Arene–alkyne derivatives of $Ru_6C(CO)_{17}$: synthesis and structure of $Ru_6C(CO)_{12}(\eta^6\text{-arene})(\mu_3\text{-}C_2Me_2)$ (arene = $C_6H_{6-n}Me_n$, $n = 0\text{–}3$) and $Ru_6C(CO)_{12}(\mu_3\text{-}C_{16}H_{16})(\mu_3\text{-}C_2Me_2)$

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Abstract

The arene–alkyne clusters $Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_6)(\mu_3\text{-}C_2Me_2)$ 1, $Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_5Me)(\mu_3\text{-}C_2Me_2)$ 2, $Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)(\mu_3\text{-}C_2Me_2)$ 3, $Ru_6C(CO)_{12}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)(\mu_3\text{-}C_2Me_2) \cdot CH_2Cl_2$ 4 and $Ru_6C(CO)_{12}(\mu_3\text{-}C_{16}H_{16})(\mu_3\text{-}C_2Me_2) \cdot C_6H_5Me$ 5 have been prepared and characterised. The molecular structures of 1, 3, 4 and 5 have been established in the solid state by single crystal X-ray diffraction, and their crystallographic packing motifs analysed.

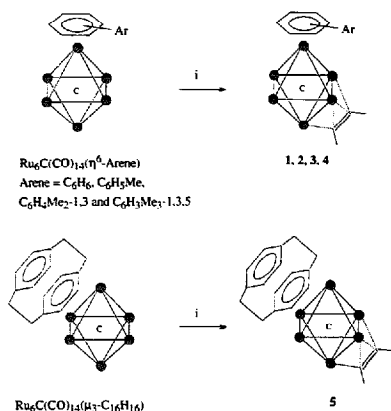*Keywords:* Ruthenium; Cluster; Arene; Alkyne

1. Introduction

The study of the synthesis and reactivity of transition metal carbonyl clusters with small organic molecules has received considerable attention in recent years; review articles of particular relevance to this paper are listed in Refs. [1,2]. In our work we have been particularly interested in the preparation of clusters with μ_3 face-capping arenes as well as the more common η^6 terminal bonding mode [2]; key papers include those listed in Refs. [3,4]. The underlying factors which govern the bonding mode adopted have also been explored, and it has been demonstrated that interchange between the two extreme bonding modes may be achieved, by thermal [5], photolytic [6] or chemical means [7]. These studies prompted us to examine the reactions of some hexaruthenium–arene clusters with alkynes, since the related reaction with the trinuclear cluster $M_3(CO)_9(\mu_3\text{-}C_6H_6)$ (M = Ru and Os) results in the migration of the benzene from the μ_3 to the η^6 terminal site [7].

2. Results and discussion

The method used to prepare the arene–alkyne clusters described in this paper involves the initial preparation of the arene cluster $Ru_6C(CO)_{14}(\eta^6\text{-arene})$, followed by the subsequent substitution of two of the 14 carbonyl ligands by the appropriate alkyne. The arene clusters $Ru_6C(CO)_{14}(\text{arene})$ (arene = C_6H_6, C_6H_5Me, $C_6H_4Me_2\text{-}1,3$ and $C_6H_3Me_3\text{-}1,3,5$) and $Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16})$ have been reported previously and were prepared by the literature methods [8,9]. The $C_{16}H_{16}$ ([2.2]paracyclophane) derivative differs from the others in the manner in which the arene bonds to the cluster. In this cluster coordination is over a trimetal face, whilst in the others the arene bonds to a single metal atom. The reactivity of these arene clusters towards a variety of ligands has previously been reported, and generally involves chemical activation by removal of CO as CO_2 using stoichiometric amounts of trimethylamine N-oxide (Me_3NO) [10,11]. Using this procedure alkynes can also be introduced into these clusters.

Treatment of $Ru_6C(CO)_{14}(\text{arene})$ with a 2 molar

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Ru$_6$C(CO)$_{14}$(η^6-Arene)
Arene = C$_6$H$_6$, C$_6$H$_5$Me,
C$_6$H$_4$Me$_2$-1,3 and C$_6$H$_3$Me$_3$-1,3,5

1, 2, 3, 4

Ru$_6$C(CO)$_{14}$(μ_3-C$_{16}$H$_{16}$)

5

Scheme 1. The synthesis of compounds 1–5. Reagents and conditions: (i) but-2-yne/2 equiv. Me$_3$NO in CH$_2$Cl$_2$.

equiv. of Me$_3$NO in the presence of but-2-yne results in the formation of Ru$_6$C(CO)$_{12}$(arene)(μ_3-C$_2$Me$_2$), in which two carbonyl ligands have been substituted by a face-capping dimethylalkyne ligand. By this route it was possible to prepare Ru$_6$C(CO)$_{12}$(η^6-C$_6$H$_6$)(μ_3-C$_2$Me$_2$) 1, Ru$_6$C(CO)$_{12}$(η^6-C$_6$H$_5$Me)(μ_3-C$_2$Me$_2$) 2, Ru$_6$C(CO)$_{12}$(η^6-C$_6$H$_4$Me$_2$-1,3)(μ_3-C$_2$Me$_2$) 3, Ru$_6$C(CO)$_{12}$(η^6-C$_6$H$_3$Me$_3$-1,3,5)(μ_3-C$_2$Me$_2$) 4 and Ru$_6$C(CO)$_{12}$(μ_3-C$_{16}$H$_{16}$)(μ_3-C$_2$Me$_2$) 5 in moderate yield (Scheme 1). Purification of these clusters was achieved chromatographically on silica using dichloromethane–hexane as eluent.

The spectroscopic data for compounds 1–5 are given in Table 1. The infrared spectra (ν_{CO}) of 1–4 are very similar, while that of 5 is quite different. This reflects the different bonding mode of the [2.2]paracyclophane ligand in 5 compared with the arene ligands in the remaining clusters. The mass spectra of all the compounds show parent peaks at values close to the calcu-

lated masses. Peaks corresponding to the sequential loss of several carbonyl ligands are also observed in all the spectra. The ^{1}H NMR spectra of compounds 1–5 contain peaks which may readily be assigned to the aromatic ring and the alkyne ligand. In each compound the face-capping dimethylalkyne ligand gives rise to a singlet resonance in the range 2.86–2.89 ppm for 1–4 and at 3.07 ppm for 5. The arene ligands in clusters 1–4 yield signals that are entirely consistent with those expected. In 5, the μ_3-[2.2]paracyclophane gives rise to four resonances at 7.45, 3.41, 3.30 and 2.79 ppm. The signal at 7.45 ppm is a singlet and corresponds to the C–H protons of the uncoordinated ring. The resonance at 3.41 ppm is also a singlet and may be assigned to the C–H protons of the μ_3-coordinated ring. The two other resonances are both multiplets and correspond to the CH$_2$ protons of the aliphatic bridges.

Compound 1 has also been prepared by an alternative route, in which the alkyne ligand is first introduced into the cluster followed by the introduction of the benzene ligand. Reaction of the previously reported cluster Ru$_6$C(CO)$_{15}$(μ_3-C$_2$Me$_2$) [12], with 2 molar equiv. of Me$_3$NO in the presence of cyclohexa-1,3-diene, results in the formation of 1 in moderate yield. Cyclohexa-1,3-diene as a precursor to benzene has been used in cluster chemistry on numerous occasions, and involves the initial coordination of the diene to the cluster unit followed by dehydrogenation to afford the coordinated benzene molecule [4].

In all known examples of clusters based on the Ru$_6$C skeleton, in which two arene ligands are present, the arenes either both adopt the η^6 bonding mode (two isomers) or one η^6 and one μ_3 bonding mode [13]. For the compounds described in this paper, the bonding mode adopted by the arene in the precursor does not undergo any alteration on replacement of the carbonyls by the incoming alkyne. In the light of previous studies this is not particularly surprising in the case of the simple arene clusters 1–4. However, in 5 both the [2.2]paracyclophane and alkyne ligands adopt μ_3 coordination modes. The reason for this is not certain, and migration of the μ_3-C$_{16}$H$_{16}$ ligand to a terminal bond-

Table 1
Spectroscopic data for compounds 1–5

| Compound	IR (CH$_2$Cl$_2$) ν(CO) (cm^{-1})	^{1}H NMR (CDCl$_3$) (ppm)	MS m/z
1	2057(m), 2019(s), 2011(s), 1996(s,br), 1958(w,br), 1938(vw)	5.79(s, 6H), 2.89(s, 6H)	1085 (1086)
2	2056(m), 2018(s), 2010(s), 1996(s,br), 1956(w,br)	5.82(m, 2H), 5.70(m, 3H), 2.88(s, 6H), 2.35(s, 3H)	1101 (1102)
3	2056(m), 2017(s), 2009(s), 1996(s,br), 1954(w,br), 1934(vw)	5.80(m, 2H), 5.72(m, 1H), 5.46(s, 1H), 2.88(s, 6H), 2.40(s, 6H)	1113 (1114)
4	2057(m), 2019(s), 2011(s), 1996(s,br), 1957(w,br), 1938(vw)	5.71(s, 3H), 2.39(s, 9H), 2.86(s, 6H)	1129 (1128)
5	2068(m), 2056(w), 2029(sh), 2017(vs), 2003(sh), 1984(w,br), 1940(v.br)	7.43(s, 4H), 3.41(s, 4H), 3.30(m, 4H), 3.07(s, 6H), 2.79(m, 4H)	1220 (1216)
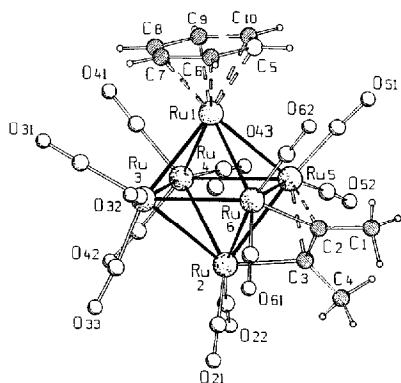
Fig. 1. The molecular structure of $Ru_6C(CO)_{12}(\eta^6-C_6H_6)(\mu_3-C_2Me_2)$ 1 in the solid state. The C atoms of the CO groups bear the same labelling as the corresponding O atoms.

ing site would have seemed likely, and followed the pattern established for other simpler arenes [11].

2.1. The molecular structure of clusters 1, 3, 4 and 5 in the solid state

The molecular structures of the species 1, 3, 4 and 5 are shown in Figs. 1–4 respectively. Relevant bond distances for compounds 1, 3 and 4 are listed in Table
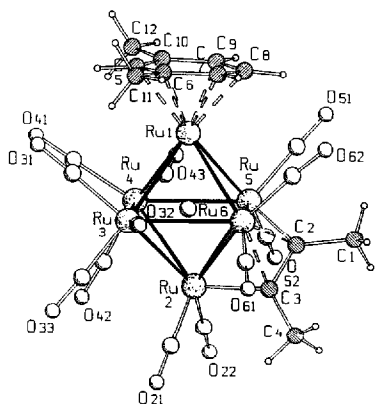

Fig. 2. The molecular structure of $Ru_6C(CO)_{12}(\eta^6-C_6H_4Me_2-1,3)(\mu_3-C_2Me_2)$ 3 in the solid state. The C atoms of the CO groups bear the same labelling as the corresponding O atoms.

Fig. 3. The molecular structure of $Ru_6C(CO)_{12}(\eta^6-C_6H_3Me_3-1,3,5)(\mu_3-C_2Me_2)$ 4 in the solid state. The C atoms of the CO groups bear the same labelling as the corresponding O atoms.

2, and those for 5 are listed in Table 3. The metal core of all the compounds comprises an octahedron encapsulating a carbido atom. In keeping with other Ru_6C species carrying a ligand which replaces all the carbonyl ligands on one metal atom, the Ru–C distance to this metal atom is shorter than the others. In the cases reported here, the Ru–C distance for the Ru atom interacting with the ring is, in structures 1, 3 and 4, shorter than the average Ru–C bond length of those remaining [1.956(5) vs. 2.051(6) Å in 1; 1.963(6) vs.

Fig. 4. The molecular structure of $Ru_6C(CO)_{12}(\mu_3-C_{16}H_{16})(\mu_3-C_2Me_2)$ 5 in the solid state. The C atoms of the CO groups bear the same labelling as the corresponding O atoms.
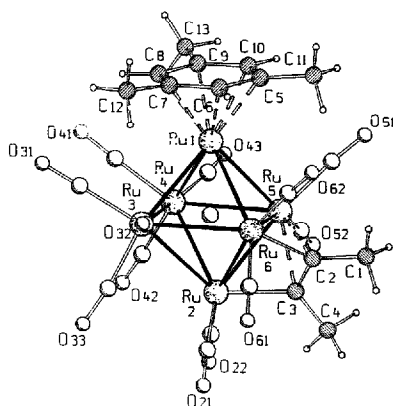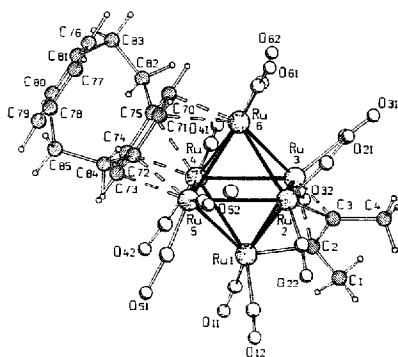
Table 2
Relevant bond lengths (Å) and angles (°) for compounds 1, 3 and 4

Ru(1)–Ru(3)	2.8667(6)	2.8852(6)	2.8792(6)
Ru(1)–Ru(4)	2.8734(6)	2.8636(6)	2.8629(6)
Ru(1)–Ru(5)	2.8785(6)	2.8476(6)	2.8985(6)
Ru(1)–Ru(6)	2.8746(6)	2.8876(6)	2.8607(6)
Ru(2)–Ru(3)	2.9384(6)	2.9118(6)	2.9273(6)
Ru(2)–Ru(4)	2.8762(6)	2.9388(6)	2.9289(6)
Ru(2)–Ru(5)	2.7881(6)	2.7942(6)	2.7607(6)
Ru(2)–Ru(6)	2.8112(6)	2.7764(6)	2.7957(5)
Ru(3)–Ru(4)	2.8534(6)	2.8301(6)	2.8553(6)
Ru(3)–Ru(6)	2.9740(6)	2.9728(6)	2.9760(6)
Ru(4)–Ru(5)	3.0132(6)	2.9521(6)	2.9216(6)
Ru(5)–Ru(6)	2.7677(6)	2.7949(6)	2.8138(6)
Ru(1)–C	1.956(5)	1.963(6)	1.956(5)
Ru(2)–C	2.039(5)	2.053(6)	2.059(5)
Ru(3)–C	2.030(6)	2.057(6)	2.010(5)
Ru(4)–C	2.061(6)	2.019(6)	2.061(5)
Ru(5)–C	2.090(6)	2.019(6)	2.089(5)
Ru(6)–C	2.035(6)	2.078(6)	2.027(5)
Ru(5)–C(2)	2.180(5)	2.054(6)	2.174(5)
Ru(6)–C(2)	2.076(5)	2.182(6)	2.064(6)
Ru(2)–C(3)	2.069(5)	2.067(5)	2.080(6)
Ru(5)–C(3)	2.182(5)		2.195(6)
Ru(6)–C(3)		2.198(6)	
Ru(1)–C(5)	2.215(5)	2.210(6)	2.264(6)
Ru(1)–C(6)	2.219(6)	2.263(6)	2.233(6)
Ru(1)–C(7)	2.234(6)	2.238(6)	2.246(6)
Ru(1)–C(8)	2.209(6)	2.190(6)	2.205(6)
Ru(1)–C(9)	2.216(6)	2.231(5)	2.251(6)
Ru(1)–C(10)	2.241(6)	2.274(6)	2.262(6)
C(1)–C(2)	1.501(7)	1.511(8)	1.490(8)
C(2)–C(3)	1.400(7)	1.395(8)	1.394(8)
C(3)–C(4)	1.499(8)	1.502(8)	1.494(8)
C(5)–C(6)	1.412(9)	1.412(8)	1.42(1)
C(5)–C(10)	1.387(9)	1.420(8)	1.41(1)
C(6)–C(7)	1.406(9)	1.416(8)	1.37(1)
C(7)–C(8)	1.412(9)	1.405(9)	1.43(1)
C(8)–C(9)	1.405(9)	1.417(9)	1.39(1)
C(9)–C(10)	1.413(9)	1.410(8)	1.401(9)
C(6)–C(11)		1.507(8)	
C(10)–C(12)		1.501(8)	
C(5)–C(11)			1.50(1)
C(7)–C(12)			1.50(1)
C(9)–C(13)			1.517(9)
C(100)–Cl(100)			1.738(7)
C(100)–Cl(101)			1.767(6)
mean Ru–C$_{CO}$	1.896(7)	1.896(6)	1.892(7)
mean C–O	1.143(7)	1.140(6)	1.140(8)
C(1)–C(2)–C(3)	124.0(5)	124.7(5)	124.5(5)
C(2)–C(3)–C(4)	124.1(5)	123.3(5)	124.8(5)
C(6)–C(5)–C(10)	120.7(5)	122.6(5)	118.4(6)
C(5)–C(6)–C(7)	120.2(6)	117.7(5)	122.1(6)
C(6)–C(7)–C(8)	119.3(6)	120.9(6)	118.1(6)
C(7)–C(8)–C(9)	119.8(5)	120.1(5)	121.3(6)
C(8)–C(9)–C(10)	120.8(6)	120.5(5)	119.1(6)
C(5)–C(10)–C(9)	119.2(6)	117.9(5)	120.8(6)
C(5)–C(6)–C(11)		122.2(5)	
C(7)–C(6)–C(11)		120.1(5)	
C(5)–C(10)–C(12)		121.3(5)	
C(9)–C(10)–C(12)		120.8(5)	
C(6)–C(5)–C(11)			129.0(7)

Table 2 (continued)

C(10)–C(5)–C(11)	121.3(7)
C(6)–C(7)–C(12)	120.7(7)
C(8)–C(7)–C(12)	121.1(7)
C(8)–C(9)–C(13)	120.7(6)
C(10)–C(9)–C(13)	120.2(6)
Cl(100)–C(100)–Cl(101)	112.4(4)

2.045(6) Å in 3; 1.956(5) vs. 2.049(5) Å in 4]. This is consistent with the arene ligand, which formally replaces a tricarbonyl unit on the metal, being a poorer π acceptor than the carbonyls, therefore necessitating an electronic compensatory effect in which the Ru–carbido bond distance is contracted. In 5, where the arene ligand

Table 3
Relevant bond distances (Å) and angles (°) for compound 5. All C$_6$ rings (including the toluene solvent C$_6$ ring) were treated as rigid hexagons with d(C–C) 1.39 Å

|			
Ru(1)–Ru(2)	2.816(4)	C(1)–C(2)–C(3)	123(3)
Ru(1)–Ru(3)	2.787(4)	C(2)–C(3)–C(4)	119(3)
Ru(1)–Ru(4)	2.898(4)		
Ru(1)–Ru(5)	2.996(4)	C(71)–C(72)–C(84)	116.5(7)
Ru(2)–Ru(3)	2.773(3)	C(73)–C(72)–C(84)	117.1(7)
Ru(2)–Ru(5)	2.939(5)	C(70)–C(75)–C(82)	117.1(6)
Ru(2)–Ru(6)	2.927(4)	C(74)–C(75)–C(82)	116.1(7)
Ru(3)–Ru(4)	2.950(4)	C(77)–C(78)–C(85)	117.5(7)
Ru(3)–Ru(6)	2.895(4)	C(79)–C(78)–C(85)	116.3(7)
Ru(4)–Ru(5)	2.892(3)	C(76)–C(81)–C(83)	115.9(7)
Ru(4)–Ru(6)	2.818(4)	C(80)–C(81)–C(83)	117.5(7)
Ru(5)–Ru(6)	2.904(4)	C(75)–C(82)–C(83)	111.7(8)
		C(81)–C(83)–C(82)	111.9(8)
Ru(1)–C	1.96(5)	C(72)–C(84)–C(85)	112.6(8)
Ru(2)–C	2.36(5)	C(78)–C(85)–C(84)	111.8(8)
Ru(3)–C	2.23(5)		
Ru(4)–C	1.70(5)	C(100)–C(101)–C(102)	114(2)
Ru(5)–C	1.97(5)	C(100)–C(101)–C(106)	126(2)
Ru(6)–C	2.17(5)		
Ru(1)–C(2)	2.04(3)		
Ru(3)–C(2)	2.15(3)		
Ru(2)–C(3)	2.01(3)		
Ru(3)–C(3)	2.18(3)		
Ru(4)–C(74)	2.30(2)		
Ru(4)–C(75)	2.40(2)		
Ru(5)–C(72)	2.15(2)		
Ru(6)–C(70)	2.24(2)		
C(1)–C(2)	1.55(5)		
C(2)–C(3)	1.46(5)		
C(3)–C(4)	1.52(5)		
C(72)–C(84)	1.61(1)		
C(75)–C(82)	1.61(1)		
C(78)–C(85)	1.60(1)		
C(81)–C(83)	1.60(1)		
C(82)–C(83)	1.53(1)		
C(84)–C(85)	1.53(1)		
C(100)–C(101)	1.51(2)		
mean Ru–C$_{CO}$	1.89(3)		
mean C–O	1.15(4)		
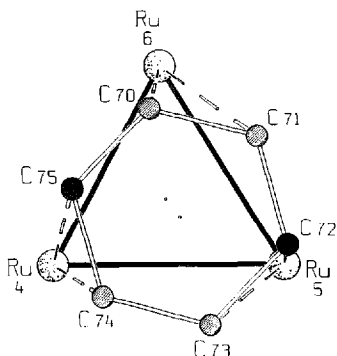
Fig. 5. Projection of the [2.2]paracylophane coordination plane in 5 showing the deviation from the eclipsing of the C=C midpoints over the Ru atoms. The remaining atoms of the cluster have been omitted for clarity. Black C atoms are those connected to the aliphatic chains.

replaces a CO ligand on each of three different Ru atoms about a triangular face, no displacement of the interstitial carbon atom in the direction of the metal face

is noted; a short distance is observed between the carbide and Ru(4), but this value has to be taken with caution due to the low quality of the data. In each structure the Ru–Ru bond lengths corresponding to the edges involved in the coordination of the alkyne fragment are shorter by about 0.1 Å with respect to the other Ru–Ru distances. Whether this is an effect of the steric constraints imposed by the μ_3-bridging ligand on the flexible Ru–Ru vectors or has electronic origins is not clear.

The coordination of the alkyne ligand to the cluster face involves the μ_3 bonding mode which is commonly observed in systems of this type and comprises one π interaction from the unsaturated bond to one Ru atom and two σ bonds to the remaining Ru atoms of the face. As usual, this results in an elongation of the C=C bond, ranging from 1.394(8)–1.400(7) Å in 1, 3 and 4 and with a value of 1.46(5) Å in 5. The elongation of the C=C bond is accompanied by bending of the methyl groups away from the cluster unit, with angles ranging from 123.3(5)–124.8(5)° in 1, 3 and 4 and angles of 123(3) and 119(3)° in 5. All the carbonyl ligands in structures 1, 3, 4 and 5 are terminally bound. The CO envelopes in clusters 1, 3 and 4 are very similar, although small conformational changes can be observed depending on the number of substituents on the rings.

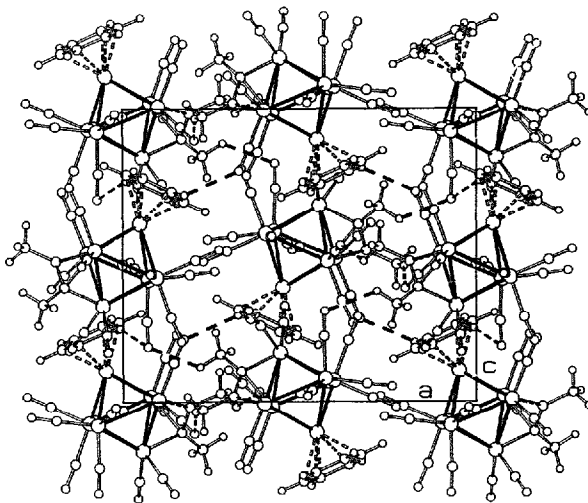Fig. 6. View down the b-axis in crystalline 1, showing the most relevant C–H · · · O hydrogen bonding interactions (C–H · · · O distances < 2.70 Å).
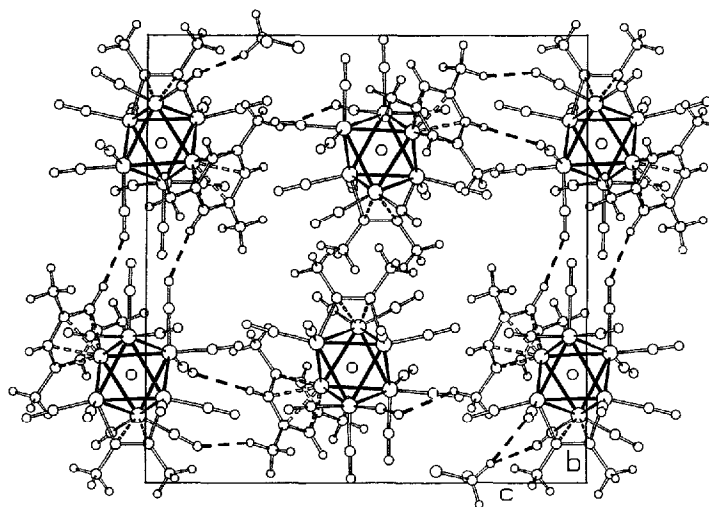
Fig. 7. View down the *a*-axis in crystalline **4**, showing the most relevant C–H · · · O hydrogen bonding interactions (C–H · · · O distances < 2.70 Å).

In **5**, the [2.2]paracyclophane ligand adopts a μ_3 bonding mode. A similar bonding arrangement has been observed for the majority of [2.2]paracyclophane clusters prepared to date [14,15]. The marked tendency for this ligand to adopt a face-bridging coordination mode compared with other arenes is apparent from the arene derivatives of the hexaruthenium carbido cluster $Ru_6C(CO)_{14}$(arene), in which the arene bonds in the η^6 mode [9].

In comparison with other facially coordinated six-membered rings, the midpoints of alternating C–C bonds in the coordinated ring of the [2.2]paracyclophane ligand are, to first approximation, eclipsed over the three Ru atoms. On close inspection, the coordinated ring shows a certain degree of torsion with respect to the underlying Ru_3 triangle (see Fig. 5), accompanied by a Ru–C(ring) distribution spread over a wide range of distances. The deviation from exact eclipsing can be viewed as the effect of the ligand rotation by 15° around an axis perpendicular to the Ru(4)–Ru(5)–Ru(6) plane and passing through Ru(4). The two bridgehead C atoms lie above the plane of the remaining four. Since NMR spectroscopy shows that the ligand is free to rotate in solution at ambient temperature, the conformational flexibility observed in the solid state is likely to arise from intermolecular forces acting on the [2.2]paracyclophane ligand which protrudes from the CO envelope. Deviation from a quasi-eclipsing confor-

mation of the paracyclophane ligand has been observed before [14]. Such variation in the orientation of face-capping benzene ligands, on the contrary, has not been

Table 4
Intermolecular C–H · · · O hydrogen bonding parameters for crystalline **1**, **3**, **4** and **5**. C–H distances have been normalised to the neutron value of 1.08 Å: H · · · O distances are given in angstroms, C–H · · · O and H · · · O–C$_{CO}$ angles in degrees

| Compound	C–H · · · O	H · · · O	C–H · · · O	H · · · O–C$_{CO}$
1	C1–H1 · · · O52	2.53	124	147
	C1–H1 · · · O61	2.40	154	114
	C4–H4 · · · O33	2.48	128	111
	C6–H6 · · · O33	2.67	155	126
	C7–H7 · · · O21	2.62	148	135
	C9–H9 · · · O62	2.65	120	133
3	C1–H1 · · · O32	2.52	133	160
4	C8–H8 · · · O41	2.63	141	156
	C6–H6 · · · O43	2.63	159	133
	C12–H12 · · · O52	2.59	158	150
	C11–H11 · · · O33	2.54	127	111
	C100–H100 · · · O51	2.68	152	166
	C100–H100 · · · O61	2.67	138	129
5	C77–H77 · · · O32	2.48	147	139
	C71–H71 · · · O41	2.56	155	140
	C84–H84 · · · O62	2.50	147	148
	C74–H74 · · · O52	2.58	149	165
	C82–H82 · · · O52	2.42	163	125
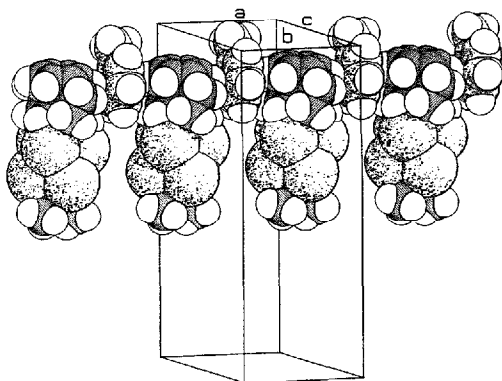
Fig. 8. Molecules arranged in piles in crystalline 5 along the a-axis; the arene clusters are intercalated along the pile by toluene solvent molecules. CO ligands have been omitted for clarity.

observed, despite the large number of species structurally characterised.

2.2. The crystal structures of 1, 3, 4 and 5

Previously, it has been noted that bis(arene) derivatives of the hexaruthenium carbido cluster $Ru_6C(CO)_{14}(arene)_2$ exhibit intermolecular graphite-like interactions involving adjacent ring systems [16]. This packing motif has not been observed in the mono(arene) derivatives, where the molecules are usually organised in the crystals in piles, with the arene planes facing a tricarbonyl unit of a neighbouring molecule; a second structural feature also found in these mono(arene) clusters involves the interlocking of the unique bridging carbonyl into the tetragonal cavity on the opposite edge of one of the surrounding molecules [9]. In compounds

1–5 the presence of alkyl substituents and the absence of bridging ligands are responsible for different packing arrangements with respect to those previously observed. The relative orientation of the molecules in the crystal is not easy to rationalise, but it can be seen that intermolecular hydrogen bonding interactions of C–H ··· O type are abundant (especially in solid 1 and 4, see Figs. 6 and 7 respectively), and contribute to the stabilisation of the crystalline edifice. It is interesting to note that in compound 4 also the hydrogen atoms belonging to the solvent molecule are involved in hydrogen bonding interactions (see Fig. 7). Relevant hydrogen bonding parameters are shown in Table 4. A hydrogen bonding network is also present in crystalline 5, and the relative geometrical parameters are listed in Table 3. The most striking feature of the molecular packing of compound 5 though is the existence of piles of cluster molecules
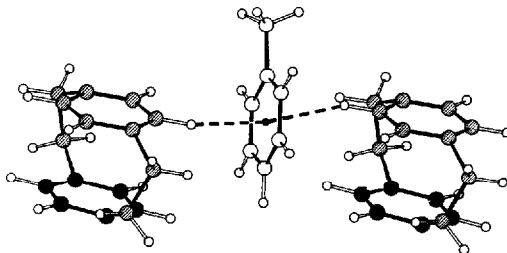

Fig. 9. Intermolecular C–H ··· π interactions (dashed lines) in crystalline 5 between CH groups belonging to the uncoordinated ring of [2.2]paracyclophane and the electron density of the π system (represented by a black spot in the geometrical midpoint of the toluene C_6 ring) of the toluene molecule. Filled C atoms represent the paracyclophane C_6 rings coordinated to the metal cluster.

along the *a*-axis of the unit cell. As can be seen in Fig. 8, the cluster molecules are intercalated by toluene solvent molecules, which are placed perpendicular to the direction of the piles. An explanation for this kind of arrangement can be found in a closer inspection of the interaction between the paracyclophane ligands and the toluene molecules. Fig. 9 shows how two opposite C–H groups, belonging to the uncoordinated C_6 rings of the paracyclophane ligands, interact via C–H $\cdots$ π interactions of 2.60 Å, with the electron density of the π system of the toluene C_6 ring. This is a well known hydrogen bonding interaction in both organic and organometallic systems [17], although examples in the organometallic field are not common.

3. Experimental

All reactions were carried out using freshly distilled solvents under an atmosphere of nitrogen. Subsequent purification of products was carried out using standard laboratory grade solvents without precautions taken to exclude air. Infrared spectra were recorded on a Perkin–Elmer 1710 Fourier-Transform instrument. Mass spectra were obtained by positive fast atom bombardment on a Kratos MS50TC. ^{1}H NMR spectra were recorded using a Bruker WM200 spectrometer. The clusters $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_6)$, $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me)$, $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_4Me_2\text{-}1,3)$, $Ru_6C(CO)_{14}(\eta^6\text{-}C_6H_3Me_3\text{-}1,3,5)$ and $Ru_6C(CO)_{14}(\mu_3\text{-}C_{16}H_{16})$ were prepared according to literature methods [8,9]. Trimethylamine–*N* oxide (Me_3NO), but-2-yne (C_2Me_2) and cyclohexa-1,3-diene ($1,3\text{-}C_6H_8$) were purchased from Aldrich chemicals. Me_3NO was dried and then sublimed prior to use.

3.1. Reaction of $Ru_6C(CO)_{14}(arene)$ with C_2Me_2 and 2 equiv. Me_3NO: synthesis of $Ru_6C(CO)_{12}(arene)(\mu_3\text{-}C_2Me_2)$ 1–5

In a typical reaction the arene cluster $Ru_6C(CO)_{14}(arene)$ (85 mg) was dissolved in CH_2Cl_2 (50 ml) and then cooled to $-78\,°C$. An excess of C_2Me_2 (1 ml) was added, followed by the dropwise addition of Me_3NO (2.2 molar equiv.) in CH_2Cl_2 (5 ml) over a 5 min period. The solution was allowed to warm to

Table 5
Crystal data and details of measurements for compounds 1, 3, 4 and 5 at 150 K

	1	3	4	5
Formula	$C_{23}H_{12}O_{12}Ru_6$	$C_{25}H_{16}O_{12}Ru_6$	$C_{27}H_{20}C_{12}O_{12}Ru_6$	$C_{40}H_{30}O_{12}Ru_6$
Formula weight	1086.76	1114.81	1213.77	1309.09
Crystal system	orthorhombic	orthorhombic	monoclinic	monoclinic
Space group	$P2_12_12_1$	$Pna2_1$	$P2_1/n$	$P2_1/n$
a (Å)	13.020(2)	14.312(4)	9.981(3)	9.784(6)
b (Å)	13.647(3)	14.368(4)	18.419(5)	26.16(1)
c (Å)	15.751(3)	14.259(4)	18.363(7)	16.016(5)
β (°)	—	—	96.820(5)	97.660
Volume (Å^3)	2798.8	2932.2	3352.0	4062.24
Z	4	4	4	4
Calc. density (g cm^{-3})	2.58	2.53	2.41	2.14
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073	0.71073
μ(Mo Kα) (mm^{-1})	3.16	3.01	2.81	2.20
Absorption correction	psi-scan	psi-scan	psi-scan	DIFABS
(min.–max. transmission)	0.250–0.298	0.299–0.327	0.284–0.350	(min.–max. correction 0.697–1.266)
$F(000)$	2006.27	2070.28	2271.34	2486.35
Crystal size (mm^3)	$0.30 \times 0.25 \times 0.20$	$0.31 \times 0.19 \times 0.19$	$0.50 \times 0.30 \times 0.25$	$0.58 \times 0.23 \times 0.12$
θ range (°)	2.5–22.25	2.5–30.0	2.5–22.5	2.5–22.5
Index ranges	$-5 < h < 14$	$-1 < h < 20$	$-10 < h < 10$	$-10 < h < 10$
	$-14 < k < 14$	$-1 < k < 20$	$0 < k < 19$	$0 < k < 28$
	$0 < l < 16$	$-1 < l < 20$	$0 < l < 19$	$0 < l < 17$
Reflections collected	3282	6761	4356	5473
Independent reflections	2064	4612	4159	4362
Independent reflections used in refinement	1996	4338	3719	2408
Refined parameters	372	390	425	272
Conventional R ($I > 2\sigma(I)$)	0.0154	0.0272	0.0384	0.1164
Goodness of fit	1.145	1.126	1.062	1.187

room temperature over 30 min. The solvent was removed in vacuo and the residue purified by TLC eluting with CH_2Cl_2–hexane (1:4, v/v). The product was extracted together with some starting material. Yields were as follows: $Ru_6C(CO)_{12}(\eta^6-C_6H_6)(\mu_3-C_2Me_2)$ **1** (40%); $Ru_6C(CO)_{12}(\eta^6-C_6H_4Me)(\mu_3-C_2Me_2)$ **2** (43%); $Ru_6C(CO)_{12}(\eta^6-C_6H_4Me_2-1,3)(\mu_3-C_2Me_2)$ **3** (32%); $Ru_6C(CO)_{12}(\eta^6-C_6H_3Me_3-1,3,5)(\mu_3-C_2Me_2)$ **4** (39%); $Ru_6C(CO)_{12}(\mu_3-C_{16}H_{16})(\mu_3-C_2Me_2)$ **5** (38%). Spectroscopic data for compounds **1–5** are listed in Table 1.

3.2. Reaction of $Ru_6C(CO)_{15}(\mu_3-C_2Me_2)$ with 1,3-C_6H_8 and 3 equiv. Me_3NO: synthesis of $Ru_6C(CO)_{12}(\eta^6-C_6H_6)(\mu_3-C_2Me_2)$ 1

The cluster $Ru_6C(CO)_{15}(\mu_3-C_2Me_2)$ (75 mg, 0.077 mmol) was dissolved in CH_2Cl_2 (50 ml) and then cooled to $-78\,^\circ C$. An excess of 1,3-C_6H_8 (1 ml) was added, followed by the dropwise addition of Me_3NO (16 mg, 0.206 molar equiv.) in CH_2Cl_2 (5 ml) over a 5 min period. The solution was allowed to warm to room temperature over 30 min. The solvent was removed in vacuo and the residue purified by TLC eluting with CH_2Cl_2–hexane (1:4, v/v). The product was extracted and characterised spectroscopically as $Ru_6C(CO)_{12}(\eta^6-C_6H_6)(\mu_3-C_2Me_2)$ **1** (28%).

3.3. Solid state characterisation of 1, 3, 4 and 5

Crystals of **1** and **4** were grown by the slow diffusion of a CH_2Cl_2–hexane layer at $-25\,^\circ C$. Crystals of **3** were grown from a solution of CH_2Cl_2–hexane at $-25\,^\circ C$. Compound **5** was crystallised from the slow evaporation of a solution of CH_2Cl_2–hexane. Single crystals of **2** were grown by the slow diffusion of a CH_2Cl_2–hexane layer at $-25\,^\circ C$, while X-ray data was collected; the data and resulting structure is of poor quality and not suitable for publication.

Diffraction data were collected on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low temperature device operating at 150 K. The crystal structures of **1**, **3**, **4** and **5** were solved by direct methods (SIR92 [18] or SHELXS [19]) and refined by full-matrix least-squares (CRYSTALS [20]). Hydrogen atoms were placed in calculated positions and re-idealised after successive refinement cycles. For **1**, **3** and **4** all non-H atoms were refined with anisotropic displacement parameters, but the rather low data quality obtained for **5** only allowed the Ru atoms to be so refined; other atoms were refined with common sets of isotropic thermal parameters, phenyl rings being modelled as rigid hexagons. Full cell and refinement data are presented in Table 5.

Crystals of **2** were obtained during this study, and were shown to have unit cell dimensions $a = 9.882(7)$, $b = 16.671(13)$, $c = 36.950(4)\,\text{Å}$, $\beta = 91.08(7)^\circ$, space group $P2_1/c$. While analysis of the diffraction data established the chemical formulation as $Ru_6C(CO)_{12}(\eta^6-C_6H_4Me)(\mu_3-C_2Me_2) \cdot xCH_2Cl_2$, with a structure similar to those of **1**, **3** and **4**, the very low data quality precluded further description of this structure.

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