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Synthesis, characterization, and X-ray crystal structure of the octabromodiosmate(III) salt $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ and its conversion to $[(C_5Me_4H)_2OsBr][Os_2HBr_4(cod)_2]$

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Abstract

Treatment of hexabromoosmic acid, H_2OsBr_6, with 4 equiv. of tetramethylcyclopentadiene ($C_5Me_4H_2$) in *tert*-butanol at reflux for 8 h affords the unusual salt $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$, **1**, which is the bis(tetramethylcyclopentadienyl)bromoosmocinium(IV) salt of the octabromodiosmate(III) dianion. The brown color of the salt suggests that the anion adopts an eclipsed conformation (D_{4h} symmetry) and this conclusion has been confirmed by a single-crystal X-ray diffraction experiment. The X-ray crystal structure indicates that the osmium atoms in the $[Os_2Br_8^{2-}]$ anion are disordered over two sites. The bromine atoms show no evidence of disorder and are disposed in a quasi-cubic arrangement; the two Os–Os vectors are almost exactly orthogonal to each other and each vector points toward a different pair of opposite square faces of the Br_8 cube. The Os–Os bond distances are 2.219(5) and 2.229(1) Å; the average Os–Br distance in the anion is 2.417(2) Å. Treatment of $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ with excess 1,5-cyclooctadiene in ethanol at gentle reflux for 3 h affords $[(C_5Me_4H)_2OsBr][Os_2HBr_4(cod)_2]$, **2**. An X-ray crystallographic study was carried out on a sample in which the cation was a mixture of $[(C_5Me_4H)_2OsBr^+]$ and $[(C_5Me_4H)_2OsH^+]$. The results demonstrate that the anion adopts a confacial bioctahedral structure in which the hydride ligand and two bromides bridge between the two osmium centers. The C=C bonds of the cod ligands are *trans* to the bridging bromide groups. The Os–Os bond distance in the anion is 2.874(1) Å. The average Os–Br distance is 2.596(2) Å for the bridging bromides and 2.565(2) Å for the terminal bromides. Compound **2** is the first example of an anionic diosmium complex containing a bridging hydride. The reaction of **1** with cod also results in the formation of bis(tetramethylcyclopentadienyl)osmocene, $(C_5Me_4H)_2Os$, **3**, which has been isolated and characterized. Treatment of $(C_5Me_4H)_2Os$ with 1.0 equiv. of $HBF_4 \cdot Et_2O$ affords the osmocinium salt $[(C_5Me_4H)_2OsH][BF_4]$.

Keywords: Osmium; Diosmium; Octahalodimetalate; Octahalodiosmate; Os–Os triple bond; Bridging hydride; Tetramethylcyclopentadiene; Octamethylosmocene; Osmocene; X-ray crystal structure

1. Introduction

Octahalodimetalate anions, $[M_2X_8^{n-}]$, are known for the elements Mo, W, Tc, Re, and Os [1]. Of these, the octahalodiosmates were discovered most recently; these dianions have $\sigma^2\pi^4\delta^2\delta^{*2}$ electronic configurations and contain triple bonds between the two osmium centers. In general, the reaction chemistry of octahalodiosmate salts has been less explored than that of their quadruply bonded $[Mo_2X_8^{4-}]$ and $[Re_2X_8^{2-}]$ counterparts, which have been shown to serve as excellent starting materials for a large number of mono- and dinuclear complexes [1]. Walton has described reactions of $[Os_2X_8^{2-}]$ salts (X = Cl, Br) with Lewis bases [2,3]. Specifically, the salts $[n\text{-}Bu_4N]_2[Os_2X_8]$ (X = Cl, Br) and $[PPN]_2[Os_2Cl_8]$, where PPN = bis(triphenylphosphoranylidene)ammonium, react with phosphines, amines, carbon monoxide, and alkyl and aryl isocyanides in alcohol solvents to afford various mononuclear osmium(II) and osmium(III) products in which the osmium–osmium triple

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bond has been cleaved. There have been no studies of the chemical reactivity of the octahalodisomate salts toward alkenes.

We previously reported the preparation of the octabromodisomate salt $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ by treatment of hexabromoosmic acid, H_2OsBr_6, with pentamethylcyclopentadiene [4]. We now present the analogous reaction of H_2OsBr_6 with tetramethylcyclopentadiene to form a similar salt, $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$, and describe the reactivity of this latter compound with 1,5-cyclooctadiene.

2. Results and discussion

2.1. Synthesis and characterization of $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$

Treatment of H_2OsBr_6 with 4 equiv. of tetramethylcyclopentadiene ($C_5Me_4H_2$) in *tert*-butanol at reflux for 8 h affords a brown precipitate of stoichiometry $(C_5Me_4H)_2Os_2Br_5$. This product is more properly formulated as the salt $[(C_5Me_4H)_2OsBr^+]_2[Os_2Br_8^{2-}]$ (**1**), which contains bis(tetramethylcyclopentadienyl)bromoosmocinium(IV) cations and octabromodiosmate(III) dianions.

$$4H_2OsBr_6 + 4C_5Me_4H_2 \rightarrow \underset{\mathbf{1}}{[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]} + 12HBr + Br_2$$

The field-desorption mass spectrum of **1** contains a parent envelope centered on *m/e* 513 that corresponds to the $[(C_5Me_4H)_2OsBr^+]$ cation. A peak envelope at *m/e* 434 due to $[(C_5Me_4H)_2Os^+]$ is also prominent; in some mass spectra, this peak envelope appears at *m/e* 433 and reflects loss of HBr rather than Br from the parent ion. The ^1H NMR spectrum of **1** is consistent with the presence of the $[(C_5Me_4H)_2OsBr^+]$ cation: it contains three singlets at δ 5.65, 2.13, and 2.14 of relative intensity 1:6:6 for the ring (methine) proton and the two inequivalent sets of ring methyls of the C_5Me_4H groups. For comparison, the ^1H NMR spectrum of the analogous $[(C_5Me_5)_2OsBr^+]$ cation shows a singlet at δ 2.06 [5]. Interestingly, the chemical shift of the ring proton in **1** is sample-dependent, varying by as much as 0.25 ppm [6].

The microanalysis suggests that the anion in **1** is octabromodiosmate and that the overall formula is $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$. This formulation has been confirmed crystallographically.

2.2. X-ray crystal structure of $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$

Single crystals of $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8] \cdot 2CH_2Cl_2$ crystallize in the $P\bar{1}$ space group with one cation and one half-anion in the asymmetric unit. Crystal data are presented in Table 1 and selected bond distances and angles are given in Table 2. In the $[(C_5Me_4H)_2OsBr^+]$ cation, the Os–Br distance is 2.540(1) Å (Fig. 1). The Os–C distances to the proton-bearing ring carbons are 2.184(9) and 2.192(9) Å, whereas the Os–C distances to the methyl-bearing ring carbons are slightly longer and range from 2.248(9) to 2.298(10) Å. For comparison, the Os–C distances in the related compound $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ all lie between 2.187(9) and 2.222(11) Å [4]. The dihedral angle between the two C_5Me_4H rings is 37.4(4)° and the Cn(1)–Os(1)–Cn(2) angle involving the centroids of the C_5Me_4H rings is 146.7(4)°. The sum of these two angles (184.1°) deviates from 180° because the Os–C distances are slightly different (i.e., the ring planes are not exactly perpendicular to the Os–centroid vectors and are instead tilted away from the Os–Br group).

Table 1
Crystallographic data for $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8] \cdot 2CH_2Cl_2$ (**1**) and $[(C_5Me_4H)_2Os(Br_{0.70}H_{0.30})][Os_2HBr_4(cod)_2]$ (**2**)

	1	**2**
Formula	$C_{38}H_{56}Cl_2Br_{10}Os_4$	$C_{34}H_{51.30}Br_{4.70}Os_3$
Formula weight	2214.53	1405.73
Dimension	0.14 × 0.14 × 0.08	0.26 × 0.04 × 0.01
Color	Black	Brown
Habit	Tabular	Platy
Diffractometer	SMART CCD	SMART CCD
Space group	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$
a (Å)	8.931(3)	18.243(7)
b (Å)	11.096(4)	8.612(3)
c (Å)	14.316(5)	23.799(9)
α (°)	96.085(6)	90
β (°)	95.007(6)	96.360(7)
γ (°)	108.011(6)	90
V (Å^3)	1330.8(8)	3716(2)
Z	1	4
T (°C)	−80	−80
λ (Å)	0.71073	0.71073
D_{calc} (Mg m^{-3})	2.763	2.556
μ_{calc} (cm^{-1})	172.52	153.07
θ Range (°)	1.95–25.40	1.59–25.41
R_{int}	0.153	0.243
$R_F[I \geqslant 2\sigma(I)]$[a]	0.0480	0.0665
R_{wF^2}(all data)[b]	0.1289	0.1333

[a] $\sum \|F_o\| - \|F_c\| / \sum \|F_o\|$.
[b] $\{\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]\}^{1/2}$.

The $[Os_2Br_8^{2-}]$ anion adopts an eclipsed geometry but the osmium atoms are disordered over two sites (Fig. 2). The occupancy factor for the major site refined to 0.879(1). The bromine atoms show no evidence of disorder and are disposed in a quasi-cubic arrangement; the two Os–Os vectors are almost exactly orthogonal to each other and each points toward a different pair of opposite square faces of the Br_8 cube. This situation resembles that of other eclipsed $[M_2X_8^{n-}]$ salts, in which the M–M units are almost invariably disordered in two or three orientations within the quasi-cubic array of eight halide atoms [1,7]. The Os–Os bond distances for the two disordered components are 2.219(5) and 2.229(1) Å, consistent with the presence of an Os–Os triple bond. These distances are slightly longer than the 2.196(1) Å distance observed for $[Os_2Br_8^{2-}]$ anions that adopt staggered conformations [8,9] but are essentially identical to the 2.219(2) and 2.222(2) Å distances observed

Table 2
Selected bond distances and angles for $[(C_5Me_4H)_2OsBr]_2$-$[Os_2Br_8] \cdot 2CH_2Cl_2$ (**1**)

Distances (Å)			
Cation			
Os(1)–C(1)	2.184(9)	Os(1)–C(11)	2.192(9)
Os(1)–C(2)	2.257(9)	Os(1)–C(12)	2.275(9)
Os(1)–C(3)	2.274(9)	Os(1)–C(13)	2.298(1)
Os(1)–C(4)	2.258(8)	Os(1)–C(14)	2.264(9)
Os(1)–C(5)	2.248(10)	Os(1)–C(15)	2.254(9)
Os(1)–Br(1)	2.540(1)		
Anion			
Os(2)–Os(2A)	2.229(1)	Os(3)–Os(3A)	2.219(5)
Os(2)–Br(2)	2.459(1)	Os(3)–Br(2A)	2.486(3)
Os(2)–Br(3)	2.451(1)	Os(3)–Br(3)	2.507(3)
Os(2)–Br(4)	2.444(1)	Os(3)–Br(4)	2.449(3)
Os(2)–Br(5)	2.450(1)	Os(3)–Br(5A)	2.473(3)
Angles (°)			
Cation			
Cn(1)–Os(1)–Cn(2)[a]	146.7(4)		
Anion			
Os(2A)–Os(2)-Br(2)	104.85(5)	Os(3A)–Os(3)–Br(2A)	103.39(18)
Os(2A)–Os(2)–Br(3)	105.78(3)	Os(3A)–Os(3)–Br(3)	102.66(18)
Os(2A)–Os(2)–Br(4)	103.47(4)	Os(3A)–Os(3)–Br(4)	103.35(17)
Os(2A)–Os(2)–Br(5)	104.69(3)	Os(3A)–Os(3)–Br(5A)	103.52(19)
Br(2)–Os(2)–Br(3)	85.89(3)	Br(2A)–Os(3)–Br(4)	87.99(10)
Br(3)–Os(2)–Br(4)	85.94(4)	Br(4)–Os(3)–Br(3)	84.62(10)
Br(4)–Os(2)–Br(5)	86.81(4)	Br(3)–Os(3)–Br(5A)	89.86(10)
Br(2)–Os(2)–Br(5)	86.62(4)	Br(2A)–Os(3)–Br(5A)	85.51(10)
Br(2)–Os(2)–Br(4)	151.67(4)	Br(2A)–Os(3)–Br(3)	153.91(13)
Br(3)–Os(2)–Br(5)	149.52(4)	Br(4)–Os(3)–Os(5A)	153.13(13)

[a] Ring centroids are designated by Cn.

in the eclipsed $[Os_2Br_8^{2-}]$ anion in $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ [4]. The somewhat longer Os–Os distance for the eclipsed conformer reflects the slightly greater steric repulsions between the bromide ligands; a similar lengthening has been seen in the eclipsed verses staggered forms of the $[Os_2Cl_8^{2-}]$ anion [2,7].

Compound **1** is chemically related to the salt $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$, except that the cation in this latter material bears a hydride instead of a bromide ligand [4]. In this previously described salt, the anion also adopts an eclipsed conformation in the solid state and was the first such example for the $[Os_2Br_8^{2-}]$ anion; all other salts containing the $[Os_2Br_8^{2-}]$ anion adopt a staggered conformation. We previously discussed the possibility that the conformations of $[Os_2X_8^{2-}]$ anions (X = Cl, Br) may be determined on the basis of the color of the salt, provided that the countercations are colorless. The brown color of **1** confirms our earlier correlation [4] that salts containing the eclipsed rotamer of of $[Os_2X_8^{2-}]$ are brown whereas salts containing the staggered conformation are green [2,8–10].

2.3. Reaction chemistry of $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ (1) with 1,5-cyclooctadiene; synthesis of $[(C_5Me_4H)_2OsBr][Os_2HBr_4(cod)_2]$

Treatment of **1** with excess 1,5-cyclooctadiene (cod) in ethanol at gentle reflux for 3 h affords a yellow solution from which green crystals of the salt $[(C_5Me_4H)_2Os$-$Br][Os_2HBr_4(cod)_2]$ (**2**) are obtained in 46% yield. The hydride source is presumably the ethanol solvent [11].

The positive-ion field desorption mass spectrum of **2** shows peak envelopes corresponding to $[(C_5Me_4H)_2Os^+]$ and $[Os_2HBr_4(cod)_2^+]$ units at *m/e* 434 and 917, respectively (the latter species is an anion in the crystal but a cation here owing to the ionization process). The ^1H NMR spectrum contains three singlets at δ 5.92, 2.14, and 2.11, which are assigned to the ring (methine) protons and two sets of

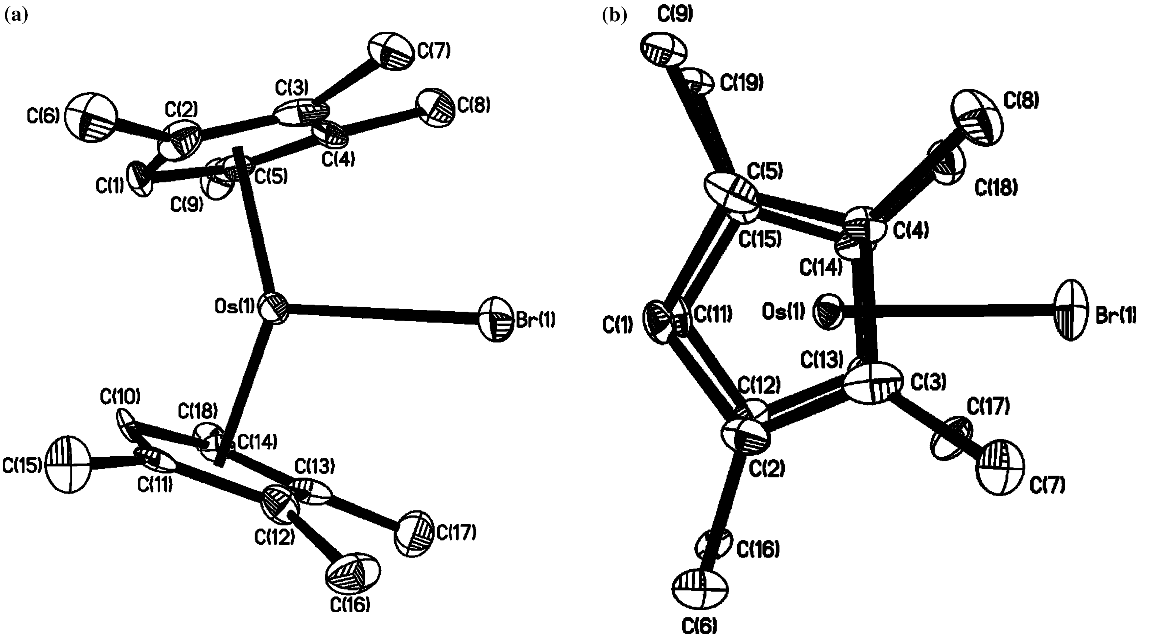

Fig. 1. ORTEP diagrams of the $[(C_5Me_4H)_2OsBr^+]$ cation of **1**: (a) side view, (b) top view. The 35% probability density surfaces are shown; hydrogen atoms are omitted for clarity.

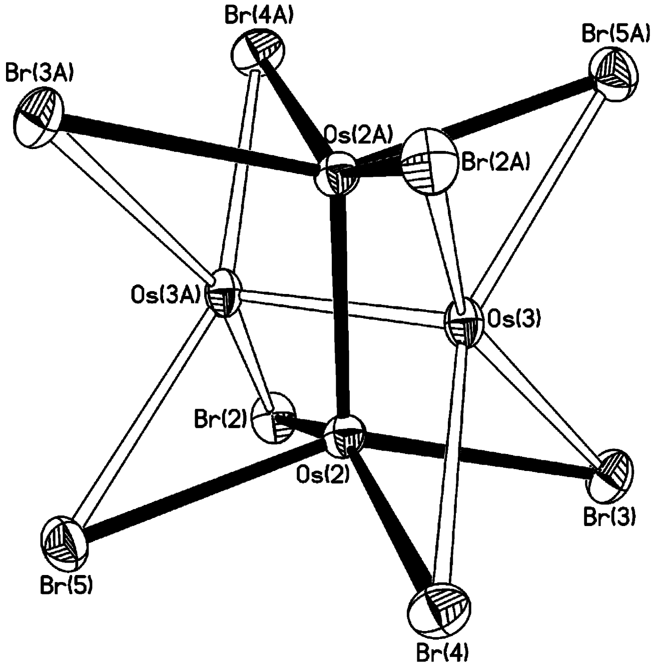

Fig. 2. ORTEP diagram of two crystallographically independent $[Os_2Br_8^{2-}]$ anions of **1**. The 35% probability density surfaces are shown.

chemically inequivalent methyl groups on the cyclopentadienyl rings of $[(C_5Me_4H)_2OsBr^+]$. Two multiplets at δ 4.25 and 4.01 and three muliplets at δ 2.58, 2.32, and 2.02–2.18 are assigned to the two sets of inequivalent vinyl protons and four sets of inequivalent aliphatic protons of the cod ligands. The hydride resonance corresponding to the anion occurs at δ −20.79. The ^1H NMR spectrum also indicates the presence of a small amount (<1–3%) of $[(C_5Me_4H)_2OsH^+][Os_2HBr_4(cod)_2^-]$. In the cation of this minor product, the osmium bears a hydride instead of a bromide ligand. The methine resonance of $[(C_5Me_4H)_2OsH^+]$ occurs at δ 4.94 and the hydride resonance appears at δ −14.90. The resonances due to the methyl groups of this minor-component cation are evidently masked by the resonances between δ 2.02–2.18 arising from the anion.

The IR spectrum of **2** does not show an Os–H stretch which suggests that the hydride in the anion is bridging; metal–hydride stretches for bridging hydrides are often weak and difficult to detect [12].

Another product in the reaction of **1** with cod is octamethylosmocene, $(C_5Me_4H)_2Os$ (**3**), which can be isolated in 20% yield [13]. To further verify the identity of the minor cation $[(C_5Me_4H)_2OsH^+]$ in **2**, we independently prepared the salt $[(C_5Me_4H)_2OsH][BF_4]$ (**4**). Protonation of $(C_5Me_4H)_2Os$ with 1.0 equiv. of HBF_4 in diethyl ether affords **4** in 42% yield. The ^1H NMR spectrum of **4** contains four singlets at δ 4.94, 2.11, 2.04, and −14.91 of relative intensity 1:6:6:1, respectively. These resonances correspond well with those assigned to the minor-component $[(C_5Me_4H)_2OsH^+]$ cation in **2**.

2.4. X-ray crystal structure of $[(C_5Me_4H)_2Os(Br_{0.70}H_{0.30})][Os_2HBr_4(cod)_2]$

Single crystals of **2** were grown from a CH_2Cl_2/Et_2O solution cooled to −20 °C for 3 months. The compound crystallizes in the $P2_1/n$ space group. Crystal data are presented in Table 1 and selected bond distances and angles are given in Table 3.

The crystallographic data strongly suggest that the bromine atom in the "$[(C_5Me_4H)_2OsBr^+]$" cation is present with a site occupancy of less than 100%. The data thus indicate that the crystal contains two different cations, $[(C_5Me_4H)_2OsBr^+]$ and $[(C_5Me_4H)_2OsH^+]$, which occupy the same site in the crystal. When we allowed the site occupancy factor for the bromine atom to vary, it refined to a value of 0.7, so that $[(C_5Me_4H)_2OsBr^+]$ and $[(C_5Me_4H)_2OsH^+]$ are present in the data crystal in a ratio of 0.70:0.30, respectively. Compound **2**, when isolated from the reaction mixture, contains very little (<3%) of the hydridoosmocinium cation $[(C_5Me_4H)_2OsH^+]$. The larger amount of this cation in the data crystal may reflect preferential crystallization (for the sample from which the data crystal was selected, the crystallization yield was less than 30%). Alternatively, it is possible that some of the $[(C_5Me_4H)_2OsBr^+]$ cations converted in solution to $[(C_5Me_4H)_2OsH^+]$ over the three month crystallization period. In any event, in the discussion below we will indicate that the cation is a mixture by assigning to it the formula $[(C_5Me_4H)_2Os(Br_{0.70}H_{0.30})^+]$.

The structure of $[(C_5Me_4H)_2Os(Br_{0.70}H_{0.30})^+]$ is very similar to that of the $[(C_5Me_4H)_2OsBr^+]$ cation in **1**. The Os–Br bond distance is 2.539(3) Å (vs. 2.540(1) Å in **1**), the Os–C distances to the methine carbons are 2.15(2) and 2.20(2) Å (vs. 2.184(9) and 2.192(9) Å in **1**), and the Os–C distances to the methyl-bearing ring carbons all lie between 2.21(2) and 2.27(2) Å (vs. 2.248(9) to 2.298(10) Å in **1**). As in **1**, the dihedral angle between the two C_5Me_4H rings of 32.8(9)° and the Cn(1)–Os(1)–Cn(2) angle of 149.3(9)° sum to a value (182.1°) that differs slightly from 180° owing to tilting of the rings with respect to the Os–centroid vectors.

The anion in **2** adopts a face-shared bioctahedral structure in which the hydride ligand and two bromides bridge between the two osmium centers (Fig. 3). The C=C bonds of the cod ligands are *trans* to the bridging bromide groups. The average Os–Br bond distance is 2.596(2) Å for the bridging bromides and 2.566(2) Å for the terminal bromides. The Os–C distances to the cod ligands in the anion average 2.16(2) Å. The Os–Os bond distance in the $[Os_2HBr_4(cod)_2^-]$ anion is 2.874(1) Å, which is short enough to be consistent with the presence of Os–Os bonding. The Os–Os bond order in **2** is, however, somewhat unclear: for each osmium center to adopt a formal electron count of 18, an Os–Os bond would be necessary. Each osmium center is, however, d^6 and quasi-octahedral; on this basis, there is no obvious need for an Os–Os bond.

Table 3
Selected bond distances and angles for $[(C_5Me_4H)_2Os(Br_{0.70}H_{0.30})][Os_2HBr_4(cod)_2]$ (**2**)

Distances (Å)			
Cation			
Os(1)–C(1)	2.196(2)	Os(1)–C(11)	2.152(15)
Os(1)–C(2)	2.270(16)	Os(1)–C(12)	2.206(14)
Os(1)–C(3)	2.215(17)	Os(1)–C(13)	2.243(15)
Os(1)–C(4)	2.248(15)	Os(1)–C(14)	2.262(14)
Os(1)–C(5)	2.221(16)	Os(1)–C(15)	2.271(14)
Os(1)–Br(1)	2.539(3)		
Anion			
Os(2)–C(21)	2.181(16)	Os(3)–C(31)	2.143(18)
Os(2)–C(22)	2.191(18)	Os(3)–C(32)	2.155(17)
Os(2)–C(25)	2.116(16)	Os(3)–C(35)	2.116(19)
Os(2)–C(26)	2.116(16)	Os(3)–C(36)	2.133(18)
Os(2)–Br(2)	2.572(2)	Os(3)–Br(3)	2.559(2)
Os(2)–Br(4)	2.604(2)	Os(3)–Br(4)	2.602(2)
Os(2)–Br(5)	2.590(2)	Os(3)–Br(5)	2.589(2)
Os(2)–Os(3)	2.873(1)		
Angles (°)			
Cation			
Cn(1)–Os(1)–Cn(2)[a]	149.3(9)		
Anion			
C(26)–Os(2)–Br(2)	120.5(4)	C(25)–Os(2)–C(26)	38.3(4)
C(25)–Os(2)–Br(2)	82.6(4)	C(21)–Os(2)–C(26)	79.9(6)
C(21)–Os(2)–Br(2)	118.1(4)	C(21)–Os(2)–C(25)	92.5(6)
C(22)–Os(2)–Br(2)	80.7(4)	C(22)–Os(2)–C(26)	93.2(6)
C(26)–Os(2)–Br(4)	152.2(4)	C(22)–Os(2)–C(25)	81.3(6)
C(25)–Os(2)–Br(4)	169.5(4)	C(21)–Os(2)–C(22)	37.9(4)
C(21)–Os(2)–Br(4)	91.7(5)	C(26)–Os(2)–Os(3)	99.1(4)
C(22)–Os(2)–Br(4)	96.3(5)	C(25)–Os(2)–Os(3)	131.7(4)
Br(2)–Os(2)–Br(4)	86.93(7)	C(21)–Os(2)–Os(3)	101.9(4)
Br(4)–Os(2)–Br(5)	86.60(6)	C(22)–Os(2)–Os(3)	134.7(4)
C(26)–Os(2)–Br(5)	89.7(4)	Br(2)–Os(2)–Os(3)	126.60(6)
C(25)–Os(2)–Br(5)	93.7(4)	Br(5)–Os(2)–Os(3)	56.29(5)
C(21)–Os(2)–Br(5)	154.3(4)	Br(4)–Os(2)–Os(3)	56.45(5)
C(22)–Os(2)–Br(5)	167.7(4)	C(35)–Os(3)–Br(3)	80.7(5)
Br(2)–Os(2)–Br(5)	87.47(7)	C(32)–Os(3)–Br(3)	81.8(4)
C(36)–Os(3)–Br(3)	119.6(5)	C(32)–Os(3)–C(36)	91.4(8)
C(31)–Os(3)–Br(3)	119.2(5)	C(31)–Os(3)–C(35)	95.8(8)
C(35)–Os(3)–Br(4)	168.7(5)	C(31)–Os(3)–C(32)	38.5(4)
C(32)–Os(3)–Br(4)	95.0(5)	C(31)–Os(3)–C(36)	80.8(7)
C(36)–Os(3)–Br(4)	152.1(5)	C(35)–Os(3)–Os(2)	133.1(5)
C(31)–Os(3)–Br(4)	87.4(5)	C(32)–Os(3)–Os(2)	132.9(4)
Br(3)–Os(3)–Br(4)	88.27(7)	C(36)–Os(3)–Os(2)	100.1(5)
Br(4)–Os(3)–Br(5)	86.67(7)	C(31)–Os(3)–Os(2)	98.4(5)
C(35)–Os(3)–Br(5)	95.2(5)	Br(3)–Os(3)–Os(2)	127.67(6)
C(32)–Os(3)–Br(5)	169.2(4)	Br(5)–Os(3)–Os(2)	56.31(5)
C(36)–Os(3)–Br(5)	92.1(6)	Br(4)–Os(3)–Os(2)	56.54(5)
C(31)–Os(3)–Br(5)	152.3(5)	Os(2)–Br(4)–Os(3)	67.00(5)
Br(3)–Os(3)–Br(5)	87.61(7)	Os(2)–Br(5)–Os(3)	67.40(5)
C(32)–Os(3)–C(35)	81.1(7)		
C(35)–Os(3)–C(36)	39.1(4)		

[a] Ring centroids are designated by Cn.

The Os–Os bond distance in **2** lies at the upper end of those for other known dinuclear complexes containing bridging hydrides (Table 4) [14–17]. Dinuclear osmium complexes containing bridging hydrides are rare; of the known polynuclear osmium compounds that contain bridging hydrides, the majority are triosmium carbonyls. To our knowledge, $[Os_2HBr_4(cod)_2^-]$ is the first example of an *anionic* diosmium complex that contains a bridging hydride.

2.5. Concluding remarks

We previously reported that the reaction of H_2OsBr_6 with *pentamethyl*cyclopentadiene affords either the dinuclear species $(C_5Me_5)_2Os_2Br_4$ [14] or the salt $[(C_5Me_5)_2OsH]_2[Os_2Br_8]$ [4] depending on the choice of solvent, the reaction time, and other reaction conditions. The dinuclear complex contains one C_5Me_5 ring per osmium center, but in the salt the osmium centers are bound either to two rings or to none. In this C_5Me_5 system, the product distribution is very sensitive to the reaction conditions. In contrast, we been unable – under any conditions – to isolate the putative dinuclear complex $(C_5Me_4H)_2Os_2Br_4$ from the reaction of H_2OsBr_6 with *tetramethyl*cyclopentadiene. Instead, we isolated only $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ and $(C_5Me_4H)_2Os$. It appears that the larger steric bulk of the C_5Me_5 ring is necessary to slow formation of osmocinium salts (i.e., to stabilize products with one ring per metal center relative to products with two rings per metal center). It is worth noting in this context that no analogues of the ruthenium complexes $(C_5Me_5)_2Ru_2X_4$ (where X = Cl, Br) have been reported with cyclopentadienyl rings other than C_5Me_5, presumably for similar reasons.

3. Experimental section

All operations were carried out under argon or vacuum using standard Schlenk techniques unless otherwise specified. Solvents were distilled under nitrogen from magnesium (ethanol), calcium hydride (dichloromethane), or sodium benzophenone (pentane, diethyl ether). *tert*-Butanol (Aldrich), tetramethylcyclopentadiene (Aldrich), hydrobromic acid (Aldrich), osmium tetroxide (Colonial Metals), and $HBF_4 \cdot Et_2O$ (Aldrich) were used as received.

Elemental analyses were performed by the University of Illinois Microanalytical Laboratory. Field-desorption (FD) mass spectra were performed on a 70-VSE-A mass spectrometer. Positive-ion fast-atom bombardment (FAB) mass spectra were acquired on a 70-VSE-C mass spectrometer. The negative ion electrospray mass spectrum was obtained on a Quattro mass spectrometer. The samples were loaded as CH_2Cl_2 solutions and the spectrometer source temperature was 25 °C. All peak envelopes matched the calculated isotope distribution patterns for the respective ions. The IR spectra were obtained on a Nicolet Impact 410 spectrometer as Nujol mulls between KBr plates. The ^1H, ^{13}C, and ^{19}F NMR data were recorded on a Varian Unity-400 spectrometer at 9.4 T. Chemical shifts are reported in δ units (positive shifts to higher frequency) relative to TMS or $CFCl_3$. Melting points were measured on a Thomas-Hoover Unimelt apparatus in sealed capillaries under argon.

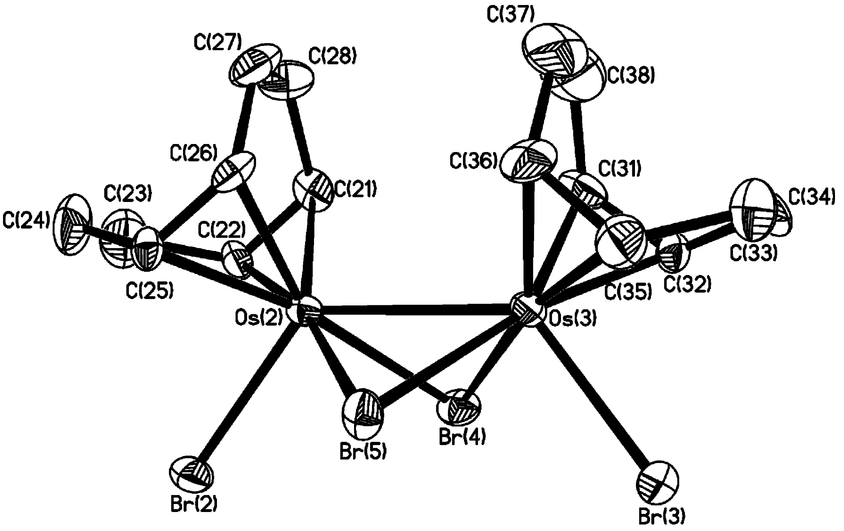

Fig. 3. ORTEP diagram of the $[Os_2HBr_4(cod)_2^-]$ anion in **2**. The 35% probability density surfaces are shown; hydrogen atoms are omitted for clarity.

3.1. Bromobis(tetramethylcyclopentadienyl)osmium(IV) octabromodiosmate(III), $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ (1)

To a solution of H_2OsBr_6 (1.99 g, 2.98 mmol) in *tert*-butanol (40 mL) was added tetramethylcyclopentadiene (0.99 mL, 11.92 mmol). The resulting dark red solution was heated to reflux for 8 h, during which time a reddish brown microcrystalline precipitate formed. The solid was collected by filtration, washed with diethyl ether (2 × 20 mL), and vacuum dried. Yield: 1.10 g (72%); m.p.: >280 °C. Anal. Calc. for $C_{36}H_{52}Br_{10}Os_4$: C, 21.2; H, 2.56; Br, 39.1. Found: C, 21.8; H, 2.81; Br, 38.8. MS (FD): 434 ($(C_5Me_4H)_2Os^+$), 513 ($(C_5Me_4H)_2OsBr^+$). ^1H NMR (CD_2Cl_2, 25 °C): δ 5.65 (s, 1H, C_5Me_4H), 2.14 (s, 6H, C_5Me_4H), 2.13 (s, 6H, C_5Me_4H). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 106.4 (s, C_5Me_4H), 99.0 (s, C_5Me_4H), 81.7 (s, C_5Me_4H), 12.5 (s, C_5Me_4H), 11.8 (s, C_5Me_4H). IR (cm^{-1}): 1506 (w), 1309 (m), 1261 (m), 1171 (w), 1148 (w), 1120 (w), 1088 (w) 1032 (sh), 1018 (m), 967 (w), 803 (w), 610 (w).

3.2. Bromobis(tetramethylcyclopentadienyl)osmium(IV) dibromodi(μ-bromo)(μ-hydrido)bis(1,5-cyclooctadiene) diosmate(II), $[(C_5Me_4H)_2OsBr][Os_2HBr_4(cod)_2]$ (2)

To a reddish brown suspension of $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ (0.70 g, 0.34 mmol) in ethanol (40 mL) was added 1,5-cyclooctadiene (0.90 mL, 7.35 mmol). The reaction mixture was heated to reflux for 3 h, during which time a yellow solution formed. The solvent was evaporated, leaving a green solid. The solid was washed with diethyl ether (3 × 20 mL) to remove bis(tetramethylcyclopentadienyl)osmium (see below) and then re-dissolved in ethanol (25 mL). The ethanol solution was concentrated to 10 mL and cooled to −20 °C for 4 h to afford green crystals. Yield: 0.24 g (46%); m.p.: >280 °C. Anal. Calc. for $C_{34}H_{51}Br_5Os_3$: C, 28.6; H, 3.60. Found: C, 28.9; H, 3.56. MS (FD): 434 ($(C_5Me_4H)_2Os^+$), 917 ($Os_2HBr_4(cod)_2^+$). ^1H NMR (CD_2Cl_2, 25 °C): δ 5.92 (s, 2H, C_5Me_4H), 4.25 (m, 4H, cod), 4.01 (m, 4H, cod), 2.58 (m, 4H, cod), 2.32 (m, 4H, cod), 2.02–2.18 (m, cod), 2.14 (s, C_5Me_4H), 2.11 (s, C_5Me_4H)], −20.79 (s, 1H, Os–H–Os). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 25 °C): δ 79.1 (s, C_5Me_4H), 65.2 (s, cod), 59.8 (s, cod), 35.8 (s, cod), 32.3 (s, cod), 12.0 (s, C_5Me_4H), 10.9 (s, C_5Me_4H). IR (cm^{-1}): 2073 (m), 1321 (m), 1263 (w), 1235 (w), 1204 (w), 1181 (w), 1163 (w), 1155 (w), 1114 (w), 1070 (w), 1033 (m), 1003 (w), 982 (w), 930 (vw), 919 (w), 908 (w), 871 (w), 847 (m), 826 (w), 816 (sh), 783 (w), 723 (w).

3.3. Bis(tetramethylcyclopentadienyl)osmium(II) $(C_5Me_4H)_2Os$ (3)

A red suspension of $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8]$ (0.45 g, 0.22 mmol) in ethanol (30 mL) was heated to reflux for 12 h yielding a black solid and a yellow solution. The solvent was evaporated, leaving a black solid. The solid was extracted into diethyl ether (3 × 20 mL) and the yellow extracts were filtered, combined, and taken to dryness in vacuum. Sublimation at 50 °C and 10^{-3} Torr yielded a white crystalline solid. Yield: 0.070 g (37%); m.p.: 128–130 °C. Anal. Calc. for $C_{18}H_{26}Os$: C, 50.0; H, 6.06. Found: C, 49.3; H, 5.59. MS (FD): 434 ($(C_5Me_4H)_2Os^+$). ^1H NMR (CD_2Cl_2, 25 °C): δ 4.25 (s, 1H, C_5Me_4H), 1.78 (s, 6H,

Table 4
Os–Os distances for binuclear osmium hydrides

Compound	Os–Os (Å)	Reference
$(C_5Me_5)_2Os_2(\mu-H)_4$	2.4567(6)	[14]
$(\eta^6-C_6H_3Me_3)_2Os_2(\mu-H)_3$	2.4741(2)	[15]
$Os_2(\mu-H)_3H(PMe_2Ph)_5$	2.551(1)	[16]
$[Os_2(\mu-H)_3(PMe_2Ph)_6][Cl]$	2.558(2)	[16]
$(\eta^6-p-MeC_6H_4CHMe_2)_2$ $Os_2\{\mu-\eta^2-OC(H)O\}(\mu-OH)(\mu-H)$	2.766(1)	[17]
$Os_2(\mu-H)_2H_2(PMe_2Ph)_6$	2.818(1)	[16]
$[(C_5Me_4H)_2Os(Br_{0.70}H_{0.30})][Os_2HBr_4(cod)_2]$	2.874(1)	This work

C_5Me_4H), 1.75 (s, 6H, C_5Me_4H). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 79.9 (s, C_5Me_4H), 78.0 (s, C_5Me_4H), 69.5 (s, C_5Me_4H), 12.5 (s, C_5Me_4H), 10.6 (s, C_5Me_4H). IR (cm^{-1}): 1419 (m), 1411 (m), 1318 (m), 1308 (m), 1169 (w), 1146 (w), 1113 (m), 1033 (s), 970 (m), 919 (w), 893 (vw), 870 (vw), 825 (m), 781 (sh), 722 (w), 682 (m), 669 (w), 634 (vw), 609 (vw), 599 (vw), 560 (w), 449 (w), 441 (w), 434 (w).

3.4. Hydridobis(tetramethylcyclopentadienyl)osmium(IV) tetrafluoroborate $[(C_5Me_4H)_2OsH][BF_4]$ (4)

To a solution of $(C_5Me_4H)_2Os$ (0.13 g, 0.30 mmol) in diethyl ether (20 mL) was added HBF_4 (0.04 mL of 54% solution in diethyl ether, 0.30 mmol). A white flocculent precipitate formed immediately. After 10 min, the solid was collected by filtration and dried in vacuum. Yield: 0.07 g (42%); m.p.: >280 °C. MS (positive ion FAB): 435 ($(C_5Me_4H)_2OsH^+$). MS (negative ion ESI): *m/e* 87 (BF_4^-). ^{1}H NMR (CD_2Cl_2, 25 °C): δ 4.94 (s, 1H, C_5Me_4H), 2.11 (s, 6H, C_5Me_4H), 2.04 (s, 6H, C_5Me_4H), −14.91 (s, 1H, Os–H). ^{13}C NMR (CD_2Cl_2, 25 °C): δ 93.4 (s, C_5Me_4H), 91.5 (s, C_5Me_4H), 78.5 (s, C_5Me_4H), 11.4 (s, C_5Me_4H), 10.4 (s, C_5Me_4H). ^{19}F NMR (CD_2Cl_2, 25 °C): δ −152.47 (s, BF_4). IR (cm^{-1}): 3171 (m), 2724 (m), 2403 (w), 2351 (w), 2318 (vw), 2150 (w), 2101 (w), 1313 (m), 1282 (m), 1168 (m), 1155 (m), 1088 (m), 1025 (m), 968 (m), 937 (m), 920 (m), 891 (m), 843 (m), 817 (m), 763 (w), 687 (w), 666 (w).

3.5. Crystallographic studies [18]

Single crystals of $[(C_5Me_4H)_2OsBr]_2[Os_2Br_8] \cdot 2CH_2Cl_2$ (**1**), grown by layering pentane onto a solution of the complex in dichloromethane and allowing the mixture to stand for 2 months at −20 °C, were mounted on glass fibers with Paratone oil (Exxon) and immediately cooled to −75 °C in a cold nitrogen gas stream on the diffractometer. [Single crystals of 2, grown by layering diethyl ether onto a solution of the complex in dichloromethane and allowing the mixture to stand for 3 months at −20 °C, were treated similarly; subsequent comments in brackets will refer to this compound. Crystals obtained over shorter crystallization periods were too small to afford useful data sets.] Standard peak search and indexing procedures, followed by least-squares refinement using 1013 [983] reflections, yielded the cell dimensions given in Table 1.

Data were collected with an area detector. The cell dimensions and average values of the normalized structure factors were most consistent with the space group $P\bar{1}$, and this choice was confirmed by successful refinement of the proposed model. [For **2**, the systematic absences $0k0$ ($k \neq 2n$) and $h0l$ ($h + l \neq 2n$) were consistent only with the space group $P2_1/n$.] The measured intensities were reduced to structure factor amplitudes and their estimated standard deviations by correction for background, Lorentz, and polarization effects. No corrections for crystal decay were necessary, but the data were corrected for absorption. The maximum and minimum transmission factors were 0.340 [0.855] and 0.061 [0.109]. Systematically absent reflections were deleted and symmetry equivalent reflections were averaged to yield the set of 4894 unique data used in the full-matrix least-squares refinement. [For **2**, three reflections ($\bar{1}11$, $\bar{1}22$, and 124) were found to be statistical outliers and were deleted; the remaining 6831 data were used in the full-matrix least-squares refinement.]

The positions of the osmium and bromine atoms were determined by using direct methods (SHELXTL). Subsequent least-squares refinement and difference Fourier calculations revealed the positions of the remaining non-hydrogen atoms. The unique osmium atom of the anion is disordered over two sites. The occupancy factors for the two sites were restrained to add to 1; the occupancy factor for the major site refined to 0.879(1). The quantity minimized by the least-squares program was $\sum w(F_o^2 - F_c^2)^2$, where $w = \{[\sigma(F_o^2)]^2 + (0.046P)^2\}^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$. [For **2**, $w = \{[\sigma(F_o^2)]^2 + (0.063P)^2\}^{-1}$.] The analytical approximations to the scattering factors were used, and all structure factors were corrected for both real and imaginary components of anomalous dispersion.

In the final cycle of least squares, anisotropic displacement factors were refined for all non-hydrogen atoms. [For **2**, the cation was found to be a mixture of $[(C_5Me_4H)_2OsBr^+]$ and $[(C_5Me_4H)_2OsH^+]$; these two species occupied the same site in the crystal. Attempts to refine the bromine as a full-occupancy atom led to unrealistically large displacement factors. To model the disorder, the Br atom was assigned a variable site occupancy factor, which refined to 0.698(7). The terminal hydride, which evidently is present with a site occupancy factor of 0.302, was not included as part of the model. Also in **2**, similarity constraints were imposed on chemically equivalent C–C distances and the anisotropic displacement factors for the carbon atoms were restrained to be near-isotropic.] Hydrogen atoms were placed in idealized positions (methyl groups were allowed to rotate about the C–C bond) with C–H = 0.93, 0.97, and 0.96 Å, for methine, methylene, and methyl groups, respectively. The displacement parameters for methine and methylene hydrogens were set equal to $1.2U_{eq}$ for the attached carbon; those for methyl hydrogens were set to $1.5U_{eq}$. [For **2**, the hydrogen atom bridging between the two osmium atoms could not be located in the difference maps.] An isotropic extinction parameter was refined to a final value of $x = 0.0010(2)$ [0.00032(4)], where F_c is multiplied by the factor $k[1 + F_c^2 x\lambda^3/\sin 2\theta]^{-1/4}$ with k being the overall scale factor. Successful convergence was indicated by the maximum shift/error of 0.001 for the last cycle. Final refinement parameters are given in Table 1. The largest peak in the final Fourier difference map (2.14 e Å^{-3}) was located 1.14 Å from Os(2). [For **2**, the largest peak in the final Fourier difference map (1.50 e Å^{-3}) was located 1.40 Å from Os(1).] A final analysis of variance between observed and calculated structure factors showed no systematic errors.

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Appendix A. Supplementary data

The ORTEP diagram of $[(C_5Me_4H)_2Os(Br_{0.70}H_{0.30})^+]$ and the ^{1}H NMR spectrum of $[(C_5Me_4H)_2OsBr][Os_2HBr_4(cod)_2]$ (**2**) are available as supplementary material. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 296785 for **1** and 296786 for **2**. Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk). Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.02.028.

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