

Hexanuclear and pentanuclear benzene carbido clusters: synthesis, characterisation and molecular structures of $[\text{Os}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$, $[\text{RuOs}_5\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$ and $[\text{RuOs}_4\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)]$

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Abstract

Reaction of the pentaosmium-carbido dianion $[\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}$ **1** with $[\text{Os}(\text{C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$ gave $[\text{Os}_6\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$ **2** in fair yield; while the corresponding reaction with $[\text{Ru}(\text{C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$ gave $[\text{RuOs}_5\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$ **3** in moderate yield. Treatment of **3** with carbon monoxide produces an unstable species $[\text{RuOs}_5\text{C}(\text{CO})_{15}(\eta^6\text{-C}_6\text{H}_6)]$ **4a**, which on standing in CH_2Cl_2 undergoes fragmentation to give the species $[\text{RuOs}_4\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)]$ **4b** or decarbonylation to **3**. Clusters **2**, **3** and **4b** have been fully characterised by both spectroscopic and crystallographic methods. The X-ray structure analysis shows that both **2** and **3** are isomorphous. Both molecules contain an octahedral cavity accommodating an interstitial C(carbido) atom, with the $\eta^6\text{-C}_6\text{H}_6$ coordinated to the Ru or Os atom in an apical position. Cluster **4b** is an unprecedented pentanuclear osmium–ruthenium mixed-metal carbido cluster containing an η^6 -coordinated benzene ligand.

Keywords: Osmium; Cluster; Arene; Carbido

1. Introduction

Organometallic compounds containing arene moieties are currently attracting considerable attention, because arenes readily form complexes with a wide range of clusters [1–8]. In particular, much attention has been focused on the transformations that organic moieties undergo when coordinated to the hexanuclear cluster metal framework [9]. Following initial reports by Lewis, Johnson and coworkers on the synthesis and structural characterisation of the first arene cluster compounds $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-arene})]$, where arene = C_6H_6 , $\text{C}_6\text{H}_5\text{Me}$, $\text{C}_6\text{H}_4\text{Me}_2$ -1,3 and $\text{C}_6\text{H}_3\text{Me}_3$ -1,3,5, prepared in low yield by heating $[\text{Ru}_3(\text{CO})_{12}]$ with the arene [9–11], came reports of the preparation and X-ray analysis of an extended range of arene derivatives obtained from alternative synthetic routes [12,13].

Although both osmium and ruthenium belong to the iron triad, they form a number of isostructural carbonyl clusters with a variety of nuclearities. The different balance of M–M and M–CO bond strengths for the two metals lead to many clusters with geometries/stoichiometries which are unique to either metal and, in

addition, synthetic routes to clusters of the two metals often differ widely. The existence of an osmium cluster does not therefore guarantee the existence of, or a synthetic route to, its ruthenium analogue and vice versa. For example, thermolysis of $[\text{Ru}_3(\text{CO})_{12}]$ in *n*-octane leads to formation of the hexanuclear carbido-cluster $[\text{Ru}_6\text{C}(\text{CO})_{17}]$; surprisingly, no $[\text{Os}_6\text{C}(\text{CO})_{17}]$ is obtained from $[\text{Os}_3(\text{CO})_{12}]$ pyrolysis [11]. Therefore, the ruthenium carbido carbonyl cluster $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ has no osmium analogue.

In fact, the hexaruthenium–carbido system has been extensively developed. However, the chemistry of osmium in this area has remained untouched, largely because of its low availability.

In this paper, we report studies of the reactions between the pentaosmium carbido cluster $[\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}$ with $[\text{M}(\text{C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$ (M = Os, Ru) to form hexanuclear carbido benzene derivatives. In addition, a new pentanuclear ruthenium–osmium carbido cluster is reported.

2. Results and discussion

The capping reaction of a metal complex fragment with a preformed pentanuclear cluster to give a sixth

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vertex is a rational way to form a hexanuclear cluster, but it is really only useful if the pentanuclear cluster itself is relatively accessible synthetically. The advantage of using such a capping procedure is that the added fragment may contain a specific organic ligand, which provides a very selective way of forming a cluster hydrocarbyl derivative [14].

Treatment of the pentanuclear carbido cluster $[\text{Os}_5\text{C}(\text{CO})_{15}]$ with $[\text{Na}_2\text{CO}_3]$ in MeOH at ambient temperature, followed by addition of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$, leads to the precipitation of an air-stable cluster dianion $[\text{N}(\text{PPh}_3)_2]_2[\text{Os}_5\text{C}(\text{CO})_{14}]$ **1**. Our synthesis of compounds **2** and **3** was developed by analogy to the ionic coupling reaction used to prepare $[\text{Ru}_6\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_6)]$ [8]. That is, by reaction of **1** with 1 equivalent of $[\text{M}(\text{C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$ ($\text{M} = \text{Os}, \text{Ru}$) to give the benzene cluster derivatives **2** and **3** respectively in moderate yields.

The benzene cluster **2** is analogous to **3**, and their spectroscopic data (IR, ^1H NMR and mass) are summarised in Table 1. Both IR and ^1H NMR data of **2** and **3** show a close resemblance to those clusters of the type $[\text{Ru}_6\text{C}(\text{CO})_{14}(\eta^6\text{-arene})]$ [1,8]. They have very similar solution IR spectral patterns in the carbonyl-stretching absorption region. The ^1H NMR spectra of both compounds consist of a singlet in the region δ 5.4 to 5.6, indicating the presence of an η^6 -terminally bound benzene ligand. This is consistent with the solid-state structures.

The molecular structures of both complexes **2** and **3** have been established by X-ray structural analyses. Since their dichloromethane solutions slowly decompose in air to give some insoluble brown precipitate, single crystals of **2** and **3** suitable for diffraction experiments were grown by slow evaporation of *n*-hexane/ CH_2Cl_2 solution at -20°C under argon over a period of several days. X-ray analyses of **2** and **3** reveal

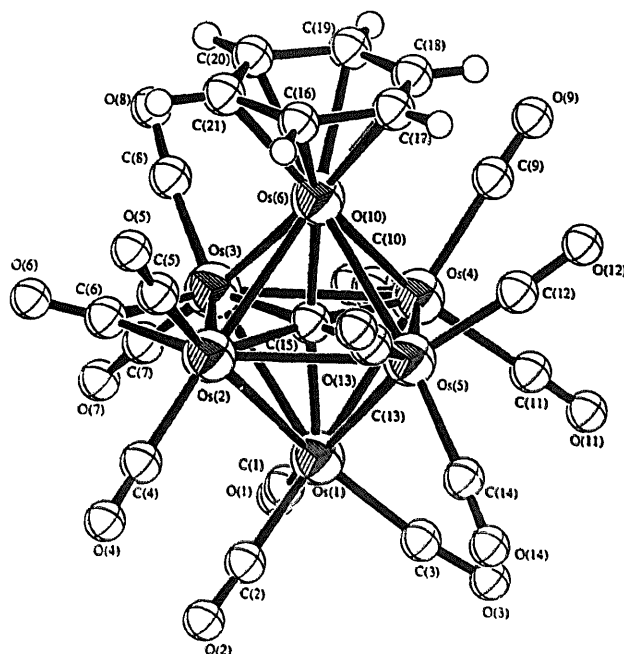


Fig. 1. The molecular structure of the complex $[\text{Os}_6\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_6)]$ **2** with the atomic numbering scheme.

that their crystal structures are isomorphous. Their molecular structures are closely related and will be discussed together. Perspective views of the complexes, together with the atomic labelling schemes, are shown in Figs. 1 and 2 respectively, selected bond distances and angles are listed in Tables 2 and 3. Both complexes possess the familiar hexanuclear cluster core present in $[\text{Ru}_6\text{C}(\text{CO})_{17}]$ [15,16] and its derivatives, in which the octahedral cavity accommodates the interstitial C(carbide) atom. It is interesting to note that the Os_6C core is unprecedented in **2**. Both **2** and **3** possess 14 carbonyl ligands, with one bridging CO position along one edge of the molecular equator, while the remaining

Table 1
Spectroscopic data for the clusters $[\text{Os}_6\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_6)]$ **2**, $[\text{RuOs}_5\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_6)]$ **3**, and $[\text{RuOs}_4\text{C}(\text{CO})_{12}(\text{C}_6\text{H}_6)]$ **4b**

Compound	IR (ν_{CO} , cm^{-1}) ^a	^1H NMR (δ , ppm) ^b	MS (m/z) ^{c,d}
2	2084 vs, 2044 s, 2033 s, 2019 s, 1991 m, 1952 w, 1782 w, br	5.49 (s, 6H)	1624 (1624)
3	2084 vs, 2044 s, 2032 s, 2020 s, 1991 m, 1952 w, 1782 w, br	5.66 (s, 6H)	1536 (1536)
4b	2084 vs, 2054 s, 2042 m, 2016 vs, 1998 m, 1980 w	5.98 (s, 6H)	1288 (1288)

^a Spectrum taken in *n*-hexane.

^b Spectrum taken in CD_2Cl_2 with TMS as internal reference.

^c Negative FAB-MS.

^d Simulated values in parentheses.

Table 2
Selected bond distances (Å) and angles (°) for complex 2

<i>Bond distances</i>			
Os(1)–Os(2)	2.980(3)	Os(1)–C(15)	2.11(4)
Os(1)–Os(3)	2.977(3)	Os(2)–C(15)	2.07(4)
Os(1)–Os(4)	2.862(3)	Os(3)–C(15)	2.05(4)
Os(1)–Os(5)	2.931(3)	Os(4)–C(15)	2.12(4)
Os(2)–Os(3)	2.835(3)	Os(5)–C(15)	2.13(4)
Os(2)–Os(5)	2.990(2)	Os(6)–C(15)	1.93(4)
Os(2)–Os(6)	2.899(2)	Os(6)–C(16)	2.20(4)
Os(3)–Os(4)	3.047(3)	Os(6)–C(17)	2.31(4)
Os(3)–Os(6)	2.892(2)	Os(6)–C(18)	2.28(5)
Os(4)–Os(5)	2.957(2)	Os(6)–C(19)	2.31(5)
Os(4)–Os(6)	2.885(2)	Os(6)–C(20)	2.29(5)
Os(5)–Os(6)	2.833(2)	Os(6)–C(21)	2.25(5)
C(16)–C(21)	1.52(6)	C(16)–C(17)	1.45(6)
C(17)–C(18)	1.32(5)	C(18)–C(19)	1.43(6)
C(19)–C(20)	1.49(7)	C(20)–C(21)	1.44(6)
<i>Bond angles</i>			
Os(1)–Os(3)–Os(2)	61.63(6)	Os(1)–Os(3)–Os(6)	86.86(6)
Os(2)–Os(3)–Os(6)	60.82(6)	Os(1)–Os(4)–Os(3)	60.41(6)
Os(1)–Os(4)–Os(6)	89.20(7)	Os(1)–Os(3)–Os(4)	56.72(6)
Os(2)–Os(3)–Os(4)	90.56(7)	Os(4)–Os(3)–Os(6)	58.06(6)
Os(1)–Os(4)–Os(5)	60.46(6)	Os(3)–Os(4)–Os(5)	88.29(7)
Os(1)–Os(5)–Os(2)	60.41(6)	Os(1)–Os(5)–Os(6)	88.85(7)
Os(6)–Os(2)–C(15)	41(1)	Os(6)–Os(3)–C(15)	43(1)
Os(6)–Os(4)–C(15)	41(1)	Os(6)–Os(5)–C(15)	42(1)

13 CO ligands show different degrees of symmetry and bonding in the two crystal lattices. A comparison of some relevant structural parameters is also noteworthy.

The metal–metal distances range from 2.835(3) to 3.037(3) Å and 2.825(2) to 3.026(2) Å in 2 and 3 respectively. Interestingly, the shortest bond length is

Table 3
Selected bond distances (Å) and angles (°) for complex 3

<i>Bond distances</i>			
Os(1)–Os(2)	2.982(2)	Os(1)–C(15)	2.07(3)
Os(1)–Os(3)	2.978(2)	Os(2)–C(15)	2.09(3)
Os(1)–Os(4)	2.868(2)	Os(3)–C(15)	2.07(3)
Os(1)–Os(5)	2.932(2)	Os(4)–C(15)	2.08(3)
Os(2)–Os(3)	2.825(2)	Os(5)–C(15)	2.09(3)
Os(2)–Os(5)	2.978(2)	Ru(1)–C(15)	2.00(3)
Os(2)–Ru(1)	2.906(3)	Ru(1)–C(16)	2.23(4)
Os(3)–Os(4)	3.026(2)	Ru(1)–C(17)	2.35(4)
Os(3)–Ru(1)	2.899(3)	Ru(1)–C(18)	2.32(5)
Os(4)–Os(5)	2.949(2)	Ru(1)–C(19)	2.32(5)
Os(4)–Ru(1)	2.890(3)	Ru(1)–C(20)	2.27(4)
Os(5)–Ru(1)	2.834(3)	Ru(1)–C(21)	2.24(4)
C(16)–C(21)	1.40(5)	C(16)–C(17)	1.43(5)
C(17)–C(18)	1.35(5)	C(18)–C(19)	1.45(6)
C(19)–C(20)	1.28(6)	C(20)–C(21)	1.41(5)
<i>Bond angles</i>			
Os(2)–Os(1)–Os(3)	56.59(5)	Os(2)–Os(1)–Os(4)	90.83(6)
Os(2)–Os(1)–Os(5)	60.46(5)	Os(3)–Os(1)–Os(4)	62.23(5)
Os(1)–Os(2)–Ru(1)	87.32(8)	Os(1)–Os(2)–Os(5)	58.95(5)
Os(5)–Os(2)–Ru(1)	57.57(7)	Os(1)–Os(3)–Os(4)	57.07(5)
Os(1)–Os(3)–Ru(1)	87.52(8)	Os(2)–Os(3)–Os(4)	90.76(6)
Os(4)–Os(3)–Ru(1)	58.34(7)	Os(1)–Os(4)–Os(3)	60.62(5)
Os(3)–Os(1)–C(15)	44.4(9)	Os(4)–Os(1)–C(15)	46.5(9)
Os(4)–Os(3)–C(15)	43.3(9)	Os(2)–Os(3)–C(15)	47.4(9)

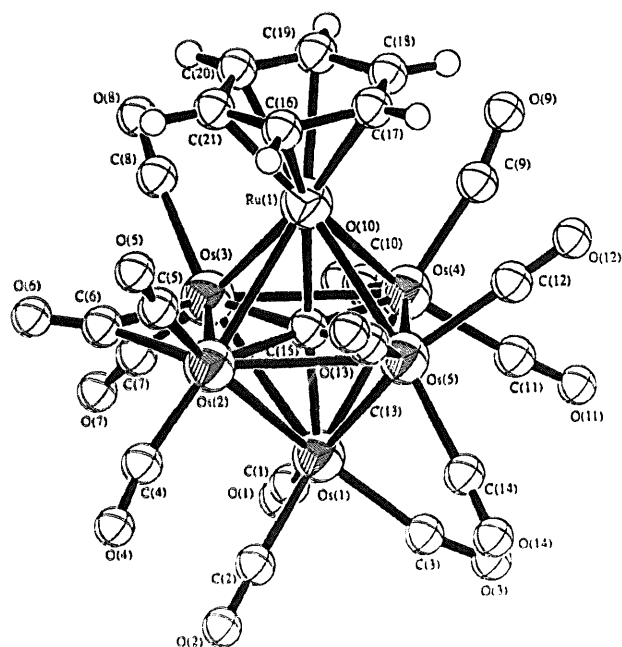
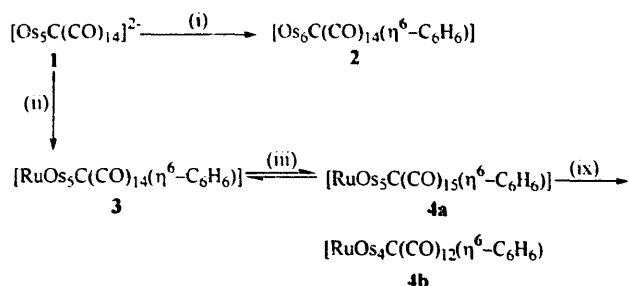


Fig. 2. The molecular structure of the complex $[\text{RuOs}_5\text{C}(\text{CO})_{14}(\eta^6\text{-C}_6\text{H}_6)]$ **3** with the atomic numbering scheme.

the one spanned by the bridging CO ligand, which is similar to those observed in other carbido clusters such as $[\text{Os}_5\text{C}(\text{CO})_{14}(\text{Au}(\text{PPh}_3)_2)_2]$ [17] and $[\text{IrOs}_5\text{C}(\text{CO})_{14}(\text{CO}_2\text{Et})]$ [18]. It is also noteworthy that the bridging carbonyl here is not bonded to the metal which has the arene bound to it. However, in the derivatives of $\text{Os}_8(\text{CO})_{18}$ with one or more substituted arenes, the bridging carbonyl is associated with the arene coordinated metal [19].



Scheme 1. Reagents and conditions: (i) $[\text{Os}(\text{C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$ in a CH_2Cl_2 solution; (ii) $[\text{Ru}(\text{C}_6\text{H}_6)(\text{MeCN})_3]^{2+}$ in a CH_2Cl_2 solution; (iii) CO bubbled through a CH_2Cl_2 solution; (ix) sealed under CO for two weeks.

The η^6 -benzene ligand is coordinated to the apical position. An essentially identical coordination is observed in **2**. The metal–C(carbide) distances in both **2** and **3** show the expected “drift” of the interstitial atom towards the metal bearing the η^6 -bound benzene. This effect is present in all arene-substituted clusters. Bond lengths Os(6)–C(15) in **2** and Ru(1)–C(15) in **3** are 1.93(4) and 2.00(3) Å respectively, while the average of the remaining Os–C(carbide) bond distances is 2.09(4) Å in both compounds. Also, the metal–C(benzene) distances are similar in **2** [2.21(5) Å] and **3** [2.25(4) Å].

Treatment of compound **3** with carbon monoxide under ambient conditions produces the unstable species $[\text{RuOs}_5\text{C}(\text{CO})_{15}(\eta^6\text{-C}_6\text{H}_6)]$ **4a**. Compound **4a** readily evolves carbon monoxide to regenerate cluster **3** on standing at room temperature. If, however, **4a** is prepared and stored at -20°C for two weeks under a CO atmosphere, a new compound **4b** is isolated after chro-

Table 4
Selected bond distances (Å) and angles ($^\circ$) for complex **4b**

	Molecule 1	Molecule 2	Molecule 1	Molecule 2
Bond distances				
Os(1)–Os(2)	2.800(2)	2.803(2)	Os(1)–Os(3)	2.848(2)
Os(1)–Os(4)	2.782(2)	2.823(2)	Os(1)–Ru(1)	2.904(4)
Os(2)–Os(3)	2.898(2)	2.900(2)	Os(2)–Ru(1)	2.818(4)
Os(3)–Os(4)	2.911(2)	2.899(2)	Os(4)–Ru(1)	2.817(4)
Os(1)–C(13)	2.17(4)	2.14(4)	Os(2)–C(13)	2.04(4)
Os(3)–C(13)	1.98(4)	1.98(4)	Os(4)–C(13)	2.11(4)
Ru(1)–C(13)	1.99(4)	2.03(4)	C(14)–C(15)	1.29(7)
C(15)–C(16)	1.46(7)	1.55(7)	C(16)–C(17)	1.29(7)
C(17)–C(18)	1.52(7)	1.47(6)	C(18)–C(19)	1.47(7)
C(14)–C(19)	1.34(7)	1.42(7)		1.37(6)
Bond angles				
Os(1)–Os(2)–Os(3)	59.95(6)	59.61(6)	Os(1)–Os(2)–Ru(1)	62.23(9)
Os(2)–Os(1)–Os(3)	61.72(6)	61.89(6)	Os(2)–Os(1)–Ru(1)	59.19(8)
Os(2)–Os(1)–Os(4)	94.67(7)	93.04(7)	Os(3)–Os(1)–Ru(1)	87.13(9)
Os(3)–Os(1)–Os(4)	66.22(6)	61.64(6)	Os(4)–Os(1)–Ru(1)	59.32(9)
Os(1)–Ru(1)–Os(4)	58.24(8)	59.46(8)	Os(1)–Ru(1)–Os(2)	58.58(8)
Os(2)–Ru(1)–Os(4)	93.6(1)	92.8(1)	Os(3)–Os(1)–C(13)	44(1)
Os(2)–Os(1)–C(13)	46(1)	48(1)	Ru(1)–Os(1)–C(13)	43(1)
Os(4)–Os(1)–C(13)	48(1)	44(1)	Os(1)–Ru(1)–C(13)	48(1)

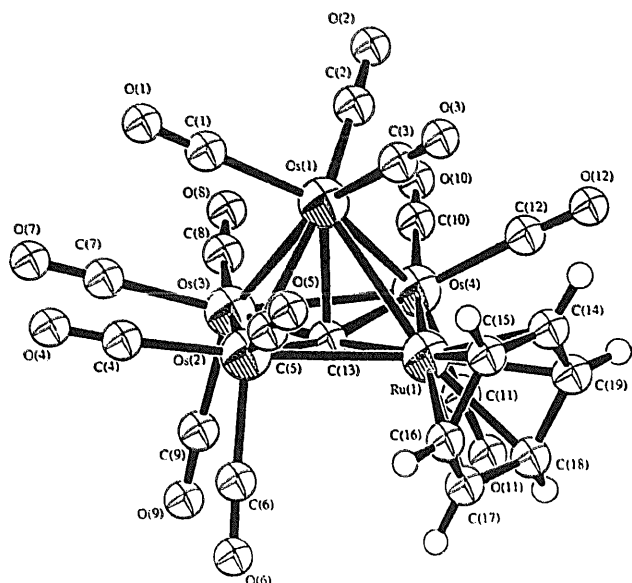


Fig. 3. The molecular structure of the complex $[\text{RuOs}_4\text{C}(\text{CO})_{12}(\text{C}_6\text{H}_6)]$ **4b** with the atomic numbering scheme. Only one of the two independent molecules present in the asymmetric unit is shown. Relevant bond distances and angles are discussed in the text.

matography on silica (TLC) with *n*-hexane/ CH_2Cl_2 (60:40 v/v) as eluent. The conversion is 50% complete after two weeks. Compound **4b** shows a different IR spectral pattern in the carbonyl region compared with the parent cluster **4a**. The ^1H NMR spectrum of **4b** displays a singlet at δ 5.98, which is also characteristic of an η^6 -coordinated benzene fragment. This signal is slightly downfield of that in **3** (δ 5.66). So, in order to structurally characterise this complex, an X-ray structural analysis was carried out on a single crystal obtained from slow evaporation of an *n*-hexane/ CH_2Cl_2 solution at -20°C for 24 h. The molecular geometry of complex **4b** and its atomic labelling are depicted in Fig. 3. Note that only one of the two crystallographically independent molecules present in the asymmetric unit of **4b** is shown. The selected interatomic bond distances and angles are given in Table 4.

The molecular structure of **4b** is based on the same square-pyramidal metal framework seen in $[\text{Os}_5\text{C}(\text{CO})_{15}]$, with the $\text{Os}(\text{CO})_3$ unit replaced by a $\text{Ru}(\text{C}_6\text{H}_6)$ fragment. Although this η^6 -benzene coordination mode has been commonly observed, to our knowledge never before has such a benzene containing pentanuclear ruthenium–osmium mixed-metal carbido cluster been isolated and structurally characterised. It is worth noting that although the central carbon atom lies 0.32 Å below the square plane, it occupies the centre of the square base. However, in the case of $[\text{Ru}_6\text{C}(\text{CO})_{12}(\eta^5\text{-C}_5\text{H}_5)_2]$ [20] and $[\text{Ru}_5\text{C}(\text{CO})_{12}(\eta^6\text{-C}_6\text{H}_6)]$ [21], the C(carbide) atom is off-centred with respect to the middle of the metal cavity and “pulled” towards the metal bearing Cp or benzene ligand.

3. Experimental

3.1. General procedures

All reactions were carried out using freshly-distilled solvents under an atmosphere of dry, purified nitrogen using standard Schlenk techniques. All chemicals were purchased from a commercial source. The complexes $[\text{Ru}(\text{C}_6\text{H}_6)(\text{MeCN})_3][\text{BF}_4]_2$ [22], $[\text{Os}(\text{C}_6\text{H}_6)(\text{MeCN})_3][\text{BF}_4]_2$ [22] and $[\text{Os}_5\text{C}(\text{CO})_{15}]$ [11,23] were prepared by literature procedures. Infra-red spectra were recorded on a Bio-Rad FTS-7 IR spectrometer, using 0.5 mm calcium fluoride solution cells. The NMR spectra were recorded on a Bruker DPX 300 NMR spectrometer with SiMe_4 as internal reference. Mass spectra were recorded on a Finnigan MAT 95 instrument by the fast atom bombardment technique. Routine separation of products was performed by thin layer chromatography on plates coated with Merck Kieselgel 60 GF₂₅₄.

3.2. Preparation of $[\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}$ 1

The compound $[\text{Os}_5\text{C}(\text{CO})_{15}]$ (100 mg, 0.72 mmol) was added to a stirred suspension of $[\text{Na}_2\text{CO}_3]$ (300 mg, 2.38 mmol) in methanol (100 cm³) until a yellow solution of $[\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}$ resulted. Filtration was followed by addition of $[\text{N}(\text{PPh}_3)_2]\text{Cl}$ (84 mg, 0.146 mmol) for precipitation [17].

3.3. Preparation of $[\text{Os}_5\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_6)]$ 2

To a solution of **1** (20 mg, 0.008 mmol) in CH_2Cl_2 (10 cm³) was added $[\text{Os}(\text{C}_6\text{H}_6)(\text{MeCN})_3][\text{BF}_4]_2$ (4.4 mg, 0.008 mmol). The reaction mixture was stirred at room temperature for 15 min during which time the reaction solution changed from light green to deep red. Excess solvent was then removed under reduced pressure, yielding a deep brown residue. This residue was then dissolved in the minimum amount of CH_2Cl_2 and subjected to preparative TLC on silica using *n*-hexane/ CH_2Cl_2 (60:40 v/v) as eluent. The red cluster **2** was isolated as the major product, $R_f = 0.4$, ca. 30% yield. Anal. Found: C, 15.58; H, 0.41. $\text{C}_{21}\text{H}_6\text{O}_{14}\text{Os}_6$ Calc.: C, 15.52; H, 0.37%.

3.4. Preparation of $[\text{RuOs}_5\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_6)]$ 3

The same procedure was applied as for the preparation of **2**, except that $[\text{Ru}(\text{C}_6\text{H}_6)(\text{MeCN})_3][\text{BF}_4]_2$ (4.4 mg, 0.008 mmol) was used instead of $[\text{Os}(\text{C}_6\text{H}_6)(\text{MeCN})_3][\text{BF}_4]_2$. Preparative TLC led to the isolation of the red cluster $[\text{RuOs}_5\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_6)]$ **3**, $R_f = 0.4$, ca. 25% yield. Anal. Found: C, 16.14, H, 0.42. $\text{C}_{21}\text{H}_6\text{O}_{14}\text{Os}_5\text{Ru}$ Calc.: C, 16.42; H, 0.39%.

3.5. Preparation of $[\text{RuOs}_4\text{C}(\text{CO})_{12}(\text{C}_6\text{H}_6)]$ **4b**

A steady stream of carbon monoxide was bubbled through a solution of $[\text{RuOs}_5\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_6)]$ **3** (20 mg, 0.016 mmol) in CH_2Cl_2 (30 cm^3). After 5 min the solution changed from red to purple. Complete consumption of the starting material was indicated by IR spectroscopy. The reaction vessel was sealed and stored at -20°C for two weeks, resulting in a brown solution. Following evaporation of most of the solvent, the mixture was subjected to preparative TLC using *n*-hexane/ CH_2Cl_2 (40:60 v/v) as eluent to afford crude red crystals of $[\text{RuOs}_4\text{C}(\text{CO})_{12}(\text{C}_6\text{H}_6)]$ **4b**, $R_f = 0.6$, ca. 30% yield. Anal. Found: C, 17.73; H, 0.53. $\text{C}_{19}\text{H}_6\text{O}_{12}\text{Os}_4\text{Ru}$ Calc.: C, 17.70; H, 0.47%.

3.6. X-ray analyses of **2**, **3** and **4b**

All pertinent crystallographic data and other experimental details are summarised in Table 5. Data were collected at ambient temperature on a Rigaku AFC7R diffractometer, using $\text{Mo K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$)

with a graphite crystal monochromator in the incident beam. The unit cell parameters were determined from 25 accurately centred reflections. Intensity data were measured with the ω - 2θ scan technique at a scan rate of $16.0^\circ\text{C min}^{-1}$ (in ω). The stability of the crystals was monitored at regular intervals using three standard reflections and no significant decay was observed. The diffracted intensities were corrected for Lorentz and polarization effects. The ψ -scan method was employed for semi-empirical absorption corrections [24]. Scattering factors were taken from Ref. [25a] and anomalous dispersion effects [25b] were included in F_c .

The structures were solved by direct methods (SIR 88) [26] and expanded by difference Fourier techniques. The solutions were refined on F by full-matrix least-squares analysis with Os and Ru atoms refined anisotropically. Hydrogen atoms were placed in their idealized positions and included in the structure factor calculations but not refined. All calculations were performed on a Silicon-Graphics workstation using the program package TEXSAN [27].

Table 5
Crystallographic data and data collection parameters for compounds **2–4b**

Compound	$\text{Os}_6\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_6)$ 2	$\text{RuOs}_5\text{C}(\text{CO})_{14}(\text{C}_6\text{H}_6)$ 3	$\text{RuOs}_4\text{C}(\text{CO})_{12}(\text{C}_6\text{H}_6)$ 4b
Empirical formula	$\text{C}_{21}\text{H}_6\text{O}_{14}\text{Os}_6$	$\text{C}_{21}\text{H}_6\text{O}_{14}\text{Os}_5\text{Ru}$	$\text{C}_{19}\text{H}_6\text{O}_{12}\text{Os}_4\text{Ru}$
Formula weight	1623.47	1534.34	1288.12
Colour, habit	red, prism	red, prism	red, prism
Crystal dimensions (mm^3)	$0.16 \times 0.21 \times 0.24$	$0.21 \times 0.25 \times 0.29$	$0.18 \times 0.23 \times 0.32$
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a (\AA)	10.809(3)	10.807(3)	15.362(2)
b (\AA)	16.146(3)	16.167(3)	16.726(2)
c (\AA)	15.294(3)	15.311(2)	18.961(3)
β ($^\circ$)	98.07(2)	98.09(1)	95.56(1)
Volume (\AA^3)	2642.7(9)	2648.6(9)	4849(1)
Z	4	4	8
Density (calc.) (g cm^{-3})	4.080	3.847	3.529
Absorption coefficient (cm^{-1})	288.37	245.34	215.43
$F(000)$	2800.00	2672.00	4512.00
Temperature (K)	298	298	301
Maximum 2θ ($^\circ$)	45.0	45.0	45.0
Scan range (ω)	$0.63 + 0.35 \tan \theta$	$0.58 + 0.35 \tan \theta$	$0.89 + 0.35 \tan \theta$
Reflections collected	3839	3845	6903
Unique reflections	3619	3625	6616
Observed reflections [$I > 3.00\sigma(I)$]	2571	2395	4492
Transmission factors	0.2228–1.000	0.4752–1.000	0.4921–1.000
Weighting scheme	$w = 0.002$	$w = 0.002$	$w = 0.004$
$w = [\sigma_c^2(F_o) + p^2/\sigma(F_o^2)]^{-1}$			
R indices (obs. data)	$R = 0.060, R' = 0.068$	$R = 0.050, R' = 0.060$	$R = 0.055, R' = 0.082$
Goodness-of-fit indicator	3.63	2.59	3.36
Largest Δ/σ	0.01	0.02	0.01
Number of parameters	195	195	339
Residual extrema in the final difference map (close to Os)	3.32 to -3.53	3.32 to -3.53	3.32 to -3.53
(e \AA^{-3})			

4. Supplementary material available

Final atomic coordinates, thermal parameters, lists of bond distances and angles, least-squares plane and structure factor tables have been deposited at the Cambridge Crystallographic Data Centre.

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