

# Synthesis and structural characterisation of trinuclear and tetranuclear ruthenium clusters containing diyne ligands derived from 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne

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Three new ruthenium diyne clusters  $[\text{Ru}_3(\text{CO})_7(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3\text{-C}_{28}\text{H}_{34}\text{O}_3)]$  **1a** (10%),  $[\text{Ru}_3(\text{CO})_7(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3\text{-C}_{28}\text{H}_{34}\text{O}_3)]$  **1b** (4%) and  $[\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^4\text{-C}_{28}\text{H}_{32}\text{O}_2)]$  **2** (12%) have been synthesized by reaction of 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne with triruthenium dodecacarbonyl in chloroform under refluxing conditions. All have been fully characterised by spectroscopic and X-ray diffraction methods. The structures of **1a** and **1b** are based on a  $\text{Ru}_3$  triangular skeleton containing a fragment of  $\text{C}_8$  chain, which arises from the coupling of two diyne molecules with the formation of a ruthenacyclopentadienyl ring and a furyl ring. Complexes **1a** and **1b** are isomeric to each other and differ only in the spatial position of the pendant alkyne moiety in the  $\text{C}_8$  hydrocarbon fragment. The organic moiety in **2** is formed by coupling of two diyne ligands and is co-ordinated to a bent  $\text{Ru}_3$  chain *via* a  $\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^4$  bonding mode. Cluster **2** is found to exhibit a charge-separated, zwitterionic formulation. Reaction of  $[\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2]$  with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne afforded another new cluster  $[\text{Ru}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-C}_{14}\text{H}_{18}\text{O}_2)]$  **3**, which consists of a diyne ligand bound to the triruthenium cluster unit *via* a typical  $\mu_3\text{-}(\eta^2\text{-})$  co-ordination mode. Thermolysis of **1a** and **2**, with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne and  $[\text{Ru}_3(\text{CO})_{12}]$ , respectively, led to  $[\text{Ru}_3(\text{CO})_5(\mu_3\text{-}\eta^5\text{:}\eta^5\text{:}\eta^6\text{-C}_{43}\text{H}_{49}\text{O}_5)]$  **4** and a tetranuclear cluster  $[\text{Ru}_4(\text{CO})_{10}(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^4\text{:}\eta^4\text{-C}_{28}\text{H}_{32}\text{O}_2)]$  **5**. Cluster **4** is closely related to **1a** by the coupling of one more diyne ligand to the triruthenium skeleton of **1a**, resulting in an unusual  $\mu_3\text{-}\eta^1\text{:}\eta^3\text{:}\eta^3$  mode. The co-ordination mode of the organic ligand in **5** is very similar to that in **2**, except that one more metal atom is involved, and one  $\eta^3$ -allyl bond is formed.

## Introduction

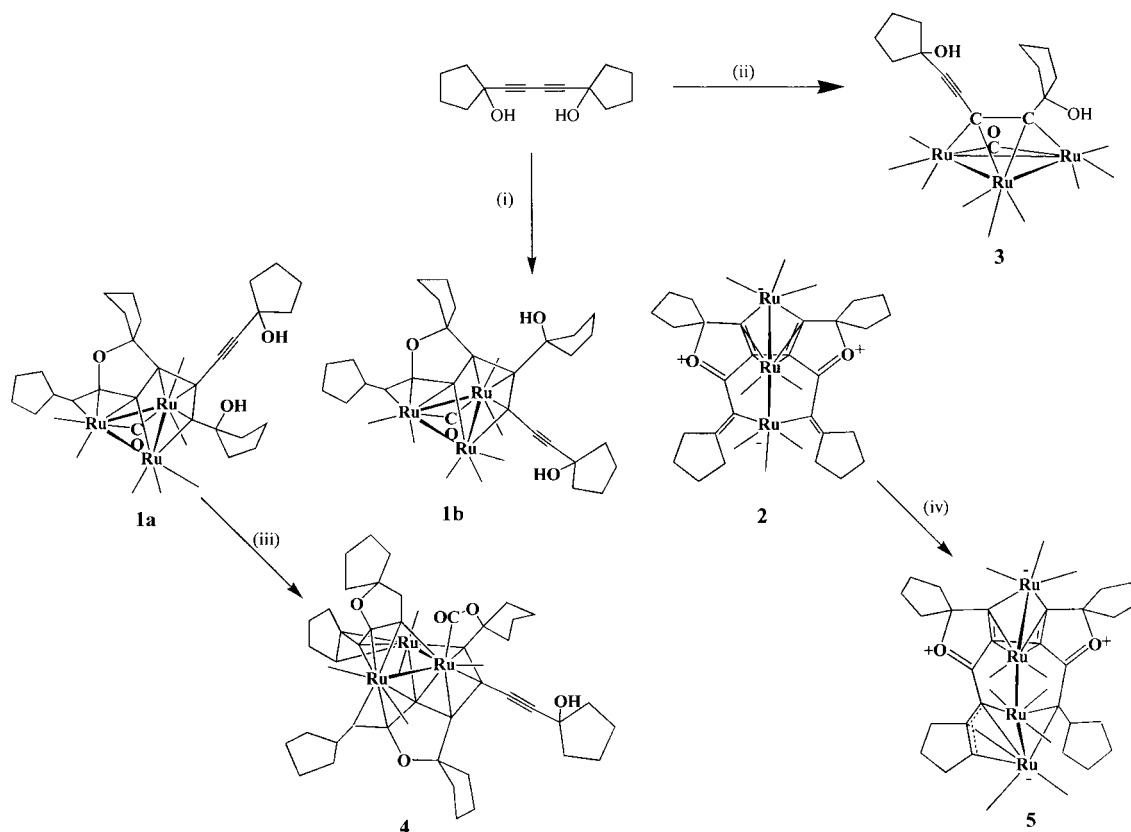
Reactions of transition metal clusters containing functionalised alkynes have been widely studied over the last two decades.<sup>1-8</sup> It was found that the presence of a terminal hydroxy group in the parent alkyne allows profound rearrangements to occur at the side chain involving dehydration,<sup>9</sup> hydrogen atom transfer,<sup>10,11</sup> and acid-induced isomerisation.<sup>12</sup> In our previous papers we have reported the reactions of  $[\text{Ru}_3(\text{CO})_{12}]$  with the hydroxy-alkyne derivatives, but-3-yn-2-ol and 9-ethynyl-9-fluorene, to afford several new clusters.<sup>13,14</sup> Recent investigations have focussed on the reactions of transition metals with ynyl and polyynyl  $[-\text{C}\equiv\text{C}-\text{R}, -(\text{C}\equiv\text{C})_x-]$  ligands which tend to link metal centres into linear arrays bearing extended carbon-carbon unsaturation, stimulating the designed synthesis of molecular wires and new rod-like materials.<sup>15-17</sup> These highly unsaturated, carbon-rich chains possess even greater potential for the construction of two- and three-dimensional multimetallic arrays if the full co-ordinating capacity of the  $\pi$  systems can be exploited.<sup>18,19</sup> Such complexes of the type  $[\text{Ru}_2(\text{CO})_6(\mu\text{-}\eta^1\text{:}\eta^1\text{-}\alpha,\beta\text{-C}\equiv\text{C}\equiv\text{CCR})(\mu\text{-PPh}_2)]$  (where  $\text{R} = \text{Bu}^t$  or  $\text{Ph}$ ) and its derivatives,  $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{:}\eta^2\text{-CH}(\text{C}_6\text{H}_4)\text{C}(\text{Ph})\equiv\text{CC}\equiv\text{CBu}^t\}(\mu\text{-PPh}_2)]$  and  $[\text{Ru}_2(\text{CO})_6\{\mu\text{-}\eta^1\text{:}\eta^2\text{-C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{C}_6\text{H}_4)\text{-CH}\}(\mu\text{-PPh}_2)]$ , have been reported by Carty and co-workers.<sup>20</sup> The behaviour of polycarbon ligands such as butadiynyls or higher polyynyls with extended  $sp$  unsaturation at the polynuclear centres has just begun to attract attention.<sup>21,22</sup> By comparison with polyne ligands co-ordinated to the metal carbonyl clusters, for which an extensive co-ordination chemistry and reactivity profile has been established,<sup>23,24</sup> relatively few organometallic functionalised diynyls have been prepared and their chemistry remains virtually unexplored. Tunik *et al* have recently published the reactions of 2,4-hexadiyne-1,6-diol

with triosmium and triruthenium carbonyl clusters to yield  $[\text{Os}_3\text{H}(\text{CO})_{10}(\mu\text{-}\eta^2\text{-C}_6\text{H}_5\text{O})]^{25}$  and  $[\text{Ru}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-HOCH}_2\text{C}_2\text{-C}_2\text{CH}_2\text{OH})]^{26}$  respectively.

In this paper we describe the reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with a hydroxy-functionalised conjugated diyne, 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne, that affords products showing interesting and unusual transformations of conjugated diynes during the process of co-ordination. The process involves  $\text{C}\equiv\text{C}$  triple bond activation,<sup>27,28</sup> intramolecular cyclization of ligands<sup>29</sup> and ligand coupling.<sup>30-32</sup>

## Results and discussion

The reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne in refluxing chloroform (68 °C) in a dinitrogen atmosphere gives a mixture of products in relatively low yields which were separated by preparative thin-layer chromatography (TLC) (Scheme 1). Three new compounds can be isolated and identified as  $[\text{Ru}_3(\text{CO})_7(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3\text{-C}_{28}\text{H}_{34}\text{O}_3)]$  **1a**,  $[\text{Ru}_3(\text{CO})_7(\mu\text{-CO})(\mu_3\text{-}\eta^2\text{:}\eta^3\text{:}\eta^3\text{-C}_{28}\text{H}_{34}\text{O}_3)]$  **1b** and  $[\text{Ru}_3(\text{CO})_8(\mu_3\text{-}\eta^2\text{:}\eta^2\text{:}\eta^4\text{-C}_{28}\text{H}_{32}\text{O}_2)]$  **2**, in 10, 4 and 12% yields, respectively [based on  $\text{Ru}_3(\text{CO})_{12}$ ]. Reaction of  $[\text{Ru}_3(\text{CO})_{10}(\text{NCMe})_2]$  with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne affords another cluster  $[\text{Ru}_3(\text{CO})_9(\mu\text{-CO})(\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^2\text{-C}_{14}\text{H}_{18}\text{O}_2)]$  **3** (30% yield). Thermolysis of **1a** and **2**, with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne and  $[\text{Ru}_3(\text{CO})_{12}]$ , respectively, leads to the formation of  $[\text{Ru}_3(\text{CO})_5(\mu_3\text{-}\eta^5\text{:}\eta^5\text{:}\eta^6\text{-C}_{43}\text{H}_{49}\text{O}_5)]$  **4** and  $[\text{Ru}_4(\text{CO})_{10}(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^4\text{:}\eta^4\text{-C}_{28}\text{H}_{32}\text{O}_2)]$  **5** (Scheme 1). All the compounds were fully characterised by FAB mass spectrometry, IR, and <sup>1</sup>H NMR spectroscopies and single-crystal X-ray crystallography. The structures of **1a** and **2** were also fully elucidated by advanced NMR techniques.



**Scheme 1** (i)  $[\text{Ru}_3(\text{CO})_{12}]$ ,  $\text{CHCl}_3$ , 61 °C; (ii)  $[\text{Ru}_3(\text{CO})_{12}(\text{NCMe})_2]$ ,  $\text{CH}_2\text{Cl}_2$ , 25 °C; (iii) excess of 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne, *n*-heptane, 98 °C; (iv) excess of  $[\text{Ru}_3(\text{CO})_{12}]$ , toluene, 111 °C.

**Table 1** Spectroscopic data for clusters **1a**, **1b** and **2–5**

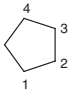
Cluster	IR, $\tilde{\nu}(\text{CO})^a/\text{cm}^{-1}$	NMR, $\delta$ (J/Hz) <sup>b</sup>	MS, $m/z^c$
<b>1a</b>	2072w, 2042vs, 2029s, 2012s, 1993w, 1874m	<sup>1</sup> H: 3.23–3.18 (1 H, m), 2.96–2.89 (3 H, m), 2.71–2.59 (2 H, m), 2.56–2.43 (1 H, m), 2.21–2.18 (1 H, m), 2.16–1.97 (11 H, m), 1.94–1.81 (10 H, m), 1.79–1.77 (1 H, m), 1.69–1.64 (1 H, m), 0.98–0.91 (1 H, m) <sup>13</sup> C: 22.39, 22.40, 23.81, 24.25, 25.05, 25.59, 25.65, 26.91, 35.63, 35.90, 38.05, 40.41, 41.29, 41.38, 44.28, 44.52, 73.91, 77.30, 87.78, 88.88, 97.26, 97.46, 115.30, 121.25, 134.64, 143.68, 143.76, 145.85, 202.06, 208.61	946(946)
<b>1b</b>	2106m, 2097w, 2056vs, 2029s, 2010s, 1867m	<sup>1</sup> H: 3.30–3.27 (1 H, m), 2.97–2.76 (3 H, m), 2.67–2.59 (2 H, m), 2.28–2.22 (1 H, m), 2.18–1.98 (10 H, m), 1.95–1.79 (12 H, m), 1.77–1.75 (1 H, m), 1.64–1.58 (1 H, m), 1.09–1.04 (1 H, m)	946(946)
<b>2</b>	2068s, 2060s, 2050vs, 2029s, 2006s, 1993vs,	<sup>1</sup> H: 2.80–2.74 (2 H, m), 2.72–2.58 (4 H, m), 2.45–2.38 (2 H, m), 2.37–2.30 (2 H, m), 2.15–2.00 (4 H, m), 2.00–1.88 (6 H, m), 1.87–1.85 (4 H, m), 1.82–1.75 (6 H, m), 1.63–1.58 (2 H, m) <sup>13</sup> C: 26.05, 26.35, 26.72, 27.54, 36.27, 38.69, 39.04, 43.85, 70.36, 70.61, 70.66, 96.63, 116.15, 126.49, 161.74, 164.55, 189.00, 193.15, 194.87, 198.06, 198.98, 205.74	928(928)
<b>3</b>	2102mw, 2070vs, 2053s, 2029s, 2007s, 1845 (br)	<sup>1</sup> H: 2.00–1.90 (8 H, m), 1.85–1.68 (8 H, m)	802(802)
<b>4</b>	2074s, 2058w, 2039s, 1989m, 1760w	<sup>1</sup> H: 4.86–4.83 (1 H, d, $J = 15.5$ ), 4.14–4.10 (1 H, q, $J = 6.5$ ), 4.07–4.04 (1 H, d, $J = 15.5$ ), 3.23–3.20 (2 H, m), 3.14–3.11 (2 H, m), 2.79–2.72 (4 H, m), 2.54–2.47 (4 H, m), 2.46–2.44 (2 H, m), 2.17–2.13 (6 H, m), 2.03–1.96 (8 H, m), 1.91–1.78 (14 H, m), 1.68–1.65 (2 H, m), 0.90–0.87 (2 H, m)	1089(1089)
<b>5</b>	2068w, 2041s, 2002vs, 1950s	<sup>1</sup> H: 3.01–2.95 (1 H, q, $J = 4.1$ ), 2.87–2.78 (1 H, m), 2.55–2.35 (2 H, m), 2.23–2.12 (2 H, m), 1.99–1.93 (2 H, m), 1.91–1.89 (10 H, m), 1.88–1.85 (8 H, m), 1.78–1.73 (2 H, m), 1.54–1.51 (2 H, m), 1.37–1.35 (2 H, m)	1085(1085)

<sup>a</sup> In  $\text{CH}_2\text{Cl}_2$ . <sup>b</sup> In  $\text{CDCl}_3$ . <sup>c</sup> Simulated values given in parentheses.

### Spectroscopic and structural characterisation of compounds **1a** and **1b**

A single red product was isolated near the bottom of the plate after preparative TLC following the thermolytic reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne. However, careful separation by repeated TLC led to two isomeric red products, **1a** and **1b**. These possess completely different <sup>1</sup>H NMR and IR spectral patterns (Table 1), but identical molecular ion peaks at  $m/z$  946. The <sup>1</sup>H NMR spectrum of **1a**

in  $\text{CDCl}_3$  comprises a complex series of multiplet resonances, many of which overlap. The four  $\text{C}_5\text{H}_8$  rings in **1a** are predicted to give rise to a total of 32 resonances which, from the integral trace of the spectrum, appears to be the case. However, no hydroxyl signal is observed. A more conclusive assignment was obtained by performing the DEPT <sup>13</sup>C and normal <sup>13</sup>C NMR experiments. The DEPT <sup>13</sup>C spectrum clearly shows the sixteen methylene carbon resonances in the  $\delta$  22.39–44.52 region. The well resolved <sup>13</sup>C NMR spectrum provides evidence for the four  $\text{C}_5\text{H}_8$  rings, two alkoxy and the pendant alkyne carbon

**Table 2** Carbon and proton assignments for rings of clusters **1a** (A–D) and **2** (A', B')


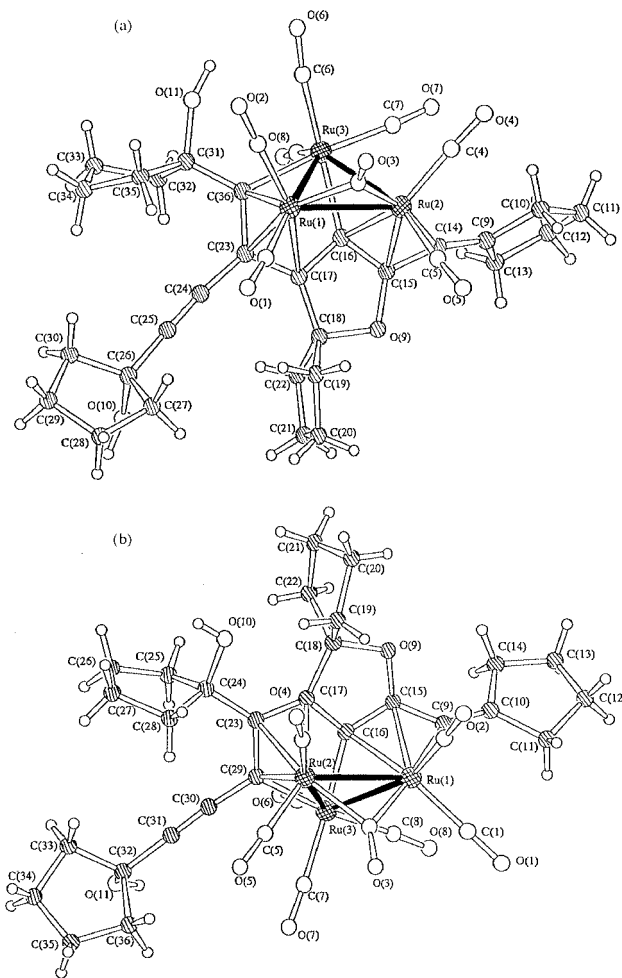
Ring	$\delta$		Position
	C	H	
A	41.38	2.02	1 or 4
		2.01	
	41.29	1.98	1 or 4
		1.96	
	22.40	2.00	2 or 3
		1.87	
	22.39	1.91	2 or 3
		1.79	
B	40.41	1.91	1 or 4
		0.94	
	38.05	2.60	1 or 4
		2.16	
	25.59	1.93	2 or 3
		1.85	
	23.81	1.89	2 or 3
		1.67	
C	35.90	2.94	1 or 4
		2.84	
	35.63	2.90	1 or 4
		2.69	
	26.91	1.93	2 or 3
		1.84	
	25.05	1.90	2 or 3
		1.88	
D	44.52	3.20	1 or 4
		2.07	
	44.28	2.46	1 or 4
		2.10	
	25.65	1.93	2 or 3
		1.84	
	24.25	1.90	2 or 3
		1.88	
A'	43.85	2.08	1 or 4
		1.84	
	39.04	2.40	1 or 4
		2.05	
	26.72	1.92	2 or 3
		1.85	
	26.05	1.94	2 or 3
		1.91	
B'	38.69	2.83	1 or 4
		2.63	
	36.27	2.71	1 or 4
		2.30	
	26.54	1.81	2 or 3
		1.61	
	26.35	1.80	2 or 3
		1.79	

atom resonances (Table 1). Eight resonances of the acetylenic carbon atoms are also observed in the range  $\delta$  97.26–145.85, and the carbonyl region displays two peaks at  $\delta$  202.06 and 208.61 in the ratio of 3 : 1, respectively. The compound has also been analysed using a combination of 2-D  $^1\text{H}$ – $^1\text{H}$  COSY, 2-D C,H-COSY and COLOC (C–H correlation spectroscopy *via* long-range couplings) experiments, which suggests that the pairs of signals arise from the geminal protons of each  $\text{C}_5\text{H}_8$  ring system. However, no attempt has been made to assign fully the actual positions of these four ring systems (A, B, C and D). Table 2 summarises the probable assignments of the protons and the carbon atoms on the four cyclopentyl rings.

Single crystals of compound **1a** suitable for X-ray analysis were obtained from slow evaporation of a chloroform–*n*-hexane solution at  $-10^\circ\text{C}$ . The crystal structure with stoichiometry **1a**· $\text{CHCl}_3$  in the asymmetric unit was established. A

**Table 3** Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for cluster **1a**

Ru(1)–Ru(2)	2.829(1)	Ru(1)–Ru(3)	2.771(1)
Ru(2)–Ru(3)	2.934(1)	Ru(1)–C(17)	2.382(10)
Ru(1)–C(23)	2.274(9)	Ru(1)–C(36)	2.181(9)
Ru(2)–C(14)	2.20(1)	Ru(2)–C(15)	2.30(1)
Ru(2)–C(16)	2.29(10)	Ru(3)–C(16)	2.04(1)
Ru(3)–C(36)	2.20(9)	O(9)–C(15)	1.39(1)
O(9)–C(18)	1.50(1)	O(10)–C(26)	1.42(1)
O(11)–C(31)	1.44(1)	C(9)–C(10)	1.47(1)
C(9)–C(13)	1.51(2)	C(9)–C(14)	1.32(1)
C(14)–C(15)	1.39(1)	C(15)–C(16)	1.39(1)
C(16)–C(17)	1.43(1)	C(17)–C(18)	1.50(1)
C(17)–C(23)	1.42(1)	C(18)–C(19)	1.51(1)
C(18)–C(22)	1.55(1)	C(19)–C(20)	1.51(2)
C(20)–C(21)	1.48(2)	C(21)–C(22)	1.47(2)
C(23)–C(24)	1.44(2)	C(23)–C(36)	1.44(1)
C(24)–C(25)	1.19(1)	C(25)–C(26)	1.47(2)
C(26)–C(27)	1.53(1)	C(26)–C(30)	1.51(1)
C(27)–C(28)	1.52(2)	C(28)–C(29)	1.53(2)
C(29)–C(30)	1.52(2)	C(31)–C(32)	1.54(1)
C(31)–C(35)	1.53(1)	C(31)–C(36)	1.52(1)
C(32)–C(33)	1.39(1)	C(33)–C(34)	1.50(2)
C(34)–C(35)	1.53(1)		
Ru(1)–Ru(2)–Ru(3)	57.45(3)	Ru(2)–Ru(1)–Ru(3)	63.17(3)
Ru(1)–Ru(3)–Ru(2)	59.38(3)	C(14)–C(15)–C(16)	122.9(10)
O(9)–C(18)–C(22)	105.2(8)	C(24)–C(25)–C(26)	175(1)
C(23)–C(24)–C(25)	172(1)		

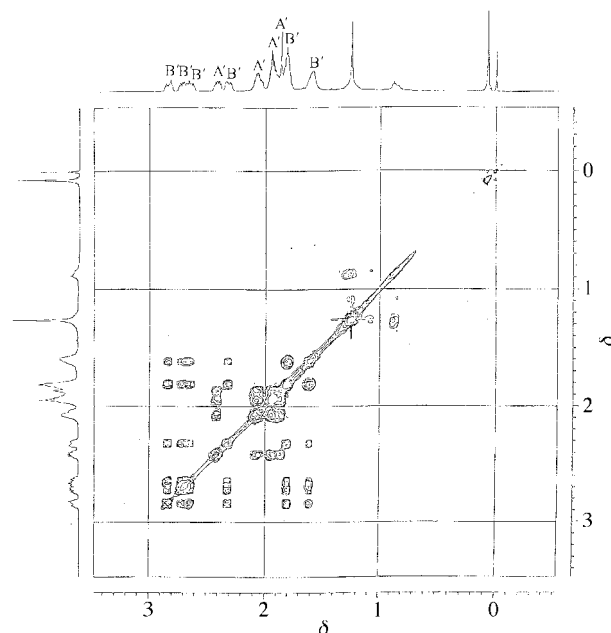
**Fig. 1** Molecular structures of clusters **1a**, (a) and **1b** (b) showing the atom-labelling scheme for non-hydrogen atoms.

perspective view of the molecular structure together with the atomic numbering scheme is illustrated in Fig. 1. Selected bond distances and angles are listed in Table 3. The metal atom framework constitutes a distorted  $\text{Ru}_3$  triangle, with Ru–Ru distances ranging from 2.771(1) to 2.934(1)  $\text{\AA}$ , and the C(3)–O(3)

**Table 4** Selected bond lengths (Å) and angles (°) for cluster **1b**

Ru(1)–Ru(2)	2.799(2)	Ru(1)–Ru(3)	2.869(2)
Ru(2)–Ru(3)	2.751(1)	Ru(1)–C(9)	2.16(2)
Ru(1)–C(15)	2.30(1)	Ru(1)–C(16)	2.34(1)
Ru(2)–C(17)	2.34(1)	Ru(2)–C(23)	2.29(1)
Ru(2)–C(29)	2.15(1)	Ru(3)–C(16)	2.02(1)
Ru(2)–C(29)	2.11(1)	O(9)–C(15)	1.35(1)
O(9)–C(18)	1.47(1)	O(10)–C(24)	1.42(1)
O(11)–C(32)	1.45(2)	C(9)–C(10)	1.31(2)
C(9)–C(15)	1.40(2)	C(10)–C(11)	1.52(2)
C(10)–C(14)	1.53(2)	C(11)–C(12)	1.66(5)
C(12)–C(13)	1.34(5)	C(13)–C(14)	1.46(4)
C(15)–C(16)	1.38(2)	C(16)–C(17)	1.44(2)
C(17)–C(18)	1.53(2)	C(17)–C(23)	1.38(2)
C(18)–C(19)	1.49(2)	C(18)–C(22)	1.55(2)
C(19)–C(20)	1.54(2)	C(20)–C(21)	1.51(2)
C(21)–C(22)	1.50(2)	C(23)–C(24)	1.52(2)
C(23)–C(29)	1.43(2)	C(24)–C(25)	1.57(2)
C(24)–C(28)	1.50(2)	C(25)–C(26)	1.50(3)
C(26)–C(27)	1.52(2)	C(27)–C(28)	1.49(2)
C(29)–C(30)	1.43(2)	C(30)–C(31)	1.18(2)
C(31)–C(32)	1.45(2)	C(32)–C(33)	1.52(2)
C(32)–C(36)	1.52(2)	C(33)–C(34)	1.51(3)
C(34)–C(35)	1.48(3)		
Ru(1)–Ru(2)–Ru(3)	62.2(4)	Ru(2)–Ru(1)–Ru(3)	58.1(4)
Ru(1)–Ru(3)–Ru(2)	59.7(4)	C(9)–C(15)–C(16)	127(1)
O(9)–C(18)–C(22)	107(1)	C(30)–C(31)–C(32)	176(1)
C(29)–C(30)–C(31)	172(1)		

unit is found to bridge Ru(1)–Ru(2) which is consistent with the band at 1874 cm<sup>-1</sup> observed in the IR spectrum. A salient structural feature of **1a** is that the two hydroxyl diyne ligands are fused together, with the loss of a water molecule, to form an interesting five-membered metallacyclic ring. One diyne moiety bonded to two Ru atoms only and adopts a  $\mu\text{-}\eta^1\text{:}\eta^2$  mode *via* the C≡C triple bond activation. The carbon atom C(36), is strongly  $\sigma$ -bound to Ru(3) and together with C(23) forms a  $\pi$  interaction to Ru(1). The pendant alkyne moiety, C(24)–C(25), is almost linear with C(23)–C(24)–C(25) and C(24)–C(25)–C(26) interbond angles being 172(1) and 175(1)°, respectively. This contact also exhibits a typical alkyne bond length of 1.19(1) Å, while the C(23)–C(36) length is 1.44(1) Å, characteristic of this type of vinylic co-ordination. The other diyne ligand is co-ordinated to the triruthenium unit in an unusual  $\mu_3\text{-}\eta^1\text{:}\eta^1\text{:}\eta^3$  fashion, *via*  $\sigma$ ,  $\pi$  and  $\pi$ -allyl bonds. The C(16) is attached to Ru(3) *via* a  $\sigma$  bond while C(17) and C(23) form a  $\pi$  interaction to Ru(1). Hence, the dimerised C<sub>4</sub> chain together with Ru(3) forms a ruthenacyclopentadiene ring. Although there are numerous examples of Group VIII complexes containing metallacyclopentadiene rings,<sup>33–35</sup> this substituted tetracarbon chain is characterised by the limited delocalisation of the three double bonds,<sup>36–38</sup> as shown by the C–C bond distances [C(16)–C(17) 1.43(1), C(17)–C(23) 1.42(1), C(23)–C(36) 1.44(1) Å]. This fragment forms one  $\pi$ -allyl bond to Ru(1). Moreover an unusual cyclisation occurs to form an oxygen-containing “C<sub>4</sub>O” ring from which one of the five-membered ring carbons, C(18), has conjugated with the cyclopentyl ring. This cyclopentyl ring is observed to skew so as to avoid the unfavourable clash between the protons located on C(21) and C(27). The C(15)–C(16) bond [1.39(1) Å] in a furyl ring exhibits a  $\pi$  interaction to Ru(2) as in the related cluster [Os<sub>3</sub>H(CO)<sub>10</sub>( $\mu\text{-}\eta^2\text{-C}_4\text{H}_3\text{O}$ )].<sup>39</sup> The C(14)–C(15)–C(16) allenyl ligand formed from the activated C≡C alkyne bond is co-ordinated to Ru(2) *via* a  $\eta^3$ -allyl bonding mode. It should be noted that the carbon atom C(9) exhibits a considerable amount of sp<sup>2</sup> character following the loss of the hydroxyl group. The C(9)–C(14) [average 1.39(1) Å] distance is significantly shorter than the adjacent C(14)–C(15)–C(16) contact suggesting the localisation of a double bond next to a delocalized  $\pi$  bond of the allenyl ligand. The organic fragment is counted as an eight electron donor so as to achieve 48 CVE for cluster **1a**.

**Fig. 2** The TOCSY spectrum of compound **2** with the <sup>1</sup>H NMR plot along the cross section at 500 MHz.

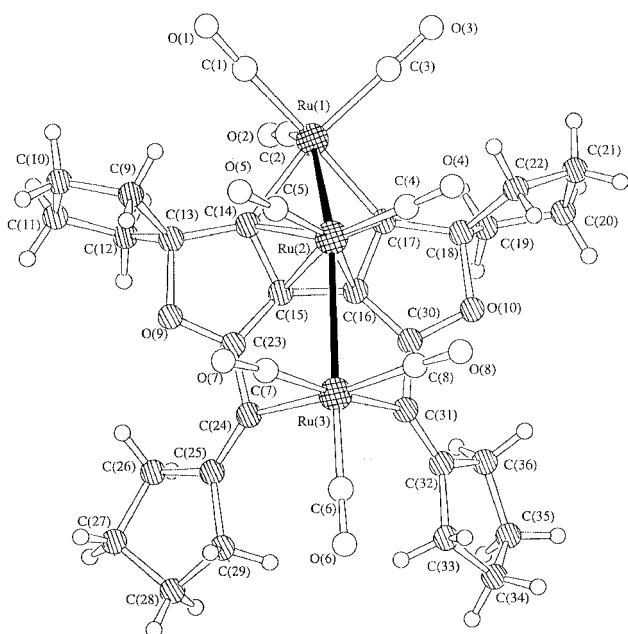
The asymmetric unit of compound **1b** consists of **1b**·½C<sub>6</sub>H<sub>14</sub>. The molecular structure is depicted in Fig. 1(b), together with the atomic numbering scheme. Selected interatomic distances and angles are given in Table 4. Infrared spectroscopy shows a broad absorption at 1867 cm<sup>-1</sup>, alluding to the presence of a bridging carbonyl ligand and a  $\nu(\text{C}\equiv\text{C})$  triple bond absorption is also observed at 2106 cm<sup>-1</sup>. The metal triangle and the hydrocarbyl ligands are essentially the same as in compound **1a**. The only difference observed lies in the position of the pendant alkyne moiety in the C<sub>8</sub> hydrocarbyl fragments. The C(29) atom of the pendant alkyne is bonded to Ru(3) *via* a  $\sigma$  bond [Ru(3)–C(29) 2.11(1) Å] while C(23) and C(29) also exhibit a  $\pi$  interaction to Ru(2) [C(23)–C(29) 1.43(2) Å]. The isolation of compounds **1a** and **1b** represents the possibility of diyne oligomerisation and OH functionalisation to give novel hydrocarbyl fragments on triruthenium clusters. Hence, this constitutes a further example of the potential of cluster compounds in the build-up of organic molecules.

#### Spectroscopic and structural characterization of compound **2**

Chromatographic separation of the reaction mixture yielded the fourth fraction which gave dark green crystals of compound **2** after recrystallisation from a solution of pure *n*-hexane by slow evaporation at –10 °C. The positive FAB mass spectrum exhibits a peak envelope at *m/z* 928 which is followed by a series of peaks corresponding to the loss of carbonyl ligands. Its IR spectrum reveals the presence of terminal carbonyl ligands only (Table 1). The <sup>1</sup>H NMR spectrum recorded in CDCl<sub>3</sub> incorporates a manifold series of overlapping multiplets in the range  $\delta$  1.58–2.80 integrating for thirty-two protons. However, a more convincing assignment was obtained by a special 2-D spectroscopic technique TOCSY (Total Correlation Spectroscopy) experiment.<sup>40,41</sup> This technique is similar to COSY, but the cross peaks arise from all of the connectivities within the spin system, not only those through three bonds. The pattern of these connectivities is unique for protons within a given spin system. Fig. 2 presents the basic <sup>1</sup>H spectrum along with cross sections as indicated on the plot of the TOCSY experiment and reveals that signals A' belong to one spin system, while B' belong to another. The compound has also been fully assigned by a combination of DEPT <sup>13</sup>C, <sup>13</sup>C NMR, 2-D <sup>1</sup>H–<sup>1</sup>H COSY, 2-D C,H-COSY and COLOC experiments, which suggests that the pairs of signals arise from the geminal protons of the C<sub>5</sub>H<sub>8</sub> ring

**Table 5** Selected bond lengths (Å) and angles (°) for cluster **2**

Ru(1)–Ru(2)	2.844(9)	Ru(2)–Ru(3)	3.019(9)
Ru(1)–C(14)	2.063(7)	Ru(1)–C(17)	2.050(7)
Ru(2)–C(14)	2.305(7)	Ru(2)–C(15)	2.177(6)
Ru(2)–C(16)	2.176(6)	Ru(2)–C(17)	2.324(7)
Ru(3)–C(7)	1.950(10)	Ru(3)–C(31)	2.182(7)
C(14)–C(15)	1.416(9)	C(15)–C(16)	1.436(9)
C(16)–C(17)	1.416(9)	C(13)–C(14)	1.512(10)
C(13)–O(9)	1.524(9)	C(23)–O(9)	1.330(8)
C(15)–C(23)	1.424(9)	C(17)–C(18)	1.518(9)
C(18)–O(10)	1.514(8)	C(30)–O(10)	1.345(8)
C(23)–C(24)	1.429(9)	C(30)–C(31)	1.414(9)
Ru(1)–Ru(2)–Ru(3)	142.98(3)	C(14)–Ru(1)–C(17)	78.0(3)

**Fig. 3** Molecular structure of cluster **2**. Details as in Fig. 1.

systems, A' and B'. Table 2 summarises the probable assignment of the protons and the carbon atoms on the four cyclopentyl rings.

The molecular structure of compound **2** is illustrated in Fig. 3 together with the atomic labelling scheme and relevant structural parameters are in Table 5. Cluster **2** consists of an open, bent arrangement of three ruthenium atoms, with an angle of 142.98(3)° for Ru(1)–Ru(2)–Ru(3), co-ordinated by eight carbonyls. The two metal–metal bonds are significantly different in length [Ru(1)–Ru(2) 2.844(9), Ru(2)–Ru(3) 3.02(1) Å] and are also considerably longer than those observed in [Ru<sub>3</sub>(CO)<sub>8</sub>(C<sub>16</sub>H<sub>22</sub>)].<sup>42</sup> The molecule possesses approximate C<sub>s</sub> symmetry with Ru(1), Ru(2) and Ru(3) lying on the mirror plane. The organic ligand system in **2** can be viewed as deriving from two dimerised molecules of the starting hydroxy-functionalised conjugated diyne ligands. One diyne ligand undergoes fragmentation to give two alkyne fragments which then couple with another diyne ligand. This is followed by cyclisation involving the OH substituent and an alkyne group to give a furyl ring, which exhibits the same manner as those observed in compounds **1a** and **1b**. This type of extensive coupling and rearrangement of functionalised diyne is believed to be triggered by ruthenium carbonyl fragments. Detailed examination of the bond parameters of the ligand system shows that the O(9)–C(23) [1.330(8) Å] and O(10)–C(30) [1.345(8) Å] distances are considerably shorter than their adjacent O(9)–C(13) [1.524(9) Å] and O(10)–C(18) [1.514(8) Å] contacts, suggesting the proximity of a double bond to a formal single bond. Bonds C(24)–C(25) and C(31)–C(32) are 1.35(10) and 1.34(9) Å respectively, also typical of double bond distances. Such a

**Table 6** Optical spectral parameters for cluster **2**

Solvent	Colour	10 <sup>-3</sup> ε/dm <sup>3</sup> mol <sup>-1</sup> cm <sup>-1</sup>	λ <sub>max</sub> /nm
<i>n</i> -Hexane	Green	4.3	632
Dichloromethane	Yellow	6.1	627
Acetone	Green	4.8	622

bonding description would require the two oxygen atoms to assume a positive charge. The Ru(1) and Ru(3) would have to carry a formal negative charge in order to maintain the charge balance. This argument is in accordance with the 18-electron rule. Based on this formulation, we could interpret the formation of a ruthenacyclopentadienyl ring [Ru(1)–C(14)–C(15)–C(16)–C(17)], maximum deviation from mean plane 0.047(6) Å] if one considers the isolobal relationship of a CR and [Ru(CO)<sub>3</sub>]<sup>-</sup> fragment. The relatively long Ru(2)–Ru(3) bond compared to Ru(1)–Ru(2) may be due to the dispersal of charge on Ru(1) into the five-membered ring. This is deduced from the significantly shorter bond distances of Ru(1)–C(14) [2.063(7) Å] and Ru(1)–C(17) [2.050(7) Å] compared to Ru(3)–C(24) [2.16(7) Å] and Ru(3)–C(31) [2.182(7) Å]. The best depiction of **2** is a charge-separated, zwitterionic formulation as shown in Scheme 1. This formulation is also consistent with its solution IR spectrum which shows unusually low carbonyl stretching frequencies for a neutral triruthenium carbonyl cluster.<sup>43</sup> The organic ligand acts as an eight electron donor to the metal framework, which accounts for a total of 48 cluster valence electrons. Taking into consideration the two negative charges residing on Ru(1) and Ru(3), the cluster **2** contains 50 CVE and obeys the EAN rule.

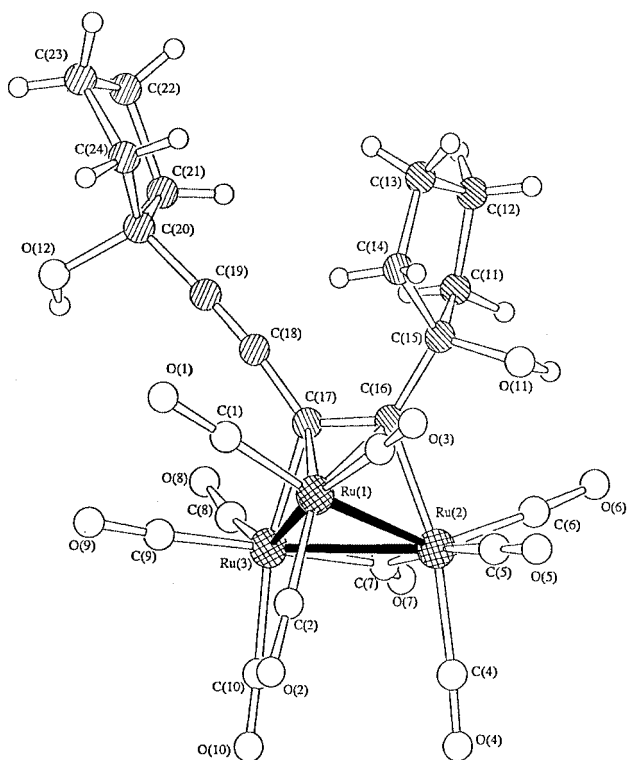
The deep colour in the solid state displayed by compound **2** prompted us to examine it by optical spectroscopy. Molecular orbital calculations by the Fenske–Hall method show that the highest occupied molecular orbital (HOMO) is largely metal-based, and the lowest unoccupied molecular orbital (LUMO) mostly based on the organic moiety.<sup>44</sup> The intense colour arises from a strong absorption of a metal-to-ligand charge-transfer (MLCT) transition. A study of compound **2** in some organic solvents by UV/VIS spectroscopy demonstrated that the MLCT transition band displays a small negative solvatochromism (hypsochromic shift). The optical spectral parameters in *n*-hexane, dichloromethane and acetone are summarised in Table 6. That is, the MLCT absorption blue shifts in progressively more polar solvent media, (μ<sub>g</sub> > μ<sub>e</sub>), where μ<sub>g</sub> and μ<sub>e</sub> are the dipole moments in the ground state and the excited state, respectively.<sup>45</sup> The electron-withdrawing ability of the furyl group in **2** substantially reduces the dipolar moment in the ground state and hence results in a lower transition energy (longer λ<sub>max</sub>).

#### Reaction of [Ru<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub>] with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne

A dichloromethane solution of [Ru<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub>] was stirred at room temperature with one molar equivalent of 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne. This resulted in a darkening of the solution and subsequent work-up results in the isolation of a single product [Ru<sub>3</sub>(CO)<sub>9</sub>(μ-CO)(μ<sub>3</sub>-η<sup>1</sup>:η<sup>1</sup>:η<sup>2</sup>-C<sub>14</sub>H<sub>18</sub>O<sub>2</sub>)] **3**. A single crystal grown from a *n*-hexane solution, was subjected to an X-ray crystallographic analysis. The molecular structure with atomic labelling is presented in Fig. 4. Selected bond parameters are given in Table 7. Cluster **3** consists of a closed triruthenium unit capped by a 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne ligand in a classical μ<sub>3</sub>-η<sup>2</sup> manner. This creates the *nido*-octahedral M<sub>3</sub>C<sub>2</sub> core geometry expected for this type of co-ordination. A hydroxycyclopentylethynyl moiety remains unco-ordinated to the triruthenium core and is essentially linear. The alkyne bond length C(18)–

**Table 7** Selected bond lengths (Å) and angles (°) for cluster **3**

Ru(1)–Ru(2)	2.735(2)	Ru(1)–Ru(3)	2.714(2)
Ru(2)–Ru(3)	2.815(1)	Ru(1)–C(16)	2.24(1)
Ru(1)–C(17)	2.26(1)	Ru(2)–C(16)	2.09(1)
Ru(3)–C(17)	2.07(1)	O(11)–C(15)	1.42(1)
C(11)–C(12)	1.54(3)	C(11)–C(15)	1.53(2)
C(12)–C(13)	1.45(2)	C(13)–C(14)	1.52(2)
C(14)–C(15)	1.50(2)	C(15)–C(16)	1.53(2)
C(16)–C(17)	1.39(2)	C(17)–C(18)	1.42(2)
C(18)–C(19)	1.21(2)	C(19)–C(20)	1.45(2)
C(14)–C(15)	1.47(2)	C(20)–C(24)	1.43(2)
C(21)–C(22)	1.63(3)	C(22)–C(23)	1.47(3)
Ru(1)–Ru(2)–Ru(3)	58.52(4)	Ru(2)–Ru(1)–Ru(3)	62.21(4)
Ru(1)–Ru(3)–Ru(2)	59.27(4)	C(17)–C(18)–C(19)	175(1)
C(18)–C(19)–C(20)	175(1)	C(16)–Ru(1)–C(17)	35.8(4)

**Fig. 4** Molecular structure of cluster **3**. Details as in Fig. 1.

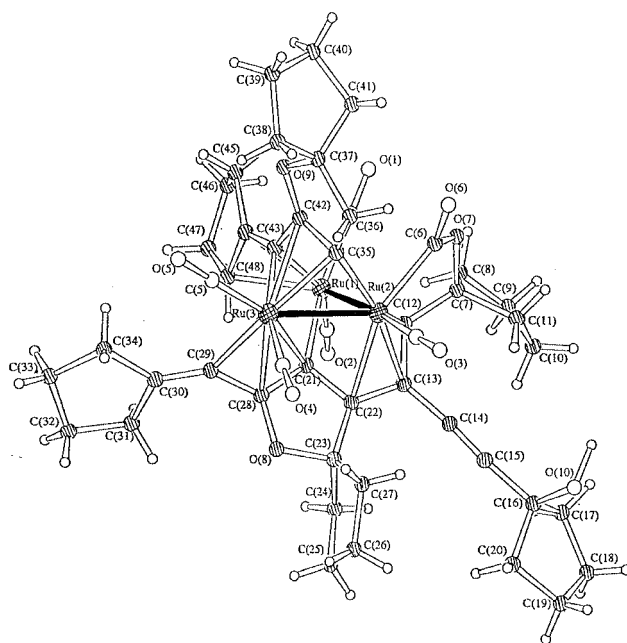
C(19) is 1.21(2) Å, typical of this type of bonds. The ruthenium unit is co-ordinated by nine terminally bound and a single asymmetrically bridging carbonyl ligand the latter being located on the Ru(2)–Ru(3) edge. The Ru-bound alkyne bond length, C(16)–C(17), shows a characteristic lengthening to 1.39(2) Å, as expected for a  $\mu_3$ - $\eta^2$  bound alkyne unit. In conclusion, the co-ordination mode observed in **3** is similar to those observed in the reaction products of dialkyl- and diaryl-acetylenes with activated derivatives of  $[\text{Ru}_3(\text{CO})_{12}]$ .<sup>46,47</sup> The spectroscopic data for compound **3** are fully consistent with the solid-state structure. An intense molecular ion peak at  $m/z$  802 is observed in the positive FAB mass spectrum. Its <sup>1</sup>H NMR spectrum shows two sets of multiplets in the range  $\delta$  1.68–2.00 for the sixteen methylene protons, but no hydroxyl signal is observed. Furthermore, the IR spectrum reveals six absorptions.

#### Thermal reaction of compound **1a** with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne

Treatment of compound **1a** with an excess of 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne in refluxing heptane solution generates a single brown product, **4**, in very low yield (5%). A large amount of unchanged **1a** and  $[\text{Ru}_3(\text{CO})_{12}]$  was also

**Table 8** Selected bond lengths (Å) and angles (°) for cluster **4**

Ru(1)–Ru(2)	2.744(5)	Ru(2)–Ru(3)	2.826(5)
Ru(1)–C(12)	2.19(4)	Ru(1)–C(21)	2.11(5)
Ru(1)–C(43)	2.204(4)	Ru(1)–C(44)	2.30(4)
Ru(1)–C(48)	2.33(4)	Ru(2)–C(6)	2.08(5)
Ru(2)–C(12)	2.07(4)	Ru(2)–C(22)	2.36(4)
Ru(2)–C(35)	2.06(4)	Ru(3)–C(28)	2.34(4)
Ru(3)–C(29)	2.17(5)	Ru(3)–C(35)	2.19(5)
Ru(3)–C(42)	2.35(5)	Ru(3)–C(43)	1.17(4)
O(6)–C(6)	1.21(6)	O(7)–C(6)	1.38(5)
O(9)–C(37)	1.51(5)	O(9)–C(42)	1.34(5)
C(35)–C(36)	1.51(6)	C(35)–C(42)	1.41(6)
C(42)–C(43)	1.42(6)	C(43)–C(44)	1.42(6)
C(44)–C(48)	1.42(6)		
Ru(1)–Ru(2)–Ru(3)	77.48(1)	C(44)–Ru(1)–C(48)	35.7(2)
C(43)–Ru(1)–C(44)	36.6(1)	C(42)–Ru(3)–C(43)	36.2(1)
C(35)–Ru(3)–C(42)	36.0(2)	C(6)–O(7)–C(7)	115.7(4)
O(6)–C(6)–O(7)	114.8(5)		

**Fig. 5** Molecular structure of cluster **4**. Details as in Fig. 1.

recovered. The molecular structure of compound **4** has been established by X-ray crystallography and is depicted in Fig. 5, together with the atomic numbering scheme. The important bond distances and angles are given in Table 8. The molecular structure reveals that coupling of one starting diyne ligand with **1a** occurs which gives rise to two discrete hydrocarbyl ligands with the loss of two water molecules. A salient structural feature is the direct coupling of one terminal carbonyl group and a OH substituent. This is evident from the IR spectrum which displays a band at 1760  $\text{cm}^{-1}$  due to the presence of a carboxylate group [C(6)–O(6) 1.21(6) and C(6)–O(7) 1.38(5) Å]. This compound is very similar to **1a** and the organic ligand is co-ordinated in a  $\mu_3$ - $\eta^2$ : $\eta^3$ : $\eta^3$  fashion to the Ru<sub>3</sub> open triangle, formally *via* two  $\sigma$  bonds Ru(1) [Ru(1)–C(12) 2.19(4), Ru(1)–C(21) 2.11(5) Å] and two  $\pi$ -allyl interactions with Ru(2) and Ru(3) [C(12)–C(13) 1.44(7), C(13)–C(22) 1.43(6), C(21)–C(28) 1.44(6), C(28)–C(29) 1.39(6) Å], respectively and acts as a nine electron donor. Another fragment, derived from C $\equiv$ C bond activation with intramolecular cyclisation of the starting diyne ligand, acts as a seven electron donor. This organic C<sub>5</sub> unit remains independently co-ordinated to the open ruthenium triangle in a  $\mu_3$ - $\eta^1$ : $\eta^3$ : $\eta^3$  mode to give a furyl ring derivative which is  $\sigma$  bonded to Ru(2) through C(35) [2.06(4) Å]. The C(36) atom exhibits a sp<sup>3</sup> centre due to hydrogen migration. Two fragments C(43)–C(44)–C(48) [1.42(6) Å] and C(35)–

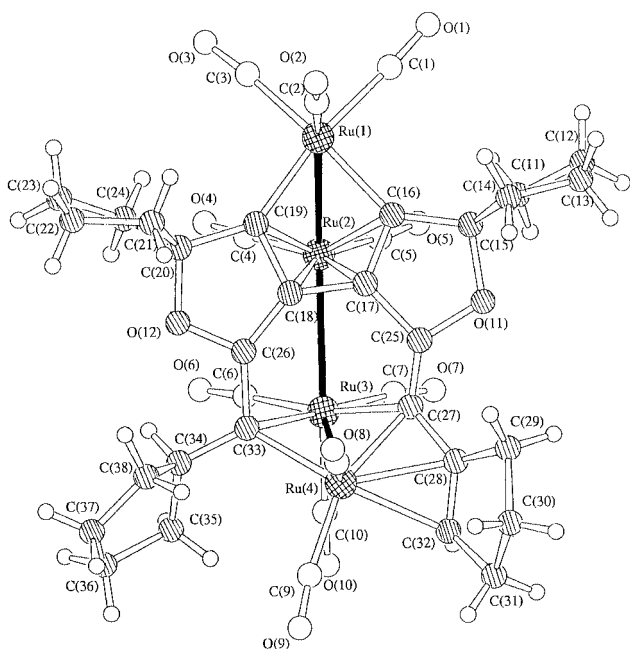


Fig. 6 Molecular structure of cluster 5. Details as in Fig. 1.

C(42)–C(43) [1.42(6) Å] form two  $\pi$ -allyl bonds to Ru(1) and Ru(3), respectively, based upon C–H activation within the open triangular ruthenium framework of 4, and the edge Ru(2)–Ru(3) [2.826(5) Å] is significantly longer than the Ru(1)–Ru(2) [2.744(5) Å]. The spectroscopic data for compound 4 are consistent with the solid-state structure. An intense molecular ion peak at  $m/z$  1089 is observed in the positive FAB mass spectrum. The two methylene protons on C(36), which are magnetically non-equivalent, give rise to two sets of doublets centred at  $\delta$  4.84 and 4.05 with a coupling constant  $J(\text{HH})$  15.5 Hz due to geminal coupling. The signal centred at  $\delta$  4.12 with  $J(\text{HH})$  6.5 Hz due to the methine proton on C(48) appears as a quartet due to overlap of the two triplets which is coupled to the non-equivalent methylene protons on C(47). Again, a rather complex pattern of overlapping multiplets due to twenty three methylene protons of the six cyclopentyl rings was observed in the range  $\delta$  0.87–3.23. The data are not sufficiently conclusive to allow a full characterisation of the actual positions of the six ring protons.

#### Thermal reaction of compound 2 with $[\text{Ru}_3(\text{CO})_{12}]$

Cluster 2 was refluxed in toluene with a slight excess of  $[\text{Ru}_3(\text{CO})_{12}]$  for 6 h to yield three products. The new component (10%) was recrystallised from a  $\text{CH}_2\text{Cl}_2$ –*n*-hexane solution to afford dark brown crystals of  $[\text{Ru}_4(\text{CO})_{10}(\mu_4\text{-}\eta^2\text{:}\eta^2\text{:}\eta^4\text{:}\eta^4\text{-C}_{28}\text{H}_{32}\text{O}_2)]$  5. The minor products were the known clusters  $[\text{Ru}_6(\text{CO})_{15}(\text{C}_6\text{H}_5\text{CH}_3)]$ <sup>48</sup> (12%) 6 and  $[\text{Ru}_6\text{H}(\text{CO})_{15}(\text{C}_5\text{H}_5)]$ <sup>49</sup> (9%) 7, respectively. A small amount of unchanged cluster 2 was also recovered. The formation of 6 is not surprising as it has frequently been isolated from the reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with toluene at elevated temperature. However, the isolation of 7 is totally unexpected. We could not explain the source of Cp in the reaction system except for the dissociation of the  $\text{C}_5\text{H}_8\text{OH}$  moiety from the 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiene ligand and then dehydration and dehydrogenation. Fig. 6 depicts the molecular structure of cluster 5 and selected bond parameters are shown in Table 9. The metal core is a bent  $\text{Ru}_4$  chain [Ru(1)–Ru(2)–Ru(3) 143.30(6), Ru(2)–Ru(3)–Ru(4) 119.09(5)°] in *syn* conformation which is similar to that found in  $[\text{Ru}_4(\mu\text{-Br})_2(\mu\text{-CO})(\text{CO})_8\{\mu\text{-C,P:P}(\text{C}_6\text{H}_4)\text{-PPhCH}_2\text{PPh}_2\}_2]$ .<sup>50</sup> The range of Ru–Ru bond lengths is 2.728(2)–2.986(2) Å. Notably the co-ordination mode of the organic ligand in 5 is very similar to that in cluster 2, except that one more Ru(4) atom is involved. One of the vinyl groups

Table 9 Selected bond lengths (Å) and angles (°) for cluster 5

Ru(1)–Ru(2)	2.792(2)	Ru(2)–Ru(3)	2.986(2)
Ru(3)–Ru(4)	2.728(2)	Ru(1)–C(16)	2.03(2)
Ru(1)–C(19)	2.02(2)	Ru(2)–C(16)	2.40(2)
Ru(2)–C(17)	2.18(2)	Ru(2)–C(18)	2.21(1)
Ru(2)–C(19)	2.33(2)	Ru(3)–C(27)	2.25(2)
Ru(3)–C(33)	2.37(2)	Ru(4)–C(27)	2.12(2)
Ru(4)–C(28)	2.24(1)	Ru(4)–C(32)	2.31(2)
Ru(4)–C(33)	2.15(2)	C(16)–C(17)	1.40(2)
C(17)–C(18)	1.45(2)	C(18)–C(19)	1.47(2)
O(11)–C(25)	1.40(2)	O(12)–C(20)	1.43(2)
C(17)–C(25)	1.50(2)	C(18)–C(26)	1.41(2)
C(25)–C(27)	1.30(2)	C(26)–C(33)	1.47(2)
Ru(1)–Ru(2)–Ru(3)	143.30(6)	Ru(2)–Ru(3)–Ru(4)	119.09(5)
C(16)–Ru(1)–C(19)	79.7(7)	C(16)–C(17)–C(18)	118(1)
C(17)–C(18)–C(19)	108(1)	C(18)–C(17)–C(25)	127(1)
C(17)–C(18)–C(26)	135(1)	C(27)–Ru(4)–C(33)	95.4(6)

attached to the  $\text{C}_5\text{H}_8$  ring and Ru(3) in 2 undergoes both C=C double bond and C–H bond activations to give a  $\eta^3$ -allyl group co-ordinated to the Ru(4) in 5 [C(27)–C(28) 1.44(2), C(28)–C(32) 1.35(2) Å]. The carbon atom C(33) of the other vinyl group, presumed to be the original carbon atom C(31) in 2, is given an alkyl bridging across the Ru(3)–Ru(4) edge followed by C=C double bond activation [Ru(3)–C(33) 2.37(2), Ru(4)–C(33) 2.15(2) Å]. Hydrogen migration also occurs to take up a hydrogen at C(34). Both carbon atoms, C(33) and C(34), exhibit a  $\text{sp}^3$  centre with a single bond length of C(33)–C(34) [1.48(2) Å]. Therefore cluster 5 becomes asymmetric. The organic ligand contributes a total of twelve electrons to the cluster 5. Assuming a negative charge residing on Ru(1) and Ru(4) respectively, cluster 5 contains 3 metal–metal bonds with 66 CVE which fits the EAN rule. The spectroscopic data for compound 5 are fully consistent with the solid-state structure. An intense molecular ion peak at  $m/z$  1085 is observed in the positive FAB mass spectrum. Its  $^1\text{H}$  NMR spectrum shows a series of multiplets in the range  $\delta$  1.35–2.87 for thirty-one protons of the four cyclopentyl rings. A downfield quartet signal centred at  $\delta$  3.00 with  $J(\text{HH})$  4.1 Hz is assigned to one proton on C(32), which is coupled to two magnetically non-equivalent methylene protons on C(31). Furthermore, its IR spectrum reveals four absorptions (Table 1).

#### Experimental

All the reactions were performed in an atmosphere of high purity nitrogen using standard Schlenk techniques. Analytical grade solvents were purified by distillation over the appropriate drying agents and in 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 using a Finnigan MAT 95 spectrometer,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra in  $\text{CDCl}_3$  on Bruker DPX 300 and DRX 500 instruments, referenced to internal  $\text{SiMe}_4$  ( $\delta$  0) and electronic absorption spectra in a microprocessor-controlled Perkin-Elmer UV/VIS spectrophotometer Lambda 3B, thermostatted by a Lauda circulating bath. The reactions were monitored by analytical thin-layer chromatography (5735 Kieselgel 60 F<sub>254</sub>, E. Merck) and the products separated on preparative thin-layer chromatographic plates coated with Merck Kieselgel 60 GF<sub>254</sub>. The compound 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiene obtained from Lancaster was used without further purification.

#### Synthesis

**Reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiene.** The compound  $[\text{Ru}_3(\text{CO})_{12}]$  (0.2 g, 0.31 mmol) was refluxed with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiene (0.07 g, 0.31 mmol) in chloroform (60 ml) for 45 min. The

**Table 10** Summary of crystal data and data collection parameters for clusters **1a**, **1b**, **2–5**

	<b>1a</b>	<b>1b</b>	<b>2</b>	<b>3</b>	<b>4</b>	<b>5</b>
Empirical formula	C <sub>36</sub> H <sub>34</sub> O <sub>11</sub> Ru <sub>3</sub> ·CHCl <sub>3</sub>	C <sub>36</sub> H <sub>34</sub> O <sub>11</sub> Ru <sub>3</sub> ·½C <sub>6</sub> H <sub>14</sub>	C <sub>36</sub> H <sub>32</sub> O <sub>10</sub> Ru <sub>3</sub>	C <sub>24</sub> H <sub>18</sub> O <sub>12</sub> Ru <sub>3</sub>	C <sub>48</sub> H <sub>49</sub> O <sub>10</sub> Ru <sub>3</sub> ·CH <sub>2</sub> Cl <sub>2</sub> ·C <sub>6</sub> H <sub>14</sub>	C <sub>38</sub> H <sub>32</sub> O <sub>12</sub> Ru <sub>4</sub>
<i>M</i>	1065.25	988.96	927.85	801.61	1260.23	1084.94
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)	<i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub> (no. 19)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)	<i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14)
<i>a</i> /Å	20.781(1)	11.692(1)	11.328(1)	9.453(1)	20.454(2)	11.876(1)
<i>b</i> /Å	9.115(1)	12.419(1)	20.565(2)	9.638(1)	10.328(1)	10.885(1)
<i>c</i> /Å	22.989(1)	28.936(1)	16.159(1)	30.759(1)	26.616(1)	29.792(2)
$\beta$ /°	109.62(2)	97.652(1)	109.09(2)	90	104.00(2)	94.05(2)
<i>U</i> /Å <sup>3</sup>	4101.7(7)	4211.3(6)	3557.3(7)	2802.4(3)	5455.67(7)	3841.6(5)
<i>Z</i>	4	4	4	4	4	4
$\mu$ (Mo-K $\alpha$ )/cm <sup>-1</sup>	13.42	11.29	13.14	16.56	9.73	16.05
No. reflections collected	35652	29565	5096	17710	39627	24583
No. unique reflections	6775	4635	4880	11378	10259	5555
No. observed reflections [ <i>I</i> > 3 $\sigma$ ( <i>I</i> )]	3076	2630	3077	1808	7423	2711
<i>R</i>	0.044	0.054	0.033	0.037	0.044	0.061
<i>R</i> '	0.048	0.052	0.034	0.044	0.047	0.068

solvent was removed *in vacuo* and the residue separated by TLC using dichloromethane–hexane (50:50 v/v) as eluent to afford three bands with *R<sub>f</sub>* values of 0.30, 0.35 and 0.80, respectively. The clusters **1a**, **1b** and **2** were isolated as solids in 10, 4 and 12% yields respectively (Found for **1a** C<sub>36</sub>H<sub>34</sub>O<sub>11</sub>Ru<sub>3</sub>: C, 45.52; H, 3.56. Calc.: C, 45.71; H, 3.63. Found for **1b** C<sub>36</sub>H<sub>34</sub>O<sub>11</sub>Ru<sub>3</sub>: C, 45.84; H, 3.49. Calc.: C, 45.71; H, 3.63. Found for **2** C<sub>36</sub>H<sub>32</sub>O<sub>10</sub>Ru<sub>3</sub>: C, 46.28; H, 3.28. Calc.: C, 46.60; H, 3.48%).

**Reaction of [Ru<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub>] with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne.** The compound [Ru<sub>3</sub>(CO)<sub>10</sub>(NCMe)<sub>2</sub>]<sup>51</sup> (0.085 g, 0.13 mmol) was stirred with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne (0.03 g, 0.13 mmol) in dichloromethane (60 ml) for 1 h at room temperature. 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 (30:70 v/v) as eluent to afford one band with *R<sub>f</sub>* 0.50. The cluster **3** was isolated as an orange solid in 30% yield (Found for C<sub>24</sub>H<sub>18</sub>O<sub>12</sub>Ru<sub>3</sub>: C, 36.08; H, 2.36. Calc.: C, 35.96; H, 2.27%).

**Thermolysis of compound 1a with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne.** The compound **1a** (0.02 g, 0.02 mmol) was refluxed with 1,4-bis(1-hydroxycyclopentyl)-1,3-butadiyne (0.005 g, 0.02 mmol) in heptane (30 ml) for 4 h. The solvent was removed *in vacuo* and the residue separated by TLC using dichloromethane–hexane (15:85 v/v) as eluent to afford one band with *R<sub>f</sub>* 0.65. The cluster **4** was isolated as a brown solid in 5% yield (Found for C<sub>48</sub>H<sub>49</sub>O<sub>10</sub>Ru<sub>3</sub>: C, 53.15; H, 4.70. Calc.: C, 52.94; H, 4.54%).

**Thermolysis of compound 2 with [Ru<sub>3</sub>(CO)<sub>12</sub>].** The compound **2** (0.024 g, 0.026 mmol) was refluxed with [Ru<sub>3</sub>(CO)<sub>12</sub>] (0.006 g, 0.026 mmol) in toluene (30 ml) for 6 h. The solvent was removed *in vacuo* and the residue separated by TLC using dichloromethane–hexane (15:85 v/v) as eluent to afford one band with *R<sub>f</sub>* 0.70, whereas the *R<sub>f</sub>* values of [Ru<sub>6</sub>C(CO)<sub>15</sub>-(C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>)] and [Ru<sub>6</sub>H(CO)<sub>15</sub>(C<sub>5</sub>H<sub>5</sub>)] are 0.55 and 0.30, respectively. The cluster **5** was isolated as a solid in 10% yield (Found for C<sub>19</sub>H<sub>16</sub>O<sub>6</sub>Ru<sub>2</sub>: C, 42.03; H, 2.84. Calc.: C, 42.06; H, 2.98%).

#### X-Ray data collection and structural determination of complexes **1a**, **1b** and **2–5**

Crystals of all new complexes suitable for X-ray analyses were mounted in Lindermann glass capillaries. Intensity data were collected at ambient temperature either on a MAR Research image plate scanner (for **1a**, **1b**, **3–5**) or an Enraf-Nonius CAD 4 diffractometer (for **2**) with graphite-monochromated Mo-K $\alpha$

radiation ( $\lambda = 0.71073$  Å) using  $\omega$  scan and  $\omega$ - $2\theta$  scan techniques, respectively. A summary of the crystallographic data and structure refinement is in Table 10. All intensity data were collected for Lorentz-polarisation effects. The  $\Psi$  scan method was employed for semiempirical absorption corrections for **2**, however, an approximation to absorption correction by inter-image scaling was applied for **1a**, **1b** and **3–5**. Scattering factors were taken from ref. 52(a) and anomalous dispersion effects<sup>52b</sup> were included in *F<sub>c</sub>*. The structures were solved by a combination of direct methods (SHELXS 86<sup>53</sup> for **1a**, **1b** and **2**; SIR 88<sup>54</sup> for **3–5**) 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). Atoms C(12) and C(13) in one of the cyclopentyl rings for structure **1b** had exceptionally large thermal parameters which were indicative of considerable positional disorder. Therefore, these two carbon atoms were modelled and refined with two alternative positions C(40) and C(41) respectively, and gave a significant improvement in subsequent refinement cycles. The absolute configuration of structure **3** was established by refining the Flack parameter to give a value 0.0095 for the reported configuration. All calculations were performed on a Silicon-Graphics computer, using the program package TEXSAN.<sup>55</sup>

CCDC reference number 186/1513.

See <http://www.rsc.org/suppdata/dt/1999/2511/> for crystallographic files in .cif format.

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