Mixed alkyne–arene-substituted carbonyl clusters; the crystal and molecular structure of $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$

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Abstract

Reaction of the alkyne-substituted cluster anion $[Os_3(CO)_9(R^1CCR^2)]^{2-}$ with the cation $[Os(\eta^6\text{-}C_6H_6)(CH_3CN)]^{2+}$ affords the neutral tetranuclear cluster $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(R^1CCR^2)$ ($R^1=R^2=Me$ (**1a**); $R^1=Me$, $R^2=Ph$ (**1b**); $R^1=R^2=Ph$ (**1c**)). The structure of **1a** has been confirmed by a single-crystal X-ray analysis. The metals adopt a 'butterfly' geometry with the alkylenic C–C vector parallel to the 'hinge' vector of the 'butterfly', and the η^6-C_6H_6 ligand occupies a terminal site on one of the 'wingtip' Os atoms. Complexes **1a** and **1b** may also be prepared by the reaction of the activated arene cluster $Os_4H_2(CO)_9(\eta^6\text{-}C_6H_6)(CH_3CN)$ with MeCCMe and MeCCPh, respectively. Under similar reaction conditions, with PhCCPh, the arene and acetonitrile ligands are substituted by the alkyne to give the known complex $Os_4H_2(CO)_9(PhCCPh)_2$ (**2c**).

Introduction

Recently, there has been considerable interest in arene-substituted carbonyl clusters, and in particular in the range of bonding modes that may be adopted by the arene ligands [1]. These clusters may be used as models for studies of arene groups chemisorbed on metal surfaces [2]. Several general methods of synthesis have been developed for these clusters [1], and one that has been exploited successfully by our research group involves the addition of the $[Os(\eta^6\text{-}C_6H_6)(CH_3CN)_3]^{2+}$ dication to a range of cluster anions [3–6]. However, under some reaction conditions, cluster breakdown occurs, and the arene-substituted cluster is not obtained. It has been observed previously that alkyne ligands stabilise cluster anions [7], and we have used this fact to synthesise mixed osmium/ruthenium clusters by the reaction of alkyne-substituted cluster anions with the dication $[Ru(\eta^6\text{-}C_6H_6)(CH_3CN)_3]^{2+}$ [3]. We now report the synthesis and characterisation of the tetra-osmium cluster $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(R^1CCR^2)$ ($R^1=R^2=Me$ (**1a**); $R^1=Me$, $R^2=Ph$ (**1b**); $R^1=R^2=Ph$ (**1c**)) by the reaction of the anion $[Os_3(CO)_9(R^1CCR^2)]^{2-}$ with the cation $[Os(\eta^6\text{-}C_6H_6)(CH_3CN)_3]^{2+}$. We have also attempted to prepare the complexes **1a**–**1c** by the reaction of the activated cluster $Os_4H_2(CO)_9(\eta^6\text{-}C_6H_6)(CH_3CN)$ [8] with the appropriate alkyne. In the case of **1a** and **1b** this reaction was successful, but with PhCCPh the known [9] complex $Os_4H_2(CO)_9(PhCCPh)_2$ (**2c**) was formed.

Experimental

All experiments were carried out at room temperature under an atmosphere of dry nitrogen, using dry and freshly distilled solvent, unless otherwise stated. The complexes $[Os_3(CO)_9(R^1C_2R^2)]^{2-}$ [4], $Os_4H_2(CO)_{10}(C_6H_6)$ [8] and $[Os(C_6H_6)(CH_3CN)_3][BF_4]_2$ [3] were prepared by literature methods.

IR spectra were recorded on a Perkin-Elmer 1710 FT-IR and ^1H NMR spectra on a Brucker WM250 or WM400 spectrometer. Mass spectra were recorded on a Kratos model MS 902 instrument.

Preparation of $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(R^1CCR^2)$ *($R^1=R^2=Me$ (1a); $R^1=Me$, $R^2=Ph$ (1b); $R^1=R^2=Ph$ (1c)*

To a cool solution (−78 °C) of $[Os_3(CO)_9(R^1CCR^2)]^{2-}$ (50 mg) in dichloromethane was added $[Os(C_6H_6)(CH_3CN)_3][BF_4]_2$ (1 mol equiv.) and the solution warmed to room temperature and stirred for 1 h. After removal of solvent, the solid residue was chromatographed by TLC using 50:50 CH_2Cl_2/hexane

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to separate $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(R^1CCR^2)$ as an orange–red solid, R_f 0.7, *c.* 50% yield.

Preparation of $Os_4H_2(CO)_9(\eta^6\text{-}C_6H_6)(CH_3CN)$

To an acetonitrile solution (20 ml) of $Os_4H_2(CO)_{10}(C_6H_6)$ (25 mg) was added dropwise 1 equiv. of Me_3NO in CH_3CN at room temperature. The mixture was stirred for 45 min. The IR spectrum showed that the starting material had been consumed, and the newly formed species was tentatively formulated as $Os_4H_2(CO)_9(\eta^6\text{-}C_6H_6)(CH_3CN)$ (IR (CH_3CN): 2062m, 2038m, 2022s, 1997s, 1975s, 1942m,sh cm^{-1}). After removal of solvent *in vacuo*, the orange–red solid was used for reactions without further purification.

Reaction of $Os_4H_2(CO)_9(\eta^6\text{-}C_6H_6)(CH_3CN)$ with R^1CCR^2

Freshly prepared $Os_4H_2(CO)_9(\eta^6\text{-}C_6H_6)(CH_3CN)$ (25 mg) was dissolved in CH_2Cl_2 and 2 equiv. of R^1CCR^2 were added to the solution and the reaction followed by IR spectroscopy.

With 2-butyne or 1-phenyl-1-propyne, the mixture was stirred for 24 h. The solvent was evaporated and the residue was subjected to TLC, eluting with 50:50 CH_2Cl_2/hexane. Compounds *1a* and *1b* were isolated as the only products from the respective reactions (*c.* 15–20% yield).

With diphenylacetylene, the colour of the solution changed instantly from orange to deep red after the addition of the acetylene and the reaction was stopped after 30 min. The solvent was evaporated and the residue chromatographed with 50:50 CH_2Cl_2/hexane. Compound **2c** was isolated as the only product (R_f 0.3, *c.* 75% yield).

X-ray crystal structure determination of $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$ (1a)

Crystals of **1a** were grown by slow evaporation of a dichloromethane:hexane (60:40) mixture and a suitable single crystal was mounted on a glass fibre with epoxy resin.

Crystal data

$C_{19}H_{12}O_9Os_4$, $M = 1145.09$, monoclinic, space group $P2_1/n$ (alt. setting $P2_1/c$, No. 14), $a = 8.190(2)$, $b = 16.338(5)$, $c = 17.222(6)$ Å, $\beta = 101.11(2)°$, $V = 2261.3$ Å^3 (by least-squares refinement of diffractometer angles from 25 automatically centred reflections in the range $20 < 2\theta < 28°$, $\lambda = 0.71073$ Å), $Z = 4$, $D_c = 3.36$ g cm^{-3}, D_m = not measured. Orange–red plate. Crystal dimensions: $0.07 \times 0.10 \times 0.24$ mm, μ(Mo Kα) = 225.1 cm^{-1}.

Data collection and processing

Enraf-Nonius CAD4 diffractometer, ω–2θ scan mode, with scan width $0.55 + 0.34 \tan \theta$, and scan speed 0.8–5.8 °/min, graphite-monochromated Mo Kα radiation, 3526 reflections measured ($4.0 < 2\theta < 46.0°$, $+h$, $+k$, $\pm l$), 3008 unique (semi-empirical absorption correction based on an ellipsoid model and psi scan data (maximum, minimum transmission factors 0.999, 0.333)), giving 2663 with $F > 3\sigma(F)$. Three check reflections showed no significant variations in intensity during data collection.

Structure solution and refinement

Direct methods (Os atoms) followed by Fourier difference techniques for the remaining non-hydrogen atoms. Full-matrix least-squares refinement with Os atoms anisotropic. Hydrogen atoms were generated geometrically. The weighting scheme $w = [\sigma^2(F) + 0.04F^2]^{-1}$, with $\sigma(F)$ from counting statistics, gave satisfactory agreement analyses. Final R and R_w values were 0.033 and 0.039, and the goodness of fit parameter $S = 1.746$. Highest peak in the final difference map 1.72 e Å^{-3} close to the metal atom positions. Final fractional atomic coordinates are presented in Table 1. All calculations were carried out on a Micro Vax II computer using the Enraf-Nonius SDP package [10].

TABLE 1. Positional parameters and their e.s.d.s

Atom	x	y	z	B (Å^2)^a
Os1	0.52260(6)	0.41570(3)	0.35299(3)	2.96(1)
Os2	0.46594(6)	0.33710(3)	0.13694(3)	3.02(1)
Os3	0.68498(6)	0.30449(3)	0.27437(3)	2.63(1)
Os4	0.62443(6)	0.46706(3)	0.21749(3)	2.53(1)
O11	0.384(2)	0.3148(8)	0.4748(7)	7.1(3)*
O12	0.182(2)	0.5361(8)	0.5196(7)	7.0(3)*
O13	0.343(2)	0.574(1)	0.3751(9)	9.6(4)*
O31	0.621(1)	0.1444(7)	0.3533(6)	5.4(2)*
O32	0.875(2)	0.2322(8)	0.1538(7)	6.7(3)*
O33	1.011(1)	0.3509(7)	0.3866(6)	5.9(2)*
O41	0.819(1)	0.4488(6)	0.0845(6)	4.9(2)*
O42	0.916(1)	0.5505(7)	0.3263(7)	6.1(3)*
O43	0.451(1)	0.6279(7)	0.1637(6)	5.9(3)*
C1	0.349(2)	0.229(1)	0.075(1)	6.4(4)*
C2	0.233(2)	0.297(1)	0.065(1)	6.4(4)*
C3	0.284(2)	0.370(1)	0.0287(9)	5.4(4)*
C4	0.439(2)	0.372(1)	0.0115(8)	4.6(3)*
C5	0.551(2)	0.305(1)	0.026(1)	5.4(4)*
C6	0.497(2)	0.232(1)	0.058(1)	6.6(4)*
C7	0.389(1)	0.4114(8)	0.2247(7)	2.9(2)*
C8	0.423(2)	0.3262(8)	0.2554(7)	3.2(2)*
C9	0.284(2)	0.269(1)	0.2686(9)	5.1(3)*
C10	0.214(2)	0.450(1)	0.2065(9)	4.7(3)*
C11	0.441(2)	0.354(1)	0.4286(9)	4.6(3)*
C12	0.703(2)	0.4460(9)	0.4300(9)	4.5(3)*
C13	0.417(2)	0.510(1)	0.370(1)	6.5(4)*
C31	0.649(2)	0.2050(8)	0.3234(7)	3.3(3)*
C32	0.797(2)	0.2607(9)	0.1985(8)	4.2(3)*
C33	0.887(2)	0.3316(9)	0.3452(8)	4.3(3)*
C41	0.744(2)	0.4560(9)	0.1335(8)	3.8(3)*
C42	0.8010	0.5179	0.2846	4.3(3)*
C43	0.5185	0.5661	0.1843	3.7(3)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$.

Results and discussion

The formation of the highly unstable, oxygen-sensitive dianion $[Os_3(CO)_9(R^1CCR^2)]^{2-}$, from the reaction of the alkyne cluster $Os_3(CO)_{10}(R^1CCR^2)$ with K–Ph_2CO or Na–Hg, in tetrahydrofuran for 0.5 h, has been reported previously [3]. We now report that the treatment of this dianion with an equimolar quantity of the dication $[Os(\eta^6\text{-}C_6H_6)(CH_3CN)_3]^{2+}$ (as its BF_4^- salt) in dichloromethane at −78 °C, followed by warming to room temperature affords the neutral cluster $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(R^1CCR^2)$ ($R^1=R^2=Me$ (**1a**); $R^1=Me$, $R^2=Ph$ (**1b**); $R^1=R^2=Ph$ (**1c**) (Scheme 1). After separation by tlc, the complexes **1a**–**1c** were fully characterised by IR, ^1H NMR and mass spectroscopy (Table 2) and, in the case of **1a**, by single-crystal X-ray diffraction. The ^1H NMR spectra of the complexes are generally very similar to that found for the related mixed-metal cluster $RuOs_3(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$ [3], which in dichloromethane, exhibits two signals at δ 3.27 (singlet, CH_3) and 5.58 (singlet, C_6H_6) of equal intensity. In all three complexes **1a**–**1c** the position of the benzene resonance is characteristic of η^6 coordination to one metal centre [11]. The IR spectra of the three complexes are also similar to those for $RuOs_3(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$ [3], exhibiting three medium to strong bands and two weaker bands in the carbonyl stretching region (1940–2100 cm^{-1}).

Complexes **1a** and **1b** may be prepared by an alternative route (see Scheme 1). The preparation of the arene-substituted cluster $Os_4H_2(CO)_{10}(\eta^6\text{-}C_6H_6)$ has recently been reported [8], and this complex may be activated by treatment with one equivalent of Me_3NO, in CH_3CN, at room temperature. After stirring for 0.5 h the new orange–red complex $Os_4(CO)_9(CH_3CN)(\eta^6\text{-}C_6H_6)$ could be isolated. The reaction of this activated complex with two equivalents of MeCCMe and MeCCPh, respectively, affords, after stirring at room temperature for 24 h, $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(R^1CCR^2)$ ($R^1=R^2=Me$ (**1a**); $R^1=Me$, $R^2=Ph$ (**1b**)), as the only discernible products. In this process the CH_3CN ligand and the two hydride ligands have been lost from $Os_4H_2(CO)_{10}(\eta^6\text{-}C_6H_6)$, and the alkyne has inserted into the tetrahedral metal core found in $Os_4H_2(CO)_{10}(\eta^6\text{-}C_6H_6)$ to give the 'butterfly' arrangement found in ***1a*** and **1b**. However, when a similar reaction using PhCCPh and $Os_4(CO)_9(CH_3CN)(\eta^6\text{-}C_6H_6)$ is carried out, complex **1c** is not isolated, but the known [9] dialkyne complex $Os_4H_2(CO)_9(PhCCPh)_2$ is obtained in good yield. In this reaction the arene ligand has been displaced by the addition of two alkyne ligands, and an X-ray structure shows that one diphenylacetylene ligand is coordinated to one Os atom in an η^2-mode while the other caps an Os_3 face in a μ_3-η^2-mode [9].

Crystallographic discussion

The molecular structure of $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$ (**1a**) is shown in Fig. 1 while selected bond parameters are presented in Table 3. The four Os atoms define a 'butterfly' metal core arrangement, and the alkyne C–C vector lies parallel to the Os(3)–Os(4) 'hinge' edge to form a quasi-octahedral Os_4C_2 unit. The arene ligand is symmetrically bound to the 'wingtip' Os(2) atom in an η^6-fashion. The nine carbonyls are all essentially linear, with three bonded to each of Os(1), Os(3) and Os(4). The overall structure is very similar to the mixed-metal cluster $RuOs_3(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$ [3], but the two crystal structures are not isomorphous. A large number of structures containing a 'butterfly' M_4C_2 core have now been reported [7], and the trends in the bond parameters in **1a** are similar to those found in $Os_4(CO)_{12}(HCCH)$ and $Os_4(CO)_{12}(HCCEt)$ [12], although in the case of

$$[Os_3(CO)_9(R^1CCR^2)]^{2-} + [Os(C_6H_6)(CH_3CN)^{2+} \longrightarrow Os_4(CO)_9(C_6H_6)(R^1CCR^2)$$

1a: $R^1=R^2=Me$
1b: $R^1=Me$, $R^2=Ph$
1c: $R^1=R^2=Ph$

$$Os_4H_2(CO)_9(C_6H_6)(CH_3CN) \xrightarrow[\text{MeCCPh}]{\text{MeCCMe}} \begin{array}{c} Os_4(CO)_9(C_6H_6)(MeCCMe) \\ \textbf{1a} \\ \\ Os_4(CO)_9(C_6H_6)(MeCCPh) \\ \textbf{1b} \end{array}$$

$$Os_4H_2(CO)_9(C_6H_6)(CH_3CN) \xrightarrow{\text{PhCCPh}} \begin{array}{c} Os_4H_2(CO)_9(PhCCPh) \\ \textbf{2c} \end{array}$$

Scheme 1.

TABLE 2. Spectroscopic data for the new complexes

Compound	IR[a] (ν_{CO} (cm^{-1}))	^{1}H NMR[b] (δ)	MS[c] (m/e)
1a	2076m, 2034s, 2021vs, 1982w, 1944w	5.81(s, 6H), 3.44(s, 6H)	1145
1b	2078m, 2036s, 2024vs, 1975w, 1946w	7.25(m, 5H), 5.75(s, 6H) 3.66(s, 3H)	1207
1c	2078m, 2038s, 2024vs, 2009w, 1989w	7.08(m, 10H), 5.84(s, 6H)	1270
2c	2084s, 2058vs, 2023vs, 2016vs, 2005s, 1989w	7.62(m, 10H), 6.87(m, 10H) -11.99(s, 1H), -13.35(s, 1H)	1378

[a] In hexane. [b] In CH_2Cl_2. [c] Mass based on ^{190}Os.

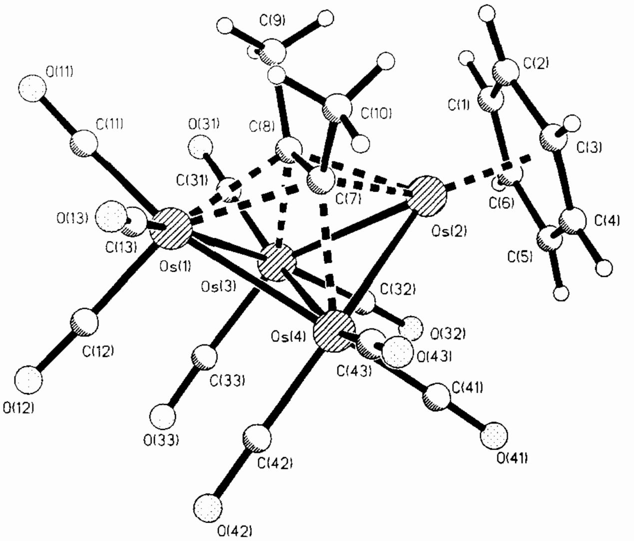

Fig. 1. The molecular structure of $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$ (**1a**) showing the atom numbering scheme.

TABLE 3. Selected bond lengths (Å) and angles (°) for $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$ (**1a**)

Os(1)–Os(3)	2.7560(8)	Os(1)–Os(4)	2.7554(7)
Os(2)–Os(3)	2.7305(6)	Os(2)–Os(4)	2.7235(7)
Os(3)–Os(4)	2.8405(7)	Os(2)–C(7)	2.13(1)
Os(2)–C(8)	2.14(1)	Os(1)–C7	2.26(1)
Os(3)–C(8)	2.13(1)	Os(4)–C(7)	2.15(1)
Os(2)–C(1)	2.19(2)	Os(2)–C(2)	2.17(2)
Os(2)–C(3)	2.22(1)	Os(2)–C(4)	2.20(1)
Os(2)–C(5)	2.22(2)	Os(2)–C(6)	2.24(2)
C(1)–C(2)	1.45(3)	C(1)–C(6)	1.30(3)
C(2)–C(3)	1.44(3)	C(3)–C(4)	1.36(2)
C(4)–C(5)	1.42(2)	C(5)–C(6)	1.42(3)
C(7)–C(8)	1.50(2)	C(7)–C(10)	1.54(2)
C(8)–C(9)	1.52(2)		
Os(3)–Os(1)–Os(4)	62.05(2)	Os(3)–Os(1)–C(7)	71.8(3)
Os(3)–Os(1)–C(8)	49.2(3)	Os(3)–Os(2)–C(7)	74.3(3)
Os(3)–Os(2)–C(8)	50.2(3)	Os(4)–Os(1)–C(7)	49.6(3)
Os(4)–Os(1)–C(8)	72.0(3)	Os(4)–Os(2)–C(7)	51.0(3)
Os(4)–Os(2)–C(8)	74.3(3)	Os(3)–Os(2)–Os(4)	62.77(2)
Os(1)–Os(3)–Os(2)	89.1(3)	Os(1)–Os(3)–Os(4)	58.97(2)
Os(1)–Os(3)–C(8)	53.1(3)	Os(2)–Os(3)–Os(4)	58.49(2)
Os(2)–Os(3)–C(8)	50.4(3)	Os(4)–Os(3)–C(8)	71.9(3)
Os(1)–Os(4)–Os(2)	90.07(2)	Os(1)–Os(4)–Os(3)	58.99(2)
Os(1)–Os(4)–C(7)	53.4(4)	Os(2)–Os(4)–Os(3)	58.73(2)
Os(2)–Os(4)–C(7)	50.0(3)	Os(3)–Os(4)–C(7)	71.6(3)
Os(1)–C(7)–Os(2)	123.9(5)	Os(1)–C(7)–Os(4)	77.0(4)
Os(1)–C(7)–C(8)	70.3(6)	Os(2)–C(7)–Os(4)	79.0(4)
Os(2)–C(7)–C(8)	70.1(8)	Os(4)–C(7)–C(8)	107.8(8)
C(8)–C(7)–C(10)	124.0(10)	Os(1)–C(8)–Os(2)	123.6(7)
Os(1)–C(8)–Os(3)	77.7(4)	Os(1)–C(8)–C(7)	71.1(6)
Os(2)–C(8)–Os(3)	79.4(5)	Os(2)–C(8)–C(7)	68.9(7)
Os(3)–C(8)–C(7)	108.7(8)	C(7)–C(8)–C(9)	122.0(10)

1a the Os–Os distances associated with the 'wingtip' Os atom coordinated to the benzene ring are *c.* 0.02 Å shorter than those associated to the 'wingtip' Os atom coordinated to the three carbonyl ligands. The Os(3)–Os(4) 'hinge' edge is *c.* 0.1 Å longer than the four 'hinge'–'wingtip' edges. The alkyne ligand forms two σ bonds with the two 'hinge' Os atoms and two π bonds with the two 'wingtip' Os atoms. The two σ bonds are essentially symmetric, but the alkyne leans towards the Os(2) arene coordinated 'wingtip' atom, with the Os(2)–C(7),C(8) distances being *c.* 0.13 Å shorter than the equivalent Os(1)–C(7),C(8) distances. A similar trend is observed in $RuOs_3(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$ [3]. The C–C alkyne bond length is similar to that found in other Os_4 and mixed metal alkyne-substituted 'butterfly' clusters [7]. The bond distances within the benzene ring do not show any systematic variations, although the high estimated standard deviations prevent an accurate analysis from being carried out. The dihedral angle in **1a** between the two 'wings' of the 'butterfly' is 111.5°, which is similar to the value of 111.0° found in $RuOs_3(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$ [3]. The arene ring acts as a six electron donor and the alkyne ligand as a four electron donor, which gives the cluster **1a** an overall count of 60 electrons which is consistent with the quasi-octahedral geometry expected by Wade's Rules.

The crystal packing diagram for **1a** (Fig. 2) shows that the cluster units are separated by normal van der Waals distances. However, recent studies on the packing of arene-substituted clusters [13] have shown that a

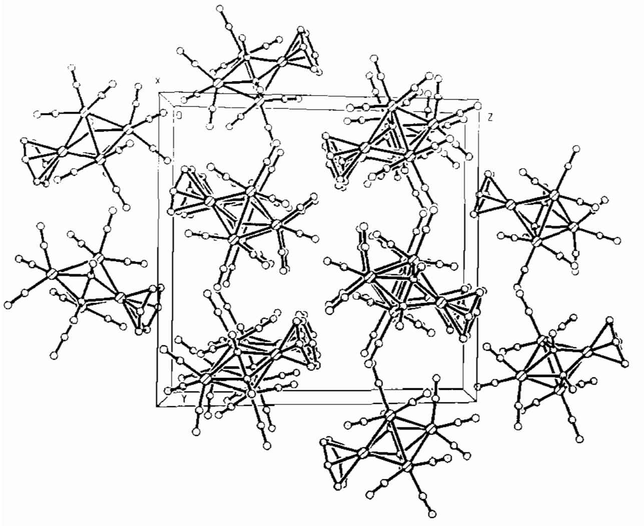

Fig. 2. The crystal packing diagram for $Os_4(CO)_9(\eta^6\text{-}C_6H_6)(MeCCMe)$ (**1a**) viewed down the *a* axis.

number of mono-arene complexes adopt a packing arrangement which favours a 'ribbon-like' arrangement of the arene fragments. An examination of Fig. 2 reveals that a similar pattern is present in the crystal structure of **1a**.

Supplementary material

Tables of thermal parameters, hydrogen atom coordinates, full lists of bond parameters, and tables of structure factors for the crystal structure are available from the authors.

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