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# Synthesis and structural characterisation of ruthenium carbonyl clusters containing hydrocarbyl ligands derived from (hydroxy)alkynes $HC{\equiv}CC(H)(OH)CH_3$

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Five new ruthenium ketonic clusters $[Ru_4(CO)_{12}\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CH_3C(H)CCC(H)CH_2C(O)CH_3\}]$ **1** (10%), $[Ru_5(CO)_{14}(\mu\text{-}H)_2\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}]$ **2** (15%), $[Ru_6(CO)_{16}\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}_2]$ **3** (15%), $[Ru_7(CO)_{19}\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}\{\mu_5\text{-}\eta^1:\eta^1:\eta^1:\eta^1:\eta^2\text{-}CCC(H)CH_3\}]$ **4** (8%), and $[Ru_5(CO)_{12}(\mu\text{-}CO)\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}(\mu_4\text{-}\eta^2\text{-}HCCCH_2CH_3)]$ **5** (10%) have been synthesised by reaction of but-3-yn-2-ol with triruthenium dodecacarbonyl, in cyclohexane, under reflux. All the compounds have been fully characterised by spectroscopic and X-ray diffraction methods. The structure of **1** is based on a $Ru_4$ butterfly skeleton containing a fragment of $C_8$ ketonic chain which arises from the coupling of two ligand molecules with the elimination of a water molecule. An interesting feature in clusters **2**, **3**, **4** and **5** is the formation of a metallocycloketonic ring with a $\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2$ coordination mode which is derived from the activation of the C≡C triple bond. Both **2** and **5** consist of a wingtip bridged butterfly core, which is also bonded with two bridged hydrides in **2** and a $\mu_4\text{-}\eta^2$ acetylide fragment in **5** respectively. Cluster **2** is also closely related to cluster **3**, in that it seems to be a monomeric unit of **3** forming a six atom raft geometry with two metallocycloketonic rings. The metal core of **4** is similar to **3**, except that one Ru–Ru bond in **4** is broken to form two more metal–metal bonds with an additional Ru atom to give a novel $Ru_7$ core, which is best described as a distorted $Ru_4$ square plane sharing an edge with an edge-bridged butterfly. Moreover, one of the metallocycloketonic rings in **3** is replaced by an allenyl $CCC(H)CH_3$ ligand, which is coordinated to an edge-bridged butterfly in **4**.

## Introduction

The chemistry of transition metal clusters containing functionalised alkynes has received considerable attention.[1–8] Early work in acetylenic alcohols, such as $HC{\equiv}CCRR'(OH)$, where R = alkyl and R′ = aryl groups, respectively, have been shown to react with triruthenium and triosmium clusters leading to hydroxy-functionalised alkyne clusters with the general formula $[HM_3(CO)_9(\mu_3\text{-}C{\equiv}CCRR'OH)]$.[9,10] The metal atoms have a great influence on the reactivity of the hydroxy function to allow reactions occuring at the side chain, such as acid-induced dehydration to give $[HRu_3(CO)_9(\mu_3\text{-}C{\equiv}CCPh{=}CH_2)]$,[9] acid-catalysed isomerisation to give $[HOs_3(\mu\text{-}OH)(CO)_9(\mu_3\text{-}C{=}C{=}CPh_2)]$,[11] and cyclization with the formation of an oxygen-containing '$C_4O$' ring.[12,13] We report here the synthesis and structural characterization of five clusters obtained in moderate yield from the reaction of $[Ru_3(CO)_{12}]$ with but-3-yn-2-ol, $HC{\equiv}CCH(OH)CH_3$. A salient feature in this reaction is that formation of these new complexes involves extensive rearrangement of ligands, namely, dehydration,[14] hydrogen atom transfer from carbon to metal atom, C≡C triple bond activation,[15,16] C–C coupling,[17–21] and cyclization with metal atoms.[22,23]

## Results and discussion

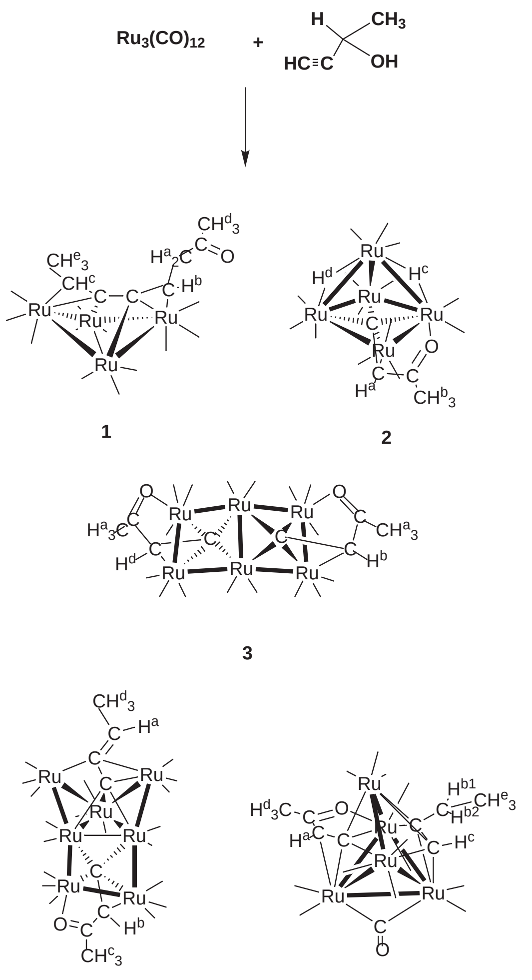
The reaction of $[Ru_3(CO)_{12}]$ with an excess of but-3-yn-2-ol in refluxing cyclohexane solution afforded five complexes, namely, $[Ru_4(CO)_{12}\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CH_3C(H)CCC(H)CH_2C(O)CH_3\}]$ **1**, $[Ru_5(CO)_{14}(\mu\text{-}H)_2\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}]$ **2**, $[Ru_6(CO)_{16}\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}_2]$ **3**, $[Ru_7(CO)_{19}\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}\{\mu_5\text{-}\eta^1:\eta^1:\eta^1:\eta^1:\eta^2\text{-}CCC(H)CH_3\}]$ **4**, and $[Ru_5(CO)_{12}(\mu\text{-}CO)\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}(\mu_4\text{-}\eta^2\text{-}HCCCH_2CH_3)]$ **5** (Scheme 1). Purification was accomplished by preparative TLC and their respective yields were 10, 15, 15, 8 and 10% [based on $Ru_3(CO)_{12}$]. Crystals of **1**–**5** suitable for X-ray determinations were obtained by slow evaporation from $CH_2Cl_2$–*n*-hexane solutions at −10 °C for 2 d. They were fully characterized by FAB mass spectrometry, IR, $^1H$ NMR and $^{13}C$ NMR spectroscopies and single-crystal X-ray diffraction techniques.

### Spectroscopic and structural characterization of 1

The positive FAB mass spectrum of **1** displays a parent molecular ion peak at *m*/*z* 862, consistent with twelve terminal carbonyl ligands and one ligated olefinic fragment. The $^1H$ NMR spectrum recorded in $CDCl_3$ under ambient conditions shows one triplet at $\delta$ 4.32 and a quartet at $\delta$ 2.71, indicative of two olefinic protons. The doublet at $\delta$ 4.29 and the singlet at $\delta$ 2.18 correspond to the methylene protons and methyl protons respectively. Moreover, the IR spectrum reveals the presence of terminal carbonyl ligands only. An X-ray diffraction analysis of **1** was undertaken and an ORTEP diagram is shown in Fig. 1 together with the atomic numbering scheme. The selected bond angles and distances are presented in Table 1. The four Ru atoms adopt a butterfly arrangement with twelve terminally bonded carbonyl ligands. The dihedral angle between the two coupled ruthenium triangles is 150.09°. The ligand capped on the butterfly framework is different to those observed in other related $Ru_4$ clusters such as $[Ru_4(CO)_{12}(MeC{=}CMe)]$,[24] $[Ru_4(CO)_{12}(\mu_4\text{-}\eta^2\text{-}HC_2Ph)]$[25] with a $\mu_4\text{-}\eta^2$ coordination mode or $[Fe_4(CO)_{12}(\mu_4\text{-}CO)]^-$, $[Ru_4H(CO)_{12}(CCPhCHPh)]$ with the interstitial carbon atom bonding in a $\mu_4$-fashion.[26,27] The two functionalized alkyne units are coupled to yield an octa-2,4-diene ketonic chain with the loss of a water molecule. The two central carbon atoms C(16) and C(15) are $\sigma$ bonded to Ru(2) [Ru(2)–C(16) 2.05(3) Å] and Ru(3) [Ru(3)–C(15) 2.04(3) Å],

**Table 1** Some selected bond lengths (Å) and angles (°) for cluster **1**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.770(3) | Ru(1)–Ru(3) | 2.895(3) |
| Ru(2)–Ru(3) | 2.848(3) | Ru(2)–Ru(4) | 2.878(3) |
| Ru(3)–Ru(4) | 2.789(3) | Ru(1)–C(16) | 2.29(3) |
| Ru(1)–C(17) | 2.35(3) | Ru(2)–C(16) | 2.05(3) |
| Ru(3)–C(15) | 2.04(3) | Ru(4)–C(14) | 2.31(3) |
| Ru(4)–C(15) | 2.29(3) | C(19)–O(13) | 1.23(3) |
| C(13)–C(14) | 1.50(4) | C(14)–C(15) | 1.40(3) |
| C(15)–C(16) | 1.40(4) | C(16)–C(17) | 1.41(4) |
| C(17)–C(18) | 1.49(4) | C(18)–C(19) | 1.53(4) |
| C(19)–C(20) | 1.47(4) | | |
| Ru(1)–Ru(2)–Ru(4) | 113.9(1) | Ru(1)–Ru(2)–Ru(3) | 62.01(8) |
| Ru(1)–Ru(3)–Ru(2) | 57.67(8) | Ru(1)–Ru(3)–Ru(4) | 112.8(1) |
| Ru(2)–Ru(3)–Ru(4) | 61.38(8) | Ru(2)–Ru(1)–Ru(3) | 60.31(8) |
| C(14)–C(15)–C(16) | 125(2) | Ru(2)–Ru(4)–Ru(3) | 60.32(8) |
| C(16)–C(17)–C(18) | 124(2) | C(15)–C(16)–C(17) | 125(2) |



**Scheme 1**

respectively. In addition, this ligand is π bonded to Ru(1) *via* C(16)–C(17) [Ru–C 2.29(3) and 2.35(3) Å] and to Ru(4) *via* C(14)–C(15) [Ru–C 2.31(3) and 2.29(3) Å]. The bonding mode of the $C_4$ ligand in **1** behaves in a same manner as that found in the $Ru_4$ square planar cluster $[Ru_4(CO)_{10}(\mu_4\text{-PPh})(\mu\text{-CO})\{\mu_4\text{-}\eta^1,\eta^1,\eta^2,\eta^2\text{-PhC(H)CCC(H)Ph}\}]$.[28] There are also other examples of clusters, such as $[Ru_4(CO)_{10}(\mu_4\text{-PPh})(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-PhC}_4\text{Ph})]$ and $[Ru_4(CO)_{10}(\mu_4\text{-PC}{\equiv}\text{CBu}^t)(\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^3{:}\eta^3\text{-Bu}^t\text{C}_4\text{Bu}^t)]$,[29] containing an unsaturated $C_4$ hydrocarbon backbone capped on a $Ru_4$ square plane in a similar bonding mode. Compound **1** has an electron count of 62 in which the ligand donates six electrons toward skeletal bonding.

**Table 2** Some selected bond lengths (Å) and angles (°) for cluster **2**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.972(1) | Ru(1)–Ru(3) | 2.829(1) |
| Ru(1)–Ru(4) | 2.874(1) | Ru(2)–Ru(4) | 2.773(1) |
| Ru(2)–Ru(5) | 3.056(1) | Ru(3)–Ru(5) | 2.866(1) |
| Ru(4)–Ru(5) | 2.825(1) | Ru(1)–O(15) | 2.125(6) |
| Ru(1)–C(15) | 2.096(9) | Ru(3)–C(16) | 2.204(9) |
| Ru(3)–C(15) | 1.088(9) | Ru(5)–C(15) | 2.143(9) |
| Ru(4)–C(15) | 2.135(9) | C(15)–C(16) | 1.47(1) |
| C(16)–C(17) | 1.44(1) | C(17)–O(15) | 1.26(1) |
| C(17)–C(18) | 1.48(1) | | |
| C(15)–C(16)–C(17) | 114.4(8) | C(16)–C(17)–C(18) | 121.5(9) |
| C(16)–C(17)–O(15) | 119.4(9) | O(15)–C(17)–C(18) | 119.1(9) |

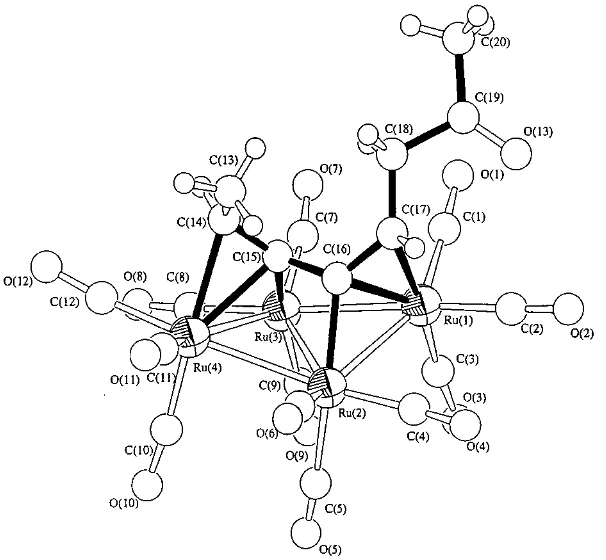


**Fig. 1** Molecular structure of $[Ru_4(CO)_{12}\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-CH}_3\text{C(H)CCC(H)CH}_2\text{C(O)CH}_3\}]$ **1** with the atom numbering scheme.

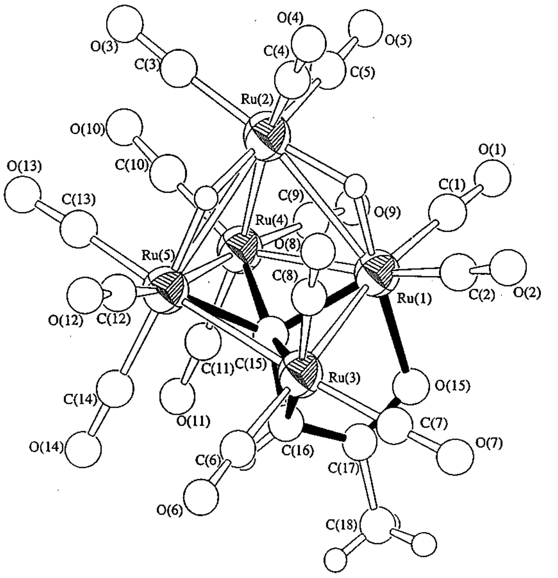


**Fig. 2** Molecular structure of $[Ru_5(CO)_{14}(\mu\text{-H})_2\{\mu_4\text{-}\eta^1{:}\eta^1{:}\eta^2{:}\eta^2\text{-CC(H)C(O)CH}_3\}]$ **2** with the atom numbering scheme.

## Spectroscopic and structural characterization of 2

The $^1H$ NMR spectrum of **2** shows two singlet signals at $\delta$ 4.52 and 2.02 with an integral ratio of 1:3 which are assigned to the alkyne proton and methyl protons respectively. Besides, there are two high field singlets at $\delta$ −21.31 and −28.45 in a ratio of 1:1 due to the presence of two bridging hydrides. The positive FAB mass spectrum exhibits a peak envelope at *m*/*z* 967,

**Table 3** Some selected bond lengths (Å) and angles (°) for cluster **3**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.780(2) | Ru(1)–Ru(3) | 2.810(2) |
| Ru(2)–Ru(4) | 2.910(2) | Ru(3)–Ru(4) | 2.656(2) |
| Ru(3)–Ru(5) | 2.820(2) | Ru(4)–Ru(6) | 2.917(2) |
| Ru(5)–Ru(6) | 2.790(2) | Ru(1)–C(17) | 2.25(2) |
| Ru(2)–C(17) | 2.14(2) | Ru(2)–C(18) | 2.20(2) |
| Ru(3)–C(17) | 2.04(2) | Ru(3)–C(21) | 2.03(2) |
| Ru(4)–C(17) | 2.11(2) | Ru(4)–C(21) | 2.10(2) |
| Ru(5)–C(21) | 2.22(2) | Ru(6)–C(21) | 2.17(2) |
| Ru(6)–C(22) | 2.22(2) | C(17)–C(18) | 1.43(2) |
| C(18)–C(19) | 1.43(2) | C(19)–O(17) | 1.24(2) |
| C(19)–C(20) | 1.48(3) | C(21)–C(22) | 1.49(2) |
| C(22)–C(23) | 1.39(2) | C(23)–O(18) | 1.22(2) |
| C(23)–C(24) | 1.51(3) | | |
| | | | |
| C(18)–C(19)–O(17) | 120(1) | C(17)–C(18)–C(19) | 115(1) |
| C(21)–C(22)–C(23) | 114(1) | C(18)–C(19)–C(20) | 121(1) |
| C(22)–C(23)–C(24) | 118(1) | C(22)–C(23)–O(18) | 123(1) |

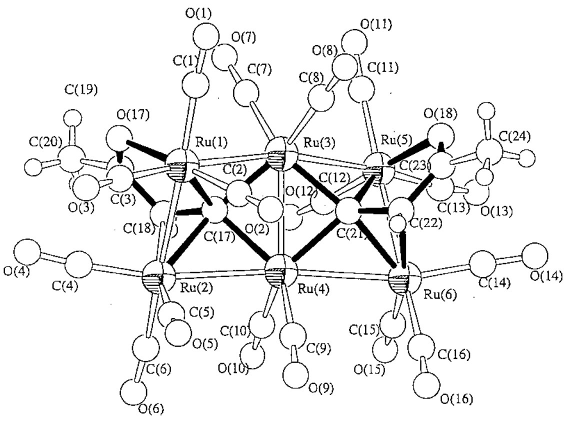


**Fig. 3** Molecular structure of $[Ru_6(CO)_{16}\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}_2]$ **3** with the atom numbering scheme.

consistent with an isotopic distribution of five Ru atoms. Furthermore, the IR spectrum reveals the presence of terminal carbonyl ligands only. The molecular structure of **2** is illustrated in Fig. 2 and some relevant bond parameters are collected in Table 2. The bond lengths of the unbridged Ru–Ru edges [average 2.83(3) Å] are found to be shorter than the hydride-bridged Ru(1)–Ru(2) and Ru(2)–Ru(5) [average 3.014(1) Å] bonds, which is a common observation in cluster chemistry.[30] The apical Ru(2) atom lies 2.33 Å above the best plane through Ru(1), Ru(3), Ru(4) and Ru(5) but is asymmetrically located with respect to the Ru(1) and Ru(5) [Ru(1)–Ru(2) 2.972(1), Ru(2)–Ru(5) 3.056(1) Å]. The alkyne ligand bonded to the cluster core adopts an unusual $\mu_4$-$\eta^1$:$\eta^1$:$\eta^2$:$\eta^2$ mode *via* the C≡C triple bond activation to form a five-membered metallocycloketonic ring involving Ru(1). The semi-interstitial carbide C(15) atom can be viewed as quadruply bridged across a distorted square base. It is however more strongly bonded to Ru(3) and Ru(4) [average Ru–C(15) 2.092 Å] than to Ru(4) and Ru(5) [average Ru–C(15) 2.139 Å], resulting in a slight displacement of this atom towards the Ru(3)–Ru(4) edge. The $^{13}$C NMR studies reveal a singlet at $\delta$ 323 which is attributed to this carbido carbon. In $[Ru_5(\mu_5\text{-}C_3PhCH)(\mu\text{-}SMe)_2(\mu\text{-}PPh_2)_2(CO)_{10}]$, a similar resonance parameter was observed for this kind of carbido atom.[31] Another interesting feature in this compound is the oxidation of the hydroxyl group of the alkyne ligand to a ketone group which is then coordinated to the Ru(1) atom. The Ru(1)–O(15) distance 2.125(6) Å is typical for the O→Ru dative bond observed in the pentanuclear clusters $[Ru_5(\mu_5\text{-}C)(CO)_{13}\{C_2H_2(CO_2Me)_2\}]$[32] and $[Ru_5(CO)_{10}(\mu\text{-}Br)(\mu\text{-}PPh_2)_2\{\mu_5\text{-}CCC(O)CH_2CH{=}CH_2\}]$.[33] A singlet at $\delta$ 224 in the $^{13}$C NMR spectrum of **2** can be assigned to this keto carbon. If the alkyne ligand in **2** contributed six electrons to cluster bonding, the total electron count for the cluster would be 76 CVE, which is consistent with a wingtip-bridged butterfly skeleton.[34–37]

## Spectroscopic and structural characterization of 3

The chromatographic separation of the reaction mixture yielded the third fraction which gave dark red crystals of **3** after recrystallization. The Ru$_6$ core geometry in **3** is best described as a twisted ladder. A perspective drawing of cluster **3** with the atomic numbering scheme is shown in Fig. 3 and some selected bond parameters are listed in Table 3. In contrast to the typical giant rhombic six-atom raft geometry with nine M–M bonds,[38–41] the metal skeleton of **3** comprises two distorted square planar units with a common edge, Ru(3)–Ru(4). The Ru–Ru bond lengths lie in the range 2.656(2)–2.917(2) Å. The Ru(3)–Ru(4) distance is significantly shorter than any of the other Ru–Ru bonds which may reflect the presence of electron unsaturation[41,42] and the steric requirements of the bridging alkyne ligands. Two alkyne ligands with a bonding mode similar to that observed in **2** were coordinated to the metal plane on the opposite side in order to minimize steric repulsion. The $^1$H NMR spectrum of **3** shows signals that are rather similar to those observed in cluster **2** since the same bridging ligands are associated with the metal core in each case. However, no hydride signal was detected for **3**. Although some examples of such rhombic geometry, $[Ru_6(CO)_{14}(\mu_2\text{-}SC_2H_5)_2\{\mu_6\text{-}C(CH_3)\text{-}CCC(CH_3)\}]$[43] and $[Os_6(CO)_{20}\{C{=}C(H)Ph\}]$,[44] containing a C$_4$ or C$_2$ alkene chain are known, structural characterization of **3** provides a rare example of hexaruthenium clusters with the two carbido-carbons quadruply bridged in a ladder plane, which may represent a particularly attractive analogue of metal surface carbides. The $^{13}$C NMR studies again reveals two singlets at $\delta$ 324 and 223 which are attributed to the carbido and keto carbons, respectively. Cluster **3** possesses 92 CVE which is two less than the expected 94 CVE unless Ru(3)–Ru(4) is considered to be a double bond. Some other six-atom raft geometries, such as $[Os_6(CO)_{20}\{C{=}C(H)Ph\}]$,[44] are known to have 92 valence electrons which are composed of four osmium triangles fused together. The structure of **3** is much more symmetrical than that of **2**. It contains a non-crystallographic two-fold rotation axis passing through Ru(3) and Ru(4).

## Spectroscopic and structural characterization of 4

Isolation by preparative TLC afforded the fourth fraction which gave slightly air-sensitive brown crystals of **4**. The $^1$H NMR spectrum of **4** is very similar to those for **2** and **3** showing the same spectral pattern in each case but with different chemical shifts. This is in accordance with the presence of a metallocycloketonic ring in these three clusters; besides, the quartet resonance at $\delta$ 4.65 and the doublet resonance at $\delta$ 1.82 correspond to the allenyl proton and methyl protons, respectively. The positive FAB spectrum exhibits a molecular ion peak at *m*/*z* 1402. A perspective drawing of **4** is depicted in Fig. 4 and selected bond parameters are given in Table 4. Complex **4** consists of an edge-bridged butterfly bonded with additional two Ru atoms *via* the Ru(3)–Ru(4) edge. The Ru–Ru distances fall into the range 2.733(4)–2.963(4) Å with the Ru(3)–Ru(4) separation being the shortest and the Ru(4)–Ru(5) vector the longest. The seven Ru atoms are ligated by two different acetylide derivatives with two different coordination modes. Like **2** and **3**, a five-membered metallocycloketonic ring bonded to four Ru [Ru(1), Ru(2), Ru(3) and Ru(4)] atoms adopts an unusual $\mu_4$-$\eta^1$:$\eta^1$:$\eta^2$:$\eta^2$ mode. The $CH_3(H)C_\gamma{=}C_\beta{=}C_\alpha$ moiety can be viewed as a allenylidene ligand[45,46] bonded to five Ru [Ru(3), Ru(4), Ru(5), Ru(6) and Ru(7)] atoms, in which the alkylated carbide atom C(24) has a strong $\sigma$-type interaction with Ru(3), Ru(4), and Ru(5) [2.09(3)–2.36(3) Å]. The C$_\beta$ atom is $\sigma$ bonded to Ru(6) [Ru(6)–C(25) 2.05(3) Å], which also forms a $\pi$ interaction to Ru(7) with C$_\alpha$ [C(24)–C(25) 1.32(4) Å]. The bond length

**Table 4** Some selected bond lengths (Å) and angles (°) for cluster **4**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.799(4) | Ru(1)–Ru(4) | 2.944(4) |
| Ru(2)–Ru(3) | 2.809(4) | Ru(3)–Ru(4) | 2.733(4) |
| Ru(3)–Ru(5) | 2.837(4) | Ru(3)–Ru(6) | 2.913(4) |
| Ru(4)–Ru(5) | 2.963(4) | Ru(4)–Ru(7) | 2.878(4) |
| Ru(5)–Ru(6) | 2.827(4) | Ru(5)–Ru(7) | 2.867(4) |
| Ru(1)–C(20) | 2.15(3) | Ru(1)–C(21) | 2.18(3) |
| Ru(2)–C(20) | 2.25(3) | Ru(2)–O(20) | 2.18(2) |
| Ru(3)–C(20) | 2.02(3) | Ru(3)–C(24) | 2.09(3) |
| Ru(4)–C(20) | 2.14(3) | Ru(4)–C(24) | 2.09(3) |
| Ru(5)–C(24) | 2.36(3) | Ru(6)–C(25) | 2.05(3) |
| Ru(7)–C(24) | 2.37(3) | Ru(7)–C(25) | 2.33(3) |
| C(24)–C(25) | 1.32(4) | C(25)–C(26) | 1.41(4) |
| Ru(6) · · · C(24) | 2.44(3) | Ru(7) · · · C(26) | 2.43(3) |
| Ru(3)–C(24)–Ru(4) | 81(1) | Ru(4)–C(24)–Ru(7) | 80(1) |
| Ru(7)–C(24)–C(25) | 72(2) | Ru(7)–C(25)–C(24) | 75(2) |
| Ru(6)–C(25)–Ru(7) | 123(1) | Ru(6)–C(25)–C(24) | 90(2) |
| C(20)–C(21)–C(22) | 115(3) | O(20)–C(22)–C(23) | 118(3) |
| C(21)–C(22)–C(23) | 120(3) | C(24)–C(25)–C(26) | 120(3) |

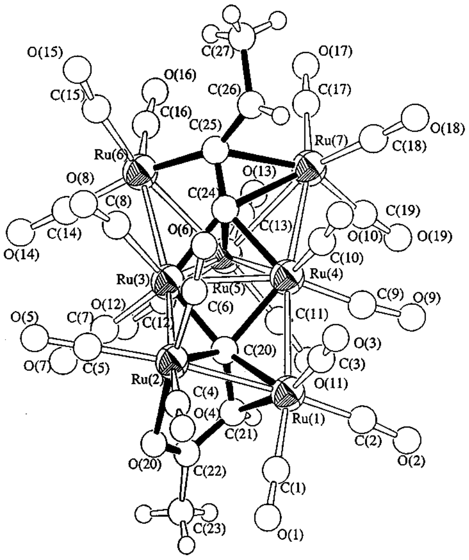


**Fig. 4** Molecular structure of $[Ru_7(CO)_{19}\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}\{\mu_5\text{-}\eta^1:\eta^1:\eta^1:\eta^1:\eta^2\text{-}CCC(H)CH_3\}]$ **4** with the atom numbering scheme.

**Table 5** Some selected bond lengths (Å) and angles (°) for cluster **5**

| | | | |
|---|---|---|---|
| Ru(1)–Ru(2) | 2.775(2) | Ru(1)–Ru(3) | 2.807(2) |
| Ru(2)–Ru(4) | 2.949(2) | Ru(2)–Ru(5) | 2.884(2) |
| Ru(3)–Ru(4) | 2.923(2) | Ru(3)–Ru(5) | 2.859(2) |
| Ru(4)–Ru(5) | 2.825(2) | Ru(1)–C(27) | 2.26(2) |
| Ru(1)–C(28) | 2.36(2) | Ru(1)–C(31) | 2.17(2) |
| Ru(2)–C(27) | 2.17(2) | Ru(2)–C(31) | 2.16(2) |
| Ru(3)–O(27) | 2.15(1) | Ru(3)–C(28) | 2.09(2) |
| Ru(4)–C(27) | 2.29(2) | Ru(4)–C(28) | 2.31(2) |
| Ru(5)–C(31) | 2.06(2) | Ru(5)–C(32) | 2.25(2) |
| Ru(2)–Ru(1)–Ru(3) | 83.39(6) | Ru(2)–Ru(4)–Ru(3) | 78.45(6) |
| Ru(2)–Ru(5)–Ru(3) | 80.57(6) | C(27)–Ru(1)–C(28) | 35.4(5) |
| C(27)–Ru(4)–C(28) | 35.6(5) | C(31)–C(32)–C(33) | 116(1) |
| C(11)–Ru(4)–C(28) | 140.9(8) | C(11)–Ru(5)–C(31) | 124.9(8) |

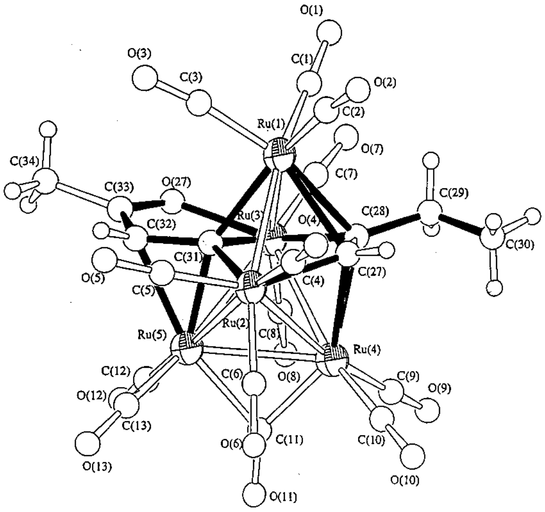


**Fig. 5** Molecular structure of $[Ru_5(CO)_{12}(\mu\text{-}CO)\{\mu_4\text{-}\eta^1:\eta^1:\eta^2:\eta^2\text{-}CC(H)C(O)CH_3\}(\mu_4\text{-}\eta^2\text{-}HCCCH_2CH_3)]$ **5** with the atom numbering scheme.

of $C_\beta$-$C_\gamma$ is 1.41(4) Å which reveals the presence of a partial double bond character. Regarding the allenylidene ligand as a six-electron donor and a metallocycloketonic ring also as a six-electron donor, the valence electron count is 106 for **4**, which is in agreement with the PSEP rule.

### Spectroscopic and structural characterization of 5

The molecular structure of **5** was established by X-ray crystallography and is shown in Fig. 5; Table 5 collects some significant bond parameters. The structure of **5** consists of two crystallographically independent molecules in the asymmetric unit. The spectroscopic data for **5** are fully consistent with the solid-state structure. An intense molecular ion peak at *m*/*z* 922 was observed in the positive FAB mass spectrum. Its $^1H$ NMR spectrum shows two singlets at $\delta$ 7.49 and 5.27 for the two sets of methyne proton. The two methylene protons on C(29), which are magnetically non-equivalent, give rise to two sets of double quartets centred at $\delta$ 3.31 and 2.85 with coupling constants $J$(HH) 7.5 Hz due to geminal coupling. The signal at $\delta$ 1.07 due to the methyl proton on C(30) appears as a triplet due to overlap of the two doublets with $J$(HH) 7.5 Hz, which is coupled to the non-equivalent methylene protons. The singlet resonance at $\delta$ 2.16 is assigned to the other methyl protons on C(34). The metal framework is essentially the same as that in cluster **2** and the structure consists of a metallocycloketonic ring, a bridging carbonyl ligand and a $\mu_4$-$\eta^2$-$CCCH_2CH_3$ ligand. The C(31) atom is asymmetrically σ bonded to the four Ru(1–3) atoms, and also π interacts with the hinge Ru(5) atom together with C(32). The oxygen atom O(27) in the metallocycloketonic ring is σ bonded to the wingtip Ru(3) atom [Ru(3)–O(27) 2.15(1) Å]. The Ru(4) and Ru(5) atoms are asymmetrically bridged by a CO ligand [Ru(4)–C(1) 1.97(2) Å; Ru(5)–C(1) 2.09(2) Å]. The acetylene ligand is σ bonded to the two wingtip Ru(2) and Ru(3) atoms, and π bonded to one hinge Ru(4) atom with one bridging Ru(1) atom. If the metallocycloketonic ring and $HCCCH_2CH_3$ are considered to be a six-electron donor and a four-electron donor respectively, cluster **5** has 76 CVE which obeys the EAN rule for the $Ru_5$ wingtip bridged butterfly.

To investigate the effect of reaction time on this reaction, heating of $Ru_3(CO)_{12}$ and but-3-yn-2-ol in cyclohexane for 24 hours has been carried out. We observed no significant increase in the yields for complexes **1**, **2** and **5**. However, much lower yields were observed for **3** and **4** together with the formation of some insoluble brown powder which cannot be further characterised. The same reaction has also been carried out in THF and $CHCl_3$ at reflux. However, only insoluble dark brown materials were obtained. No clusters **1**–**5** can be isolated in significant amount. Attempts have been made to examine the relationship between cluster **2**, **3** and **4**. Reaction of **2** with an excess of $Ru_3(CO)_{12}$ does not lead to **3** nor **4**. No reaction is observed between **3** and $Ru_3(CO)_{12}$. Hence, it is believed that the formation of complexes **1**–**5** follows independent reaction pathways.

## Conclusion

In view of the importance of the acetylenic metal cluster chemistry to surface chemistry, the formation of various novel

**Table 6** Spectroscopic data for clusters **1**–**5**

| Cluster | IR, ν(CO)[a]/cm$^{-1}$ | $^1$H NMR,[b] δ(*J*/Hz) | MS[c] (*m*/*z*) |
|---|---|---|---|
| **1** | 2094s, 2064s, 2037vs, 2014w | 4.32 (1H, t, $J = 3.7$, $H^b$), 4.29 (2H, d, $J = 3.7$, $H^a$), 2.71 (1H, q, $J = 5.6$, $H^c$), 2.18 (3H, s, $H^d$), 1.72 (3H, d, $J = 5.6$, $H^e$) | 862 (863) |
| **2** | 2099w, 2062vs, 2048s, 2018m [C=O (KBr) 1558m] | 4.52 (1H, s, $H^a$), 2.02 (3H, s, $H^b$), −21.31 (1H, s, $H^c$ or $H^d$), −28.45 (1H, s, $H^d$ or $H^c$) | 967 (968) |
| **3** | 2070s, 2058s, 2006m [C=O (KBr) 1541m] | 3.84 (2H, s, $H^b$), 2.10 (6H, s, $H^a$) | 1190 (1190) |
| **4** | 2070vs, 2056vs, 2032m, 2012m | 4.65 (1H, q, $J = 5.8$, $H^a$), 4.21 (1H, s, $H^b$), 2.09 (3H, s, $H^c$), 1.82 (3H, d, $J = 5.8$, $H^d$) | 1402 (1403) |
| **5** | 2095s, 2066s, 2043vs, 2026s, 2014s, 1981 (sh) | 7.49 (1H, s, $H^c$), 5.27 (1H, s, $H^a$), 3.31 (1H, dq, $J = 7.5$, 15.7, $H^{b1\text{ or }b2}$), 2.85 (1H, dq, $J = 7.5$, 15.7, $H^{b1\text{ or }b2}$), 2.16 (3H, s, $H^d$), 1.07 (3H, t, $J = 7.5$, $H^e$) | 922 (923) |

[a] In $CH_2Cl_2$. [b] In $CDCl_3$. [c] Simulated values given in parentheses.

**Table 7** Summary of crystal data and data collection parameters for clusters **1**–**5**

| Cluster | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Empirical formula | $Ru_4C_{20}H_{10}O_{13}$ | $Ru_5C_{18}H_6O_{15}$ | $Ru_6C_{24}H_8O_{18}$ | $Ru_7C_{27.50}H_9O_{20}Cl$ | $Ru_5C_{21}H_{14}O_{10}$ |
| *M* | 852.57 | 967.59 | 1190.74 | 1402.30 | 991.65 |
| Crystal colour, habit | Purple, block | Orange, block | Red, block | Brown, plate | Red, plate |
| Crystal size/mm | 0.14 × 0.30 × 0.32 | 0.11 × 0.13 × 0.17 | 0.22 × 0.22 × 0.29 | 0.10 × 0.23 × 0.26 | 0.07 × 0.26 × 0.29 |
| Crystal system | Monoclinic | Monoclinic | Triclinic | Monoclinic | Triclinic |
| Space group | $P2_1/c$ (no. 14) | $C2/c$ (no. 15) | $P\bar{1}$ (no. 2) | $C2/c$ (no. 15) | $P\bar{1}$ (no. 2) |
| *a*/Å | 11.102(5) | 25.000(2) | 9.542(1) | 40.140(10) | 9.966(1) |
| *b*/Å | 9.987(4) | 14.835(3) | 12.192(1) | 8.889(7) | 17.564(1) |
| *c*/Å | 23.312(5) | 17.302(3) | 15.699(1) | 23.179(8) | 18.051(2) |
| α/° | — | — | 93.30(1) | — | 114.22(1) |
| β/° | 100.62(3) | 127.44(1) | 99.45(1) | 113.28(3) | 100.49(1) |
| γ/° | — | — | 113.25(1) | — | 97.22(1) |
| *U*/Å$^3$ | 2540(1) | 5094(1) | 1640.1(3) | 7597(6) | 2761.8(6) |
| *Z* | 4 | 8 | 2 | 8 | 4 |
| $D_c$/g cm$^{-3}$ | 2.255 | 2.523 | 2.411 | 2.452 | 2.385 |
| *T*/K | 298 | 298 | 298 | 298 | 298 |
| *F*(000) | 1640 | 3632 | 1120 | 5272 | 1872 |
| μ(Mo-Kα)/cm$^{-1}$ | 23.97 | 29.69 | 27.70 | 28.58 | 27.39 |
| ω-Scan width/° | 1.73 + 0.35 tan θ | 1.31 + 0.35 tan θ | — | 1.47 + 0.35 tan θ | — |
| No. of plates | — | — | 65 | — | 65 |
| Scan time/min | — | — | 5 | — | 5 |
| 2θ Range collected/° | 2.0–45 | 2.0–45 | 2.0–51.2 | 2.0–45 | 2.0–51.2 |
| Scan speed/° min$^{-1}$ | 16.0 | 16.0 | — | 16.0 | — |
| No. reflections collected | 3762 | 3576 | 10887 | 5451 | 14987 |
| No. unique reflections | 3550 | 3483 | 4253 | 5359 | 6552 |
| No. observed reflections [$I > 3\sigma(I)$] | 1986 | 2540 | 2251 | 2348 | 3425 |
| *R* | 0.066 | 0.036 | 0.053 | 0.062 | 0.050 |
| $R_w$ | 0.097 | 0.038 | 0.062 | 0.078 | 0.052 |
| Goodness of fit, *S* | 3.24 | 1.64 | 1.49 | 2.43 | 1.77 |
| Maximum Δ/σ | 0.02 | 0.01 | 0.03 | 0.03 | 0.02 |
| No. of parameters | 214 | 178 | 223 | 263 | 371 |
| Maximum, minimum density in Δ*F* map/e Å$^{-3}$ (close to Ru) | 1.83, −1.43 | 0.99, −0.89 | 1.01, −0.93 | 2.00, −1.80 | 0.84, −0.44 |

hydrocarbyl ketonic fragments on a metal cluster surface is intrinsically interesting. The results reported in this paper show that the five clusters are obtained by a combination of dehydration, hydrogen atom transfer and oxidation of a secondary alcohol to give a ketone. Cluster **1** consists of a $Ru_4$ butterfly skeleton with a $C_8$ ketonic chain fragment. Clusters **2**–**5** are interesting examples of metal carbonyls with a metallocycloketonic ring *via* a $\mu_4$-$\eta^1$:$\eta^1$:$\eta^2$:$\eta^2$ bonding mode and the O→Ru dative interaction due to the activation of hydroxyl group is observed. Moreover, the cluster **3** has a hexaruthenium skeleton, with seven M–M bonds, which is different from those commonly observed for the hexanuclear raft compounds. Cluster **4** is one of a very rare collection of a distorted $Ru_4$ square plane sharing an edge with an edge-bridged butterfly.

## Experimental

All the reactions were performed under an atmosphere of high purity nitrogen using standard Schlenk techniques. Analytical grade solvents were purified by distillation over the appropriate drying agents and under an inert nitrogen atmosphere prior to use. Infrared spectra were recorded on a Bio-Rad FTS-7 spectrometer using a 0.5 mm solution cell. Positive-ion fast atom bombardment mass spectra were obtained using a Finnigan MAT 95 spectrometer, $^1$H NMR and $^{13}$C NMR spectra were recorded in $CDCl_3$ on a Bruker DPX 300 NMR instrument, referenced to internal $SiMe_4$ ($\delta = 0$). The reactions were monitored by analytical thin-layer chromatography (5735 Kieselgel 60 $F_{254}$, E. Merck) and the products were separated in air on preparative thin-layer chromatographic plates coated with Merck Kieselgel 60 $GF_{254}$. The compound but-3-yn-2ol obtained from Lancaster was used without further purification.

### Synthesis

The compound $[Ru_3(CO)_{12}]$ (0.5 g, 0.78 mmol) was refluxed in cyclohexane (60 ml) with but-3-yn-2-ol (0.5 ml) for 8 h. Infrared spectroscopy and TLC indicated complete consumption of the starting material. The solvent was removed *in vacuo* and the residue separated by TLC using dichloromethane–hexane (15:85 v/v) as eluent to afford five bands with $R_f$ values of 0.30, 0.45, 0.55, 0.70 and 0.80 respectively. All the clusters **1**–**5** were isolated as solids in 10, 15, 15, 8 and 10% yields respectively [based on $Ru_3(CO)_{12}$] (Found for $Ru_4C_{20}H_{10}O_{13}$ **1**: C, 28.45; H, 1.32. Calc.: C, 28.19; H, 1.19%. Found for $Ru_5C_{18}H_6O_{15}$ **2**: C, 22.51; H, 0.50. Calc.: C, 22.34; H, 0.63%. Found for $Ru_6C_{24}H_8O_{18}$ **3**: C, 24.45; H, 0.98. Calc.: C, 24.21; H, 0.68%. Found for $Ru_7C_{27}H_8O_{20}$ **4**: C, 23.96; H, 0.75. Calc.: C, 23.85; H, 0.59%. Found for $Ru_5C_{21}H_{14}O_{10}$ **5**: C, 25.59; H, 1.20. Calc.: C, 25.45; H, 1.43%). Table 6 summarises the IR, $^1H$ NMR and FAB mass spectroscopies for all the new compounds.

### X-Ray data collection and structural determination of complexes 1–5

Crystals of clusters **1**–**5** suitable for X-ray analysis were obtained by slow evaporation of their respective dichloromethane–*n*-hexane solution at −10 °C for 2 d. Single crystals of **1**, **2**, **3** and **5** were mounted on a glass fibre using epoxy resin, however, crystal **4**, together with solvate of stoichiometry $0.5CH_2Cl_2$, was sealed in a 0.3 mm Lindermann glass capillary. Data were collected at ambient temperature either on a Rigaku AFC7R diffractometer (for **1**, **2** and **4**) or a MAR research image plate scanner (for **3** and **5**) with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) using the *ω–2θ* and *ω* scan techniques respectively. A summary of the crystallographic data and structure refinement is listed in Table 7. All intensity data were collected for Lorentz and polarization effects. The Ψ scan method was employed for semi-empirical absorption corrections for **1**, **2** and **4**, however, an approximation to absorption correction by inter-image scaling was applied for **3** and **5**. Scattering factors were taken from ref. 47(*a*) and anomalous dispersion effects[47b] were included in $F_c$. The structures were solved by a combination of direct methods (SHELXS 86[48] for **1**, **2**, **3** and **4**; SIR 88[49] for **5**) and Fourier-difference techniques and refined on $F$ by full-matrix least-squares analysis. The hydrogen atoms of the organic moieties were generated in their ideal positions (C–H 0.95 Å) while all metal hydrides were estimated by potential-energy calculations.[50] All calculations were performed on a Silicon-Graphics computer, using the program package TEXSAN.[51]

CCDC reference number 186/1145.

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