longest Ru–Ru bonds are between this atom and Ru(1,3). The Ru–CO interactions are longest for the CO groups below the Ru_4 rhombus [1.917(9)–1.966(9) Å], which are on average some 0.039 Å longer than the other Ru–CO bonds. The metal connectivity of the various Ru atoms ranges from 2 to 4.

The vinylidene ligand is attached *via* atom C(1) to three Ru atoms of a tetrahedral face [Ru–C 2.072(7)–2.119(7) Å] and by an asymmetric η^2 interaction of C(1)–C(2) with Ru(2) [Ru(2)–

C(1,2) 2.305(7), 2.187(9) Å]. The two H atoms were located in the refinement and the CH_2 plane is inclined to the Ru(1,2,3) plane; there is a plane of symmetry passing through atoms Ru(2,4,5)C(1,2), rendering them chemically equivalent. The C(1)–C(2) distance of 1.44(1) Å is consistent with a π -bonded C=C double bond and is considerably shorter than that found in the related complex $\text{Os}_5(\mu_4\text{-CCHPh})(\text{CO})_{15}$ [1.51(3) Å].¹⁸

$\text{Ru}_6(\mu_4\text{-CCH}_2)_2(\text{CO})_{16}$ **7.** There is a centre of symmetry within this molecule. The cluster core here comprises two edge-sharing butterflies with overall 2 symmetry. Each butterfly contains a $\mu_4\text{-CCH}_2$ ligand, as found in **5** above. The geometrical parameters of the vinylidene ligands are similar to those found for **5**, with Ru–C(1) bonds 2.069(7), 2.124(7) and 2.139(6) Å; the Ru(1)–C(1,2) interaction [2.222(8), 2.181(6) Å] is much stronger and more symmetrical than that found in **5**. The bridging Ru atom is 1.014(2) Å below the Ru_3 plane, with the Ru(1,2,3)/Ru(1',2',3') dihedral angle being 86.36(4)°.

The cluster framework found in **7** is unprecedented. The Ru(2)–Ru(2') separation, *i.e.* the bond shared by both butterflies, is short enough at 2.686(1) Å to be considered as an Ru=Ru double bond [*cf.* the Ru–Ru separation of 2.854 Å in

Table 2 Selected bond lengths (Å), bond angles (°) and dihedral angles (°) for complexes **5** and **7**

	5	7
Ru(1)–Ru(2)	2.8198(9)	2.756(1)
Ru(1)–Ru(3)	2.778(1)	2.838(1)
Ru(1)–Ru(4)	2.8229(8)	
Ru(1)–Ru(5)	2.816(1)	
Ru(2)–Ru(2')		2.686(1)
Ru(2)–Ru(3)	2.8307(9)	2.943(1)
Ru(2)–Ru(3')		2.712(1)
Ru(3)···Ru(3')		3.246(1)
Ru(3)–Ru(4)	2.8321(9)	
Ru(3)–Ru(5)	2.8136(8)	
Ru(4)–Ru(5)	2.753(1)	
Ru(1)–C(1)	2.072(7)	2.181(6)
Ru(1)–C(2)		2.222(8)
Ru(2)–C(1)	2.305(7)	2.069(7)
Ru(2)–C(1')		2.139(6)
Ru(2)–C(2)	2.187(9)	
Ru(3)–C(1)	2.093(7)	2.124(7)
Ru(5)–C(1)	2.119(7)	
C(1)–C(2)	1.44(1)	1.39(1)
Ru(<i>n</i>)–CO(<i>n</i> 1, <i>n</i> 2)	1.873(9)–1.927(9)	1.887–1.933(9) ^a
average	1.897	1.905
Ru(<i>n</i>)–CO(<i>n</i> 3) (<i>n</i> = 1–4)	1.917(8)–1.966(9)	
average	1.936	
C–O	1.12(1)–1.14(1)	1.12–1.16(1)
average	1.13	1.13
Ru(1)–C(1)–C(2)	127.7(6)	
Ru(2)–C(1)–C(2)		127.1(6)
Ru(3)–C(1)–C(2)	125.8(6)	130.4(6)
Ru(5)–C(1)–C(2)	134.5(6)	
Ru(1,2,3)/Ru(1,3,4)	12.89(4)	
Ru(1,2,3)/Ru(1,3,5)	55.31(4)	
Ru(1,2,3)/Ru(2,2',3)		50.37(4)
Ru(1,2,3)/Ru(2,2',3')		81.95(4)
Ru(1,2,3)/Ru(1',2',3')		86.36(4)
Ru(2,2',3)/Ru(2,2',3')		46.35(5)

^a All Ru–CO except Ru(2)–C(2) 1.832(9) Å.

Ru₃(CO)₁₂].¹⁵ Conversely, the Ru(3)···Ru(3') vector [3.246(1) Å] is too long for there to be any significant bonding interaction. Electron counts on individual ruthenium atoms are precise and the cluster as a whole is an 88 e.v.e. system.

Complexes **1** and **2** are the parent compounds for a wide range of analogues derived from various mono- (for **1** and **2**) and di-substituted alkynes (for **1**).^{1,2} As such, their structural parameters do not differ significantly from other structurally characterised examples. Preliminary theoretical studies¹⁹ have shown that two high-lying MOs with significant s character are associated with the H atoms and probably align one H for transfer from the alkyne to the cluster during the formation of **2**. This process likely occurs in concert with movement of the μ-CO ligand to the adjacent Ru atom, following which loss of CO from the six-coordinate Ru atom enables the H atom to adopt a bridging position. Thus, as noted before, there is a ready conversion of the 1-alkyne to (alkynyl + H) mediated by the Ru₃ cluster.

Complex **4** is similarly the prototype of many related compounds. The first of these was obtained from C₂Ph₂²⁰ and its molecular structure was described in 1977.²¹ Formal addition of an Ru(CO)₃ fragment to **2** to give **4** is accompanied by reversion of the H atom from the cluster to the alkynyl group to reform the alkyne. Alternatively, the formation of **4** can be considered to be a replacement of the μ-CO ligand in **1** by the isolobal Ru(CO)₃ fragment [*cf.* the relationship between Fe₂(CO)₉ and Fe₃(CO)₁₂, for example]. We conclude that the alkyne is stabilised by the Ru₄ cluster as a result of the further interaction of the π system with the fourth Ru atom.

The C₂H₂ fragment in **5** adopts the tautomeric vinylidene formulation, being accommodated within the cleft formed by

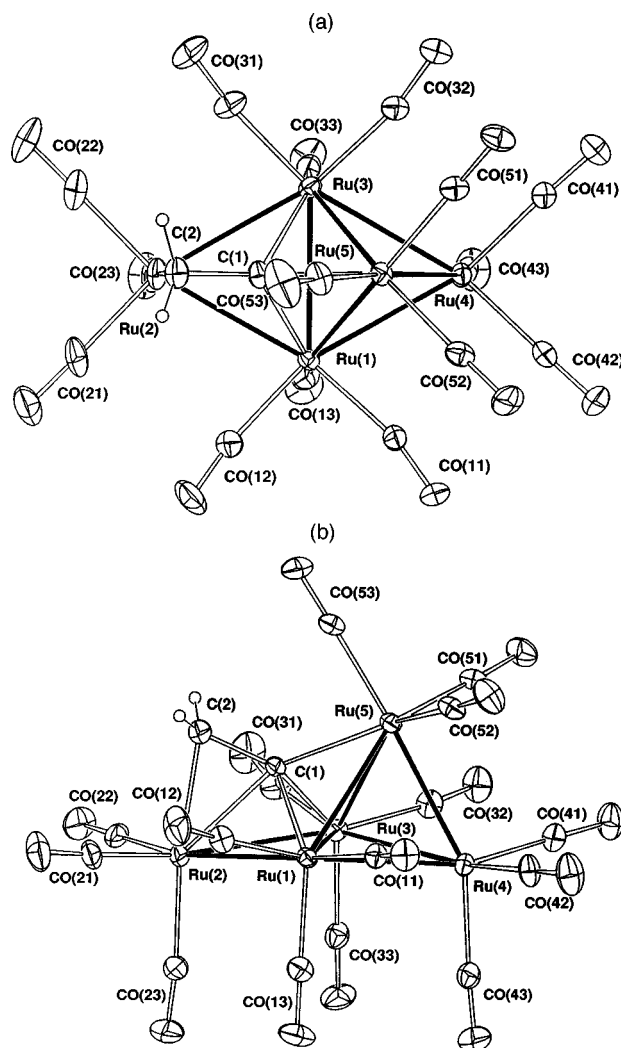


Fig. 4 Projections of Ru₅(μ₄-CCH₂)(CO)₁₅ **5**, (a) normal to, and (b) oblique to the Ru₄ plane, showing atom numbering scheme.

the fifth Ru atom bridging an edge of an Ru₄ tetrahedron. The pentagonal bipyramidal C₂Ru₅ structure (incorporating the HCCH tautomer of the alkyne) is not found. Similar edge-bridged tetrahedral cores have been found in Ru₅(μ₄-η²-CNMe₂)₂{μ-C(NMe₂)}(CO)₁₃ and Ru₅(μ-H)(μ₄-η²-CNMe₂)(CO)_{12-n}(PMe₂Ph)_n (*n* = 0, 2)²² and in Ru₆(μ₄-η²-CO)₂(CO)₁₃-(η⁶-arene) (arene = C₆H₃Me₃,²³ C₆Me₆,²⁴) and Ru₆(μ-H)(μ₄-η²-CO)₂(μ-CO)(CO)₁₂(η-C₅R₅) (C₅R₅ = C₅H₅,²⁵ C₅H₄Me,²⁶ C₅Me₅²⁶), supporting μ₄-L (L = aminocarbonyl or carbonyl) ligands, respectively.

The Ru₆ cluster in **7** has a surprising and unprecedented structure. Following **5**, one might have expected the Ru₆ core to adopt the doubly edge-bridged tetrahedral structure. This core has several precedents, especially notable being those containing μ₄-η²-CO ligands, which are isoelectronic with the μ₄-η²-CCH₂ ligands found in **5** and **7**. However, in **7**, while the cluster has a formal resemblance to a doubly-bridged tetrahedron, the “bridged” edges differ significantly from those found in the μ₄-CO complexes mentioned above, where two edges of the same face are bridged. In **7**, one edge of each of two opposite faces is bridged. Concomitantly, formal electron transfer from one edge to that opposite results in cleavage of the former and formation of an Ru=Ru double bond in the latter.

We have noted above that bridging an Ru–Ru vector with a C–C ligand in the ⊥ mode results in considerable shortening, even when a μ-H ligand is also present, so that when two such ligands are present, as in **7**, an enhanced effect is found [*cf.* **2**, Ru(1)–Ru(2) 2.790(1); **5**, Ru(1)–Ru(3) 2.778(1); **7**, Ru(2)–Ru(2') 2.686(1) Å]. Evidently, these ligands act as conduits to feed

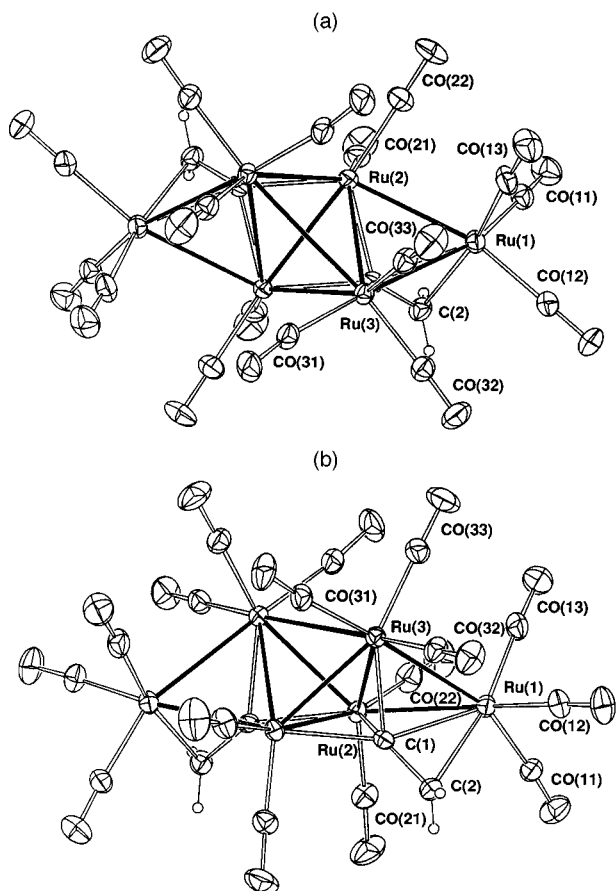


Fig. 5 Projections of $\text{Ru}_6(\mu_4\text{-CCH}_2)_2(\text{CO})_{16}$ **7**, (a) normal to, and (b) oblique to one of the Ru_4 planes, showing atom numbering scheme.

electron density into the bridged bond; in **7**, a consequent effect is the lengthening of the $\text{Ru}(3)\text{-Ru}(3')$ vector.

Conclusions

This study has confirmed the formation of the $\mu_3\text{-C}_2\text{H}_2$ complex **1** from ethyne and $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ and its extreme tendency to give **2** via a hydrogen-shift from the coordinated alkyne to the cluster with concomitant loss of a CO molecule. While this transformation occurs at temperatures little higher than ambient, harsher but nevertheless still mild conditions result in further transformations of the hydrido-ethynyl cluster to higher nuclearity products, two of which have been isolated from the preparation of **1**. Formation of **4** results from trapping of an $\text{Ru}(\text{CO})_3$ group with rearrangement back to the alkyne. In contrast, when two $\text{Ru}(\text{CO})_3$ groups are added to form the Ru_5 cluster in **5**, the cluster-bonded H atom migrates to the CH group to give the well-known vinylidene ligand. Formation of **7** represents a dimerisation of the original Ru_3 cluster with similar H migration reactions and loss of two CO groups.

As previously described,¹⁴ coupling of two ethyne molecules and rearrangement results in the C_4 ligand found in **6**; cluster enlargement has also occurred. While coupling of two alkynes to give $2\eta^1:\eta^4\text{-C}_4$ ligands is a common reaction on Ru_3 clusters,^{1,2,27} the H rearrangements observed here are unusual. The hydride, carbide, and methyl acetylidene ligands residing in the open Ru_6 core of **8** result from disproportionation of two molecules of ethyne. The latter may be related to the formation of a minor product obtained from $\text{Ru}_6\text{C}(\text{CO})_{17}$ and $\text{HC}\equiv\text{CPh}$, namely $\text{Ru}_6\text{C}(\mu_3\text{-CPh})(\mu\text{-CO})(\text{CO})_{12}(\eta\text{-C}_5\text{H}_3\text{Ph}_2\text{-1,3})$, formation of which involves cleavage of a $\text{C}\equiv\text{C}$ triple bond in one molecule of alkyne, with incorporation of the CH group by coupling with two molecules of $\text{HC}\equiv\text{CPh}$ to form the C_5 ligand.²⁸ The CPh group remaining is face-bonded to the Ru_6C

cluster. Similar reactions whereby the $\text{C}\equiv\text{C}$ triple bonds in alkynes are cleaved on $\{\text{CoCp}\}_3$ clusters have been described and considered theoretically.²⁹ In this case, however, dehydrogenation of the resulting $\mu_3\text{-CH}$ group to carbide with H migration to the cluster provides some novelty.

As in many complexes of this type, where the overall globularity of the species is maintained, we find this reflected fairly generally in the crystal packings, perhaps best exemplified in the close-packed layers of **5**.

Experimental

General reaction conditions

Reactions were carried out under an atmosphere of nitrogen; solvents were distilled under nitrogen before use. Elemental microanalyses were determined by Canadian Microanalytical Company, Delta, BC, Canada.

Instrumentation

IR: Perkin-Elmer 1700X FT IR. NMR: Bruker CXP300 or ACP300 (^1H NMR at 300.13 MHz, ^{13}C NMR at 75.47 MHz). FAB MS: VG ZAB 2HF (using 3-nitrobenzyl alcohol as matrix, exciting gas Ar, FAB gun voltage 7.5 kV, current 1 mA, accelerating potential 7 kV).

Starting materials

Ethyne (BOC Ltd) was purified by passing through concentrated H_2SO_4 , water and drying through a tower of CaCl_2 . $\text{Ru}_3(\text{CO})_{12}$ was prepared according to ref. 30.

Reaction of ethyne with $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$

The pale yellow solution of $\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2$ [prepared from $\text{Ru}_3(\text{CO})_{12}$ (200 mg, 0.312 mmol) as described in ref. 31] was concentrated under vacuum to ca. 10 ml and CH_2Cl_2 saturated with ethyne (2 ml) was added at r.t. The solution immediately became red. After passing ethyne through the mixture for 5 min, solvent was removed *in vacuo* and the residue was separated by preparative TLC (silica gel, hexane-benzene 4:1) into three bands and a baseline (which was not further investigated).

Band 1 (orange, R_f 0.64) afforded $\text{Ru}_3(\mu_3\text{-C}_2\text{H}_2)(\mu\text{-CO})(\text{CO})_9$ **1** (78 mg, 41%) as orange crystals (from $\text{CH}_2\text{Cl}_2\text{-MeOH}$), mp 93 °C. IR (cyclohexane): $\nu(\text{CO})$ 2099w, 2062vs, 2054vs, 2031vs, 2012m, 1991 (sh), 1885w (br) cm^{-1} . ^1H NMR (CDCl_3): δ 8.60 (s, 2H) [lit.⁸ values: $\nu(\text{CO})$ 2099m, 2061vs, 2055vs, 2031s, 2012m, 1988w, 1885m (br) cm^{-1} . ^1H NMR: δ 8.59s]. FAB mass spectrum: m/z 610, $[\text{M} - \text{H}]^+ \equiv [\text{M}]^+$; 582–386, $[\text{M}' - n\text{CO}]^+$ ($n = 1\text{--}8$); most intense peak is $[\text{M}' - 2\text{CO}]^+$.

Band 2 (red, R_f 0.56) contained $\text{Ru}_5(\mu_4\text{-CCH}_2)(\text{CO})_{15}$ **5** (2.7 mg, 1.5%), red crystals (from C_6H_6). IR (cyclohexane): $\nu(\text{CO})$ 2098w, 2081 (sh), 2069vs, 2046s, 2037s, 2014m, 1975w (br) cm^{-1} . ^1H NMR (CDCl_3): δ 4.23 (s, 2H, CH_2). FAB mass spectrum: m/z 952, M^+ ; 924–812, $[\text{M} - n\text{CO}]^+$ ($n = 1\text{--}5$); 793, $[\text{M} - 5\text{CO} - \text{O}]^+$; 765–603, $[\text{M} - n\text{CO} - \text{O}]^+$ ($n = 6\text{--}12$).

From band 3 (R_f 0.46) was obtained $\text{Ru}_4(\mu_4\text{-C}_2\text{H}_2)(\text{CO})_{12}$ **4** (11.3 mg, 7%) as dark red crystals, mp 191–193 °C (decomp.) (Found: C, 22.29; H, 0.32. $\text{C}_{14}\text{H}_2\text{O}_{12}\text{Ru}_4$ calc.: C, 21.94; H, 0.26%). IR (cyclohexane): $\nu(\text{CO})$ 2098w, 2070s, 2045s, 2037vs, 2019m, 2011m, 1990w (br), 1977w (br) cm^{-1} . ^1H NMR (CDCl_3): δ 10.01 (s, 2H). FAB mass spectrum: m/z 766, $[\text{M} - 2\text{H}]^+$; 738–570, $[\text{M} - 2\text{H} - n\text{CO}]^+$ ($n = 1\text{--}7$); strongest peak is $n = 1$.

Thermolysis of $\text{Ru}_3(\mu_3\text{-C}_2\text{H}_2)(\mu\text{-CO})(\text{CO})_9$ **1**

A solution of **1** (160 mg, 0.26 mmol) in hexane (50 ml) was stirred at 50 °C until TLC showed that no starting complex remained (3 h). After cooling, the solvent was removed and a CH_2Cl_2 extract of the residue was separated by preparative

Table 3 Crystal data and refinement details for complexes **1**, **2**, **4**, **5** and **7**

Compound	1	2	4	5	7
Formula	C ₁₂ H ₂ O ₁₀ Ru ₃ 609.4	C ₁₁ H ₂ O ₉ Ru ₃ 581.3	C ₁₄ H ₂ O ₁₂ Ru ₄ 766.5	C ₁₇ H ₂ O ₁₅ Ru ₅ 951.6	C ₂₀ H ₄ O ₁₆ Ru ₆ ·CH ₂ Cl ₂ 1191.6
Crystal system	Monoclinic	Monoclinic		Orthorhombic	
Space group	<i>P</i> 2 ₁ (no. 4)	<i>P</i> 2 ₁ / <i>c</i> (no. 14)		<i>Pbca</i> (no. 61)	<i>P</i> 4 ₁ 2 ₁ 2 ^a (no. 92)
<i>a</i> /Å	9.605(1)	13.099(4)	9.558(1)	21.312(2)	9.470(5)
<i>b</i> /Å	9.516(3)	15.619(4)	19.203(3)	15.290(6)	
<i>c</i> /Å	9.189(3)	16.345(4)		14.8226(9)	35.094(8)
β/°	100.93(2)	105.86(2)			
<i>V</i> /Å ³	824.7	3217	1519.7	4830	3150
<i>Z</i>	2	4	3	8	4
<i>D</i> _c /g cm ⁻³	2.45	2.40	2.51	2.62	2.52
<i>F</i> (000)	572	2176	1074	3552	2232
Crystal size/mm	0.17 × 0.27 × 0.05	0.18 × 0.24 × 0.10	0.18 × 0.21 × 0.40	0.34 × 0.12 × 0.12	0.16 × 0.20 × 0.32
μ/cm ⁻¹	27.6	28.2	29.8	31.3	30.5
<i>A</i> * (min, max)	1.14, 1.49	1.37, 1.59	1.28, 1.34	1.38, 1.50	1.57, 1.81
2θ _{max} /°	60	55	60	55	60
<i>N</i>	2533	7376	1526	4236	2747
<i>N</i> _o	2097	4552	1360	2983	1986
<i>R</i>	0.030	0.037	0.021	0.031	0.033
<i>R</i> _w	0.029	0.036	0.019	0.031	0.029

^a The two possible chiralities/space groups were indistinguishable.

TLC (silica gel, hexane–benzene 4:1) into six bands and a baseline, from which nothing tractable was isolated.

Band 1 (*R*_f 0.80) contained Ru₃(CO)₁₂ (21.2 mg, 12.5%), identified from its IR ν(CO) spectrum.

Band 2 (yellow, *R*_f 0.76) afforded Ru₃(μ-H)(μ₃-C₂H)(CO)₉ **2** (77.8 mg, 51%) as pale yellow crystals from benzene. IR (cyclohexane): ν(CO) 2101w, 2084 (sh), 2074s, 2056s, 2025vs, 1999 (sh), 1993m cm⁻¹. ¹H NMR (CDCl₃): δ -21.22 (s, 1H, RuH), 5.45 (s, 1H, ≡CH) [lit.⁸ values: ν(CO) 2095m, 2066vs, 2051vs, 2022vs, 2018s, 1990m cm⁻¹; ¹H NMR: δ -19.48 (s), 10.64 (s)]. FAB mass spectrum: *m/z* 582, [M - H]⁺; 554, [M - H - CO]⁺; 526, [M - H - 2CO]⁺; 498, [M - H - 3CO]⁺.

Band 3 (*R*_f 0.61) contained Ru₅(μ₄-CCH₂)(CO)₁₅ **5** (5.6 mg, 2.4%), identified as above.

Very dark red crystals of Ru₆(μ₄-CCH₂)₂(CO)₁₆ **7** (3 mg, 1%) were isolated from band 4 (*R*_f 0.52). IR (cyclohexane): ν(CO) 2098w, 2077s, 2060s, 2046vs, 2035s, 2020m, 2009w, 1999w, 1981vw, 1973vw, 1961vw cm⁻¹. ¹H NMR (CDCl₃): δ 4.34, 4.48 (AB quartet, 2 × d, 2 × 1H, *J*(HH) = 5 Hz, CH₂). FAB mass spectrum: *m/z* 1079, [M - CO]⁺; 1051–883, [M - *n*CO]⁺ (*n* = 2–7).

Bands 5 (*R*_f 0.25) and 6 (*R*_f 0.19) afforded respectively dark red crystals of Ru₆(μ-H)(μ₄-C)(μ₄-CCMe)(μ-CO)(CO)₁₆ **8** (12 mg, 8%) and orange crystals of Ru₅(μ₅-CHCHCCH₂)(CO)₁₅ **6** (16 mg, 6.2%).¹⁴

Thermolysis of **9**

A solution of **9** (50 mg, 0.09 mmol) in hexane (10 ml) was heated at reflux point overnight. Solvent was removed from the black reaction mixture and a CH₂Cl₂ extract of the residue was purified by TLC. Two bands developed: band 1 (*R*_f 0.63) contained Ru₃(CO)₁₂ (1.9 mg, 4%), identified from its IR ν(CO) spectrum. Band 2 (*R*_f 0.58) afforded Ru₄(μ₄-C₂Me₂)(CO)₁₂ **10** (2.6 mg, 5%) as very dark red crystals from C₆H₆–hexane. IR (cyclohexane): ν(CO) 2093w, 2065s, 2037vs, 2015m, 2004m, 1973w (br) cm⁻¹. ¹H NMR (CDCl₃): δ 3.21 (s, Me) [lit.¹³ values: ν(CO) (CHCl₃) 2090w, 2064s, 2036 (sh), 2032vs, 2004m (br) cm⁻¹; δ(¹H) 3.19].

Crystallography

Unique data sets were measured at ca. 295 K within the specified 2θ_{max} limits using an Enraf-Nonius CAD4 diffractometer (2θ/θ scan mode; monochromatic Mo-Kα radiation, λ 0.71073 Å); *N* independent reflections were obtained, *N*_o with *I* > 3σ(*I*) being considered 'observed' and used in the full

matrix least squares refinements after gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (*x*, *y*, *z*, *U*_{iso})_H were refined. Conventional residuals *R*, *R'* on |*F*| are quoted, statistical weights derivative of σ²(*I*) = σ²(*I*_{diff}) + 0.0004σ⁴(*I*_{diff}) being used. Computation used the XTAL 3.2 program system³² implemented by S.R. Hall; neutral atom complex scattering factors were employed. Crystal data and refinement details are given in Table 3.

Abnormal features and variations in procedure. **1** Hydrogen atom parameters were not refined, being constrained at 'improved' difference map estimates. **7** Solvent hydrogen atom parameters were estimated and constrained during refinement, site occupancy being set at unity after trial refinement.

CCDC reference number 186/1369.

See <http://www.rsc.org/suppdata/dt/1999/1445/> for crystallographic files in .cif format.

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