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**STRUCTURE AND REACTIVITY OF THE ANIONIC ALKENEOSMIUM CLUSTER, [1,1,1,2,2,2,3,3,3,3-DECACARBONYL-2-BROMO-1- $\eta^2$ -*trans*-1,1,1,4,4,4-HEXAFLUORO BUT-2-ENE-*triangulo*-TRIOSMIUM]<sup>-</sup>:**

**X-RAY CRYSTAL STRUCTURES OF**

**[ $(\text{Ph}_3\text{P})_2\text{N}][\text{Os}_3(\text{CO})_{10}(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)\text{Br}]^-$ ,**  
**[ $(\text{Ph}_3\text{P})_2\text{N}][\text{Os}_3(\text{CO})_9(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})]$ , AND**  
**[ $\text{HOs}_3(\text{CO})_9(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})$ ]<sup>\*</sup>**

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**Summary**

The  $\eta^2$ -alkenebromoosmium cluster  $[\text{Os}_3(\text{CO})_{10}(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)\text{Br}]^-$  (1) when refluxed in dichloromethane gives  $[\text{Os}_3(\text{CO})_9(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})]^-$  (2). On reaction with  $[\text{Me}_3\text{O}]\text{BF}_4$  1 gives  $[\text{HOs}_3(\text{CO})_{10}\text{Br}]$  and  $[\text{Os}_3(\text{CO})_{11}(\text{trans-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)]$  (3), whilst reaction with  $\text{MeSO}_3\text{F}$  affords 3 and  $[\text{HOs}_3(\text{CO})_9(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})]$  (4). To confirm structural conclusions based on <sup>1</sup>H NMR, mass spectra and IR data, single crystal X-ray structures of the starting material and the two  $\mu\text{-Br}$  products have been determined. Crystals of  $[\text{Os}_3(\text{CO})_{10}(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)\text{Br}][\text{PPN}]$  (PPN =  $(\text{Ph}_3\text{P})_2\text{N}$ ) are monoclinic, space group  $P2_1/c$ , with  $a$  15.521(4),  $b$  8.863(3),  $c$  37.497(11) Å,  $\beta$  95.11(2)°,  $Z = 4$ , and final  $R = 0.047$ . Crystals of  $[\text{Os}_3(\text{CO})_9(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})][\text{PPN}]$  are orthorhombic, space group  $Pbca$ , with  $a$  15.725(5),  $b$  20.194(8),  $c$  32.295(12) Å,  $Z = 8$ , and final  $R = 0.068$ . Crystals of  $[\text{HOs}_3(\text{CO})_9(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})]$  are monoclinic, space group  $C2/c$ , with  $a$  27.670(3),  $b$  9.225(2),  $c$  16.799(3) Å,  $\beta$  92.24(4)°,  $Z = 8$  and final  $R = 0.082$ . In all three structures the alkene ligand is  $\eta^2$ -bonded to one Os atom but

\* Dedicated to Professor H.J. Emeléus on the occasion of his 80th birthday on 22nd June, 1983. Professor Emeléus was Head of Department whilst I was a Research Student at Cambridge and also during my first five years on the Staff. I owe much to his support and encouragement.

the differing relative positions of the bromine atoms have a significant effect on the C–C alkene distance. The outcome of the reactions studied is interpreted in terms of the stabilising effect of the  $\text{CF}_3$  substituents on the complexed alkene, both with respect to displacement and ligand modification.

Unsaturated organic ligands show a strong tendency to participate in multicentre bonding with polynuclear complexes and, as a result, simple alkene complexes of transition metal clusters are relatively rare. For example, the reaction of  $[\text{H}_2\text{Os}_3(\text{CO})_{10}]$  with ethylene gives a hydridovinyl species,  $[\text{HOs}_3(\text{CO})_{10}(\mu\text{-CH=CH}_2)]$  [1,2] and the reaction of  $[\text{Os}_3(\text{CO})_{12}]$  with ethylene gives the vinylidene complex,  $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}=\text{CH}_2)]$  [3]. The complexes  $[\text{Os}_3(\text{CO})_{11}(\text{C}_2\text{H}_4)]$  [4] and  $[\text{HOs}_3(\text{CO})_9(\text{C}_2\text{H}_4)(\text{SMe})]$  [5] have been reported and these clusters owe their existence to the ability of their respective precursors,  $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$  and  $[\text{HOs}_3(\text{CO})_9(\text{SMe})]$ , to react with ethylene via generation of a vacant coordination site under mild conditions. We have reported the formation of alkene clusters [6], where the alkene is substituted with the strongly electronegative group  $\text{CF}_3$ , wherein the alkene–metal interaction can be represented in terms of the formation of a three-membered metallocycle containing two normal two-centre two-electron bonds in addition to the C–C linkage, which approaches that expected for a single bond distance [6–8].

Few reactions of simple cluster alkene complexes have been reported apart from the pyrolysis of  $[\text{Os}_3(\text{CO})_{11}(\text{C}_2\text{H}_4)]$  in octane to give the vinylidene complex,  $[\text{H}_2\text{Os}_3(\text{CO})_9(\text{C}=\text{CH}_2)]$  together with  $[\text{Os}_3(\text{CO})_{12}]$  [9].  $[\text{HOs}_3(\text{CO})_9(\text{C}_2\text{H}_4)(\text{SMe})]$  is also pyrolysed in octane with ejection of the alkene to give the precursor, in which the SMe ligand resumes a face-capping position on the cluster, although in the presence of excess  $\text{C}_2\text{H}_4$  the vinyl complex  $[\text{HOs}_3(\text{CO})_9(\text{CH}=\text{CH}_2)\text{S}]$  is obtained [10].

We now describe in detail the pyrolysis and attempted protonation and methylation of the anionic alkene cluster derivative  $[\text{Os}_3(\text{CO})_{10}(\text{trans-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{-CF}_3)\text{Br}]^-$  (**1**) [11,12]. These reactions in the main give cluster products in which the alkene ligand is unaffected and remains  $\eta^2$ -bonded to a single osmium atom, demonstrating the remarkable stabilising power of the  $\text{CF}_3$  substituents on this type of linkage.

## Results and discussion

The high yield route (ca. 75%) to the anion  $[\text{Os}_3(\text{CO})_{10}(\text{trans-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{-CF}_3)\text{Br}]^-$  (**1**) from the reaction of  $[\text{HOs}_3(\text{CO})_{10}(\text{CF}_3\text{C}:\text{C}(\text{H})\text{CF}_3)]$  [6] with  $[\text{Et}_4\text{N}]\text{Br}$  has been previously described [11].

(a) *Thermolysis of 1*. When an amber solution of **1** in dichloromethane is raised to reflux ( $40^\circ\text{C}$ ), a change in colour to amber-red takes place within a few minutes. The colour deepens over 24 h after which TLC shows the formation of one product, along with a little starting material. Evaporation of the solvent and crystallisation from hot methanol gave **2** as scarlet needles (40%). The IR spectrum of **2** is considerably different from that of the starting material **1**, and lacked the weak band at  $1829\text{ cm}^{-1}$  assignable to the incipient bridging carbonyl ligand in **1**. The semi-bridging nature of this ligand is thought to be due to the need to alleviate the

polarity induced in the molecule by the terminal bromide ligand, and the absence of such a CO ligand in **2** suggests the loss of this polarity. An X-ray analysis confirms this suggestion and shows that the bromide in **2** adopts a bridging position.

The loss of CO rather than the alkene ligand during the above pyrolysis reaction is in direct contrast to the outcome of the previously studied pyrolysis of  $[\text{Os}_3(\text{CO})_{11}(\text{C}_2\text{H}_4)]$  [9] and  $[\text{HOs}_3(\text{CO})_9(\text{C}_2\text{H}_4)(\text{SMe})]$  [10]. It is unexpected in that carbonyl loss from an anionic complex usually occurs less readily than from a neutral one, since the increased electron density available at the cluster for back donation to the carbonyl group increases the strength of the metal-carbonyl bond. In this case, however, the electron-withdrawing properties of the  $\text{CF}_3$  substituted alkene ligand may reduce the electron density on the Os atom to which it is attached, thereby weakening the bonds from this atom to its associated CO ligands. Certainly the relatively mild conditions under which CO loss takes place suggests that the required activation energy is low.

The lack of reaction of the alkene ligand itself on pyrolysis of **1** could be due to the readiness with which the terminal Br ligand can adopt a  $\mu_2$ -bonding mode, thereby satisfying the electron deficiency resulting from departure of the CO group. That the Br ligand is important in allowing the pyrolysis of **1** to proceed under such mild conditions was demonstrated by an attempt to pyrolyse the related anionic complex  $[\text{HOs}_3(\text{CO})_{10}(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)]^-$  [12] under the same conditions. No reaction was detected after several hours and unchanged starting material was recovered quantitatively. This unwillingness of the  $\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3$  ligand to transfer a proton to the metal atom framework as compared to the previously known cluster alkene complexes containing  $\text{C}_2\text{H}_4$  is, perhaps, hardly surprising in view of the ease with which the reverse proton transfer from metal to ligand has been shown to occur [8].

(b) *Reactions of 1 with  $[\text{Me}_3\text{O}]\text{BF}_4$  and  $\text{MeSO}_3\text{F}$ .* Treatment of a dichloromethane solution of  $[\text{Os}_3(\text{CO})_{10}(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)\text{Br}][\text{PPN}]$  (**1**) with an excess of  $[\text{Me}_3\text{O}]\text{BF}_4$  gave, after 12 h, approximately 50% conversion to two pale yellow neutral complexes in roughly equal yields, separated by chromatography (see Scheme 1). The remaining ionic material was identified as residual starting material by an infrared spectrum. One of the products was identified as the known complex  $[\text{HOs}_3(\text{CO})_{10}\text{Br}]$  on the basis of its IR and mass spectra [13], with the proton presumably coming from the acid impurity commonly found in the oxonium salt. However, since treatment of **1** with a variety of acids such as  $\text{H}_2\text{SO}_4$  or  $\text{HSO}_3\text{F}$  in many different solvent media gave little or no neutral material, the  $[\text{Me}_3\text{O}]^+$  must also play a role in the formation of this product. The second complex showed  $\nu(\text{C}-\text{F})$  absorptions in its IR spectrum indicating the presence of the organic ligand, and the IR and mass spectra were identical to those observed for  $[\text{Os}_3(\text{CO})_{11}(\text{trans}-\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)]$  (**3**) [8]. The formation of this product is interesting in that abstraction of bromine has occurred on attack by the "methylating" agent, and the complex has scavenged a carbonyl ligand. Methyl bromide is presumed to be liberated. Although this process was not anticipated, it has been previously observed, and methylating agents have been employed as halide abstractors in mononuclear platinum chemistry [14].

When  $\text{MeSO}_3\text{F}$  is used as the methylating agent, the reaction with **1** follows a different course. Again two neutral complexes, present in yields of 30 and 50% were isolated, but in this case both products were shown by their IR spectra to contain the



TABLE 2  
SUMMARY OF CRYSTAL DATA

	$C_{50}H_{32}BrF_6NO_{10}Os_3P_2$ (1)	$C_{49}H_{32}BrF_6NO_9Os_3P_2$ (2)	$C_{13}H_3BrF_6NO_9Os_3$ (4)
<i>M</i>	1633.3	1605.3	1067.5
Crystal system	Monoclinic	Orthorhombic	Monoclinic
<i>a</i> (Å)	15.521(4)	15.725(5)	27.670(3)
<i>b</i> (Å)	8.863(3)	20.194(8)	9.225(2)
<i>c</i> (Å)	37.497(11)	32.395(12)	16.799(3)
$\beta$ (°)	95.11(2)	(90)	92.24(4)
Space group	$P2_1/c$	$Pbca$	$C2/c$
<i>U</i> (Å <sup>3</sup> )	5137.68	10255.28	4284.8
<i>Z</i>	4	8	8
$D_c$ (g cm <sup>-3</sup> )	2.111	2.079	3.308
<i>F</i> (000)	3064	6016	3976
$\mu$ (Mo- $K_{\alpha}$ )(cm <sup>-1</sup> )	82.76	82.9	189.8
Crystal size(mm)	0.33×0.27×0.21	0.29×0.26×0.13	0.16×0.14×0.10
Unique data	5650 <sup>a</sup>	4805 <sup>a</sup>	3424 <sup>b</sup>
No of variables	407	274	302
Final <i>R</i>	0.047	0.068	0.082
Final <i>R'</i> [ $w = 1/\sigma^2(F)$ ]	0.048	0.069	0.087
Diffractometer	Syntex P2 <sub>1</sub>	Stoe-Siemens AED	Philips PW1100

<sup>a</sup> $F > 4\sigma(F)$ , <sup>b</sup> $F > 6\sigma(F)$

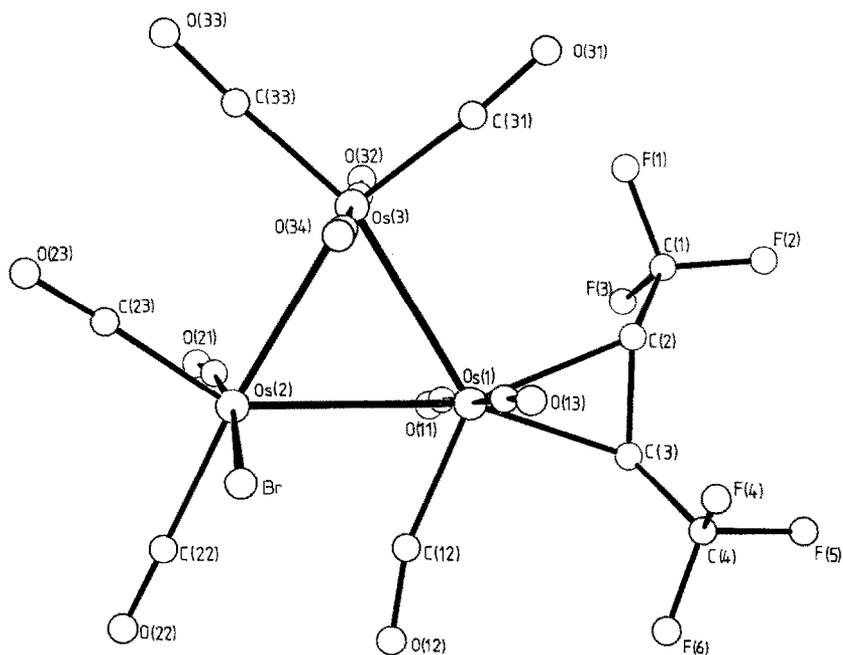


Fig. 1. Molecular structure of  $[\text{Os}_3(\text{CO})_{10}(\text{trans}\text{-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)\text{Br}]^-$  (1).

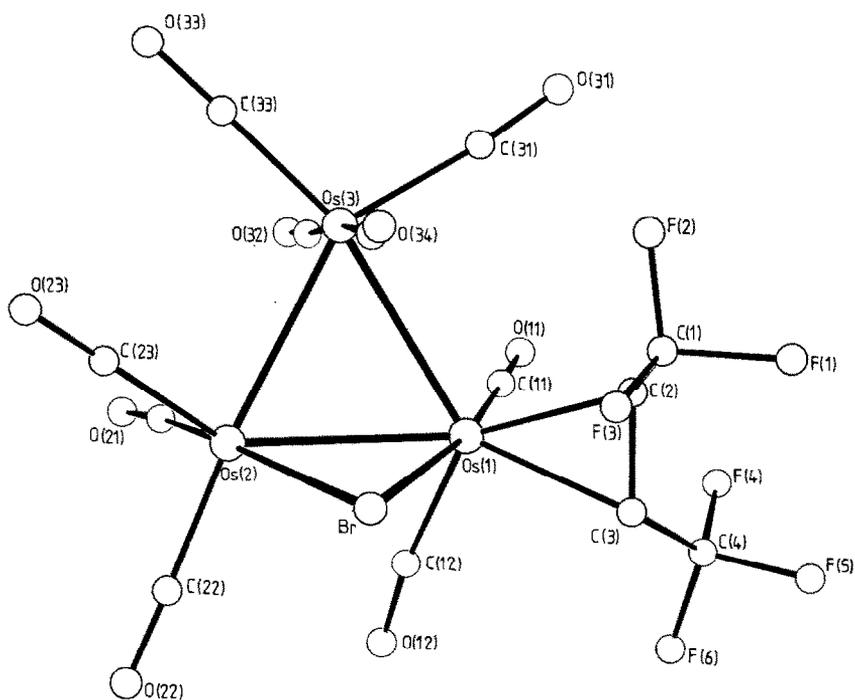


Fig. 2. Molecular structure of  $[\text{Os}_3(\text{CO})_9(\text{trans}\text{-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})]^-$  (2).

TABLE 3  
SELECTED INTERATOMIC DISTANCES (Å) FOR 1, 2 AND 4

	1	2	4
<i>(a) Metal-metal bonds</i>			
Os(1)-Os(2)	2.901(2)	2.757(1)	2.914(2)
Os(1)-Os(3)	2.892(2)	2.847(1)	2.868(2)
Os(2)-Os(3)	2.853(2)	2.828(1)	2.820(2)
<i>(b) Metal-bromine bonds</i>			
Os(1)-Br		2.646(3)	
Os(2)-Br	2.628(2)	2.577(3)	2.583(4)
Os(3)-Br			2.587(4)
<i>(c) Metal-carbon bond</i>			
Os(1)-C(2)	2.171(14)	2.098(21)	2.24(3)
Os(1)-C(3)	2.120(15)	2.147(21)	2.16(4)
<i>(d) Os-C (carbonyl)</i>			
Range	1.834-1.954(20)	1.784-1.925(23)	1.68-1.95(5)
Mean	1.908	1.865	1.871
<i>(e) Ligand distances</i>			
C(1)-C(2)	1.484(22)	1.47(4)	1.46(5)
C(2)-C(3)	1.489(21)	1.40(3)	1.46(6)
C(3)-C(4)	1.493(22)	1.48(4)	1.49(6)
Range	1.301-1.343(22)	1.30-1.44(4)	1.33-1.43(7)
Mean	1.325	1.345	1.38
<i>(f) C-O (carbonyl)</i>			
Range	1.110-1.182(26)	<sup>a</sup>	1.09-1.38(7)
Mean	1.152	1.158	1.191

<sup>a</sup> The carbonyl distances for **2** were constrained during refinement.

scopic data used to identify the new compounds described here are presented in Table 1). The parent ion for the hydrido complex was observed at  $m/z$  1073 ( $^{192}\text{Os}$ ) corresponding to the formulation  $[\text{HOs}_3(\text{CO})_9(\text{CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})]$  (**4**), with an X-ray analysis confirming this formulation (*vide infra*).

Acid impurity again appears to be responsible for the presence of the hydride ligand in **4**. The elimination of this impurity is difficult and unfortunately it seems to react preferentially precluding the observation of methylated products. Methylation of **1** may, in any event, not be a favoured process since the electron-withdrawing properties of the  $\text{CF}_3$  substituents are likely to inhibit electrophilic attack at the alkene ligand, and only one example of the methylation of a trinuclear cluster at the metal atoms is known [15]. Methylation at the oxygen of a carbonyl group is better documented [16] but generally requires the presence of a bridging CO ligand, a criterion which, despite the incipient CO bridge, is not fully met by **1**.

*(c) X-ray crystal structures of compounds 1, 2, and 4.* Crystal data for these three compounds are given in Table 2 and selected interatomic distances (Table 3) and intermolecular angles (Table 4) are tabulated together for easy comparison. The fractional atomic coordinates for **1**, **2** and **4** are given in Tables 5, 6 and 7 respectively in the Experimental section. The molecular structures are shown in the respective Fig. 1-3.

The molecular structure of **1** (Fig. 1) is derived from that of  $[\text{Os}_3(\text{CO})_{12}]$  [17] with an axial carbonyl ligand on one metal atom replaced by a bromine ligand, and an

TABLE 4  
SELECTED INTRAMOLECULAR ANGLES (°) FOR 1, 2 AND 4

(a) Angles at osmium	1	2	4
Os(2)–Os(1)–Os(3)	59.0(1)	60.6(1)	58.4(1)
Os(1)–Os(2)–Os(3)	60.3(1)	61.3(1)	60.0(1)
Os(1)–Os(3)–Os(2)	60.7(1)	58.1(1)	61.6(1)
Os(2)–Os(1)–C(2)	158.6(4)	147.2(6)	156(1)
Os(3)–Os(1)–C(2)	99.9(4)	101.9(6)	98(1)
Os(2)–Os(1)–C(3)	160.4(4)	144.6(1)	165(1)
Os(3)–Os(1)–C(3)	140.4(4)	139.7(5)	136(1)
C(2)–Os(1)–C(3)	40.6(6)	38.5(8)	39(2)
C(2)–Os(1)–C(11)	91.6(6)	91.7(9)	93(2)
C(3)–Os(1)–C(11)	85.8(6)	98.9(9)	90(2)
C(2)–Os(1)–C(12)	136.0(6)	133.6(9)	126(2)
C(3)–Os(1)–C(12)	95.7(6)	95.8(9)	87(2)
C(2)–Os(1)–C(13)	86.1(6)		87(2)
C(3)–Os(1)–C(13)	93.9(6)		97(2)
Os(2)–Os(1)–C(11)	88.6(4)	113.0(6)	86(1)
Os(3)–Os(1)–C(11)	98.6(4)	86.5(6)	85(1)
Os(2)–Os(1)–C(12)	65.4(4)	71.0(6)	78(1)
Os(3)–Os(1)–C(12)	123.5(4)	124.4(7)	137(1)
Os(2)–Os(1)–C(13)	92.7(4)		90(1)
Os(3)–Os(1)–C(13)	79.5(4)		86(1)
Os(1)–Os(2)–C(21)	90.6(5)	108.3(7)	90(1)
Os(3)–Os(2)–C(21)	89.9(5)	93.1(6)	115(1)
Os(1)–Os(2)–C(22)	115.0(6)	113.9(6)	99(1)
Os(3)–Os(2)–C(22)	175.3(6)	173.8(6)	144(1)
Os(1)–Os(2)–C(23)	145.1(4)	139.3(6)	166(1)
Os(3)–Os(2)–C(23)	84.8(4)	84.0(6)	107(1)
Os(1)–Os(3)–C(31)	98.3(6)	88.9(5)	86(1)
Os(2)–Os(3)–C(31)	157.7(6)	146.8(5)	133(1)
Os(1)–Os(3)–C(32)	79.4(5)	88.8(6)	90(1)
Os(2)–Os(3)–C(32)	90.0(5)	84.3(6)	115(1)
Os(1)–Os(3)–C(33)	160.4(5)	165.0(7)	173(1)
Os(2)–Os(3)–C(33)	101.7(5)	107.0(7)	111(1)
Os(1)–Os(3)–C(34)	97.2(4)	86.8(7)	
Os(2)–Os(3)–C(34)	86.4(4)	89.1(7)	
C(11)–Os(1)–C(12)	89.0(6)	88.5(9)	93(2)
C(11)–Os(1)–C(13)	176.7(6)		170(2)
C(12)–Os(1)–C(13)	94.3(6)		96(2)
C(21)–Os(2)–C(22)	90.6(7)	92.2(9)	91(2)
C(21)–Os(2)–C(23)	91.8(6)	93.2(9)	91(2)
C(22)–Os(2)–C(23)	99.8(7)	99.0(9)	96(2)
C(31)–Os(3)–C(32)	93.2(8)	91.6(8)	97(2)
C(31)–Os(3)–C(33)	100.1(8)	106.1(9)	101(2)
C(31)–Os(3)–C(34)	89.5(7)	93.3(9)	
C(32)–Os(3)–C(33)	92.9(7)	91.8(9)	91(2)
C(32)–Os(3)–C(34)	175.9(6)	173.3(9)	
C(33)–Os(3)–C(34)	89.7(6)	91.2(10)	
Os(1)–Os(2)–Br	94.3(1)	59.4(1)	87(1)
Os(3)–Os(2)–Br	98.6(1)	88.7(1)	57(1)
C(21)–Os(2)–Br	171.5(5)	164.4(7)	172(1)

TABLE 4 (continued)

(a) Angles at osmium	1	2	4
C(22)–Os(2)–Br	80.9(5)	85.3(6)	96(1)
C(23)–Os(2)–Br	88.3(4)	102.4(6)	91(1)

	2	4	
Br–Os(1)–C(2)	97.2(6)	Br–Os(3)–C(31)	91(1)
Br–Os(1)–C(3)	91.1(6)	Br–Os(3)–C(32)	171(1)
Br–Os(1)–C(11)	169.9(6)	Br–Os(3)–C(33)	90(1)
Br–Os(1)–C(12)	88.7(7)	Br–Os(3)–Os(1)	88(1)
Br–Os(1)–Os(2)	56.9(1)	Br–Os(3)–Os(2)	57(1)
Br–Os(1)–Os(3)	87.0(1)		
Os(1)–Br–Os(2)	63.7(1)	Os(2)–Br–Os(3)	66(1)

(b) Os–C–O	1	2	4
Range	164.6–179(2)	169.8–178.2(20)	157–179(4)
Mean	174.6	175.1	173

(c) Angles within the alkene ligand	1	2	4
F(1)–C(1)–F(2)	105(1)	99(2)	102(3)
F(1)–C(1)–F(3)	107(1)	104(2)	108(3)
F(2)–C(1)–F(3)	102(1)	109(3)	107(3)
F(1)–C(1)–C(2)	115(1)	110(2)	112(3)
F(2)–C(1)–C(2)	111(1)	115(3)	111(3)
F(3)–C(1)–C(2)	115(1)	119(3)	102(3)
C(1)–C(2)–C(3)	119(1)	118(2)	119(3)
C(1)–C(2)–Os(1)	123(1)	126(2)	125(2)
C(3)–C(2)–Os(1)	68(1)	73(1)	68(2)
C(2)–C(3)–Os(1)	72(1)	69(1)	73(2)
C(4)–C(3)–Os(1)	125(1)	119(2)	121(3)
C(2)–C(3)–C(4)	119(1)	117(2)	114(4)
C(3)–C(4)–F(4)	112(1)	118(2)	114(4)
C(3)–C(4)–F(5)	112(1)	115(2)	113(4)
C(3)–C(4)–F(6)	113(1)	116(2)	109(4)
F(4)–C(4)–F(5)	104(1)	102(2)	104(4)
F(4)–C(4)–F(6)	106(1)	104(2)	109(4)
F(5)–C(4)–F(6)	108(1)	99(2)	104(4)

equatorial carbonyl on another Os atom replaced by the fluoroalkene group. The dihedral angle between the planes defined by the atoms, Os(1)Os(2)Os(3) and Os(1)C(2)C(3) is  $4^\circ$  and the  $\text{CF}_3$  groups are *trans* with respect to each other. There is also an incipient bridging carbonyl group spanning the Os(1)–Os(2) edge with Os(1)–C(12) 1.929(15) Å and Os(2)... C(12) of 2.73(2) Å. This presumably helps to reduce the electron deficiency on Os(2) which is present unless the negative charge on the cluster is entirely localised on this atom.

In the structures of the two products **2** and **4** (Fig. 2 and 3, respectively) the

TABLE 5  
FRACTIONAL COORDINATES FOR 1

Atom	x	y	z
Os(1)	1.0040(1)	0.2750(1)	0.3569(1)
Os(2)	0.9391(1)	0.2943(1)	0.4270(1)
Os(3)	1.0082(1)	0.5568(1)	0.3959(1)
Br	0.7769(1)	0.3251(2)	0.4014(1)
C(1)	1.1628(11)	0.3803(17)	0.3107(4)
C(2)	1.0693(8)	0.3435(17)	0.3107(4)
C(3)	1.0422(10)	0.1823(16)	0.3086(4)
C(4)	0.9823(11)	0.1301(22)	0.2777(4)
F(1)	1.1836(7)	0.5126(12)	0.3260(4)
F(2)	1.1911(7)	0.3817(16)	0.2797(3)
F(3)	1.2152(6)	0.2786(12)	0.3297(3)
F(4)	0.9231(8)	0.2341(14)	0.2677(3)
F(5)	1.0232(7)	0.1063(15)	0.2486(3)
F(6)	0.9402(9)	0.0081(14)	0.2846(3)
C(11)	1.1075(9)	0.1874(13)	0.3792(4)
O(11)	1.1687(6)	0.1233(12)	0.3913(3)
C(12)	0.9411(9)	0.0994(16)	0.3705(4)
O(12)	0.9091(7)	-0.0192(11)	0.3716(3)
C(13)	0.9023(10)	0.3744(16)	0.3336(4)
O(13)	0.8430(7)	0.4268(14)	0.3181(3)
C(21)	1.0497(11)	0.2473(20)	0.4491(4)
O(21)	1.1118(8)	0.2067(18)	0.4642(3)
C(22)	0.8927(11)	0.1060(21)	0.4445(6)
O(22)	0.8670(9)	-0.0007(13)	0.4549(4)
C(23)	0.9159(8)	0.4249(15)	0.4648(4)
O(23)	0.8986(6)	0.5025(12)	0.4877(3)
C(31)	1.0428(12)	0.6801(20)	0.3606(5)
O(31)	1.0644(11)	0.7670(16)	0.3393(5)
C(32)	1.1221(11)	0.4847(16)	0.4086(5)
O(32)	1.1936(7)	0.4549(14)	0.4171(4)
C(33)	1.0132(9)	0.6931(16)	0.4343(5)
O(33)	1.0190(8)	0.7825(14)	0.4578(4)
C(34)	0.8885(10)	0.6159(15)	0.3828(4)
O(34)	0.8205(7)	0.6594(12)	0.3753(3)
N	0.5417(6)	0.2087(10)	0.1202(3)
P(1)	0.5217(2)	0.1880(3)	0.1601(1)
P(2)	0.5329(2)	0.1300(3)	0.0820(1)
C(101)	0.6075(5)	0.2777(11)	0.1882(2)
C(102)	0.5997(5)	0.3043(11)	0.2244(2)
C(103)	0.6679(5)	0.3701(11)	0.2457(2)
C(104)	0.7740(5)	0.4092(11)	0.2307(2)
C(105)	0.7518(5)	0.3826(11)	0.1945(2)
C(106)	0.6836(5)	0.3168(11)	0.1732(2)
C(111)	0.5125(4)	-0.0023(9)	0.1744(2)
C(112)	0.4359(4)	-0.0802(9)	0.1646(2)
C(113)	0.4295(4)	-0.2333(9)	0.1727(2)
C(114)	0.4997(4)	-0.3084(9)	0.1905(2)
C(115)	0.5763(4)	-0.2305(9)	0.2002(2)
C(116)	0.5827(4)	-0.0775(9)	0.1922(2)
C(121)	0.4207(5)	0.2762(9)	0.1692(2)
C(122)	0.3812(5)	0.3784(9)	0.1446(2)
C(123)	0.3038(5)	0.4482(9)	0.1515(5)

TABLE 5 (continued)

Atom	x	y	z
C(124)	0.2660(5)	0.4158(9)	0.1830(2)
C(125)	0.3055(5)	0.3136(9)	0.2076(2)
C(126)	0.3829(5)	0.2438(9)	0.2007(2)
C(201)	0.4403(4)	0.2006(9)	0.0546(2)
C(202)	0.4506(4)	0.2788(9)	0.0230(2)
C(203)	0.3785(4)	0.3379(9)	0.0028(2)
C(204)	0.2961(4)	0.3188(9)	0.0143(2)
C(205)	0.2859(4)	0.2406(9)	0.0460(2)
C(206)	0.3579(4)	0.1815(9)	0.0661(2)
C(211)	0.5277(4)	-0.0715(8)	0.0828(2)
C(212)	0.4560(4)	-0.1535(8)	0.0685(2)
C(213)	0.4553(4)	-0.3103(8)	0.0715(2)
C(214)	0.5263(4)	-0.3852(8)	0.0888(2)
C(215)	0.5980(4)	-0.3032(8)	0.1031(2)
C(216)	0.5987(4)	-0.1463(8)	0.1001(2)
C(221)	0.6262(5)	0.1762(8)	0.0590(2)
C(222)	0.6767(5)	0.3015(8)	0.0694(2)
C(223)	0.7452(5)	0.3436(8)	0.0499(2)
C(224)	0.7632(5)	0.2605(8)	0.0198(2)
C(225)	0.7127(5)	0.1352(8)	0.0093(2)
C(226)	0.6442(5)	0.0930(8)	0.0289(2)

alkene ligand has maintained its *trans*-configuration and is  $\eta^2$ -bound to Os(1) occupying a similar equatorial site to that which it occupies in the structure of **1**. The terminal axial Br atom in **1** on Os(2) adopts a bridging position between Os(1) and

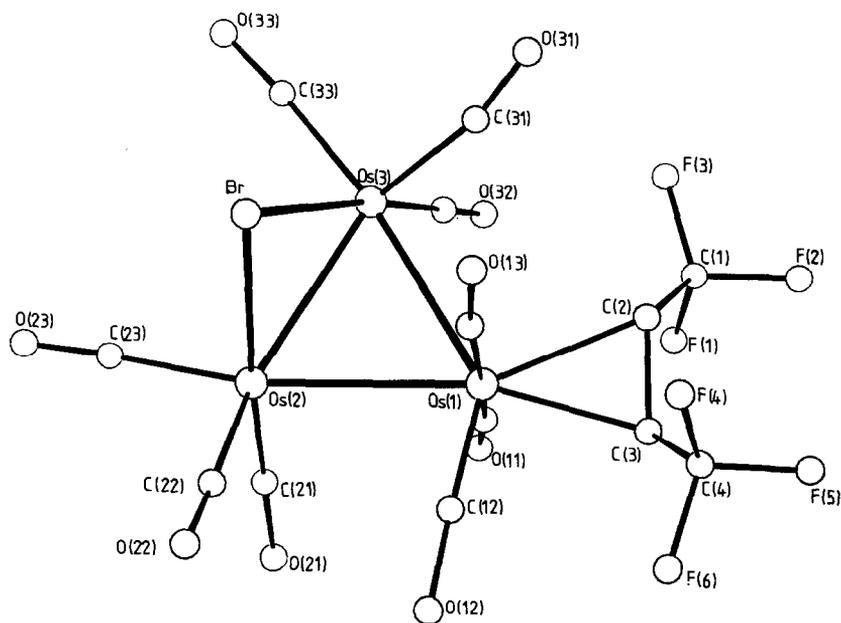


Fig. 3. Molecular structure of  $[(\mu\text{-H})\text{Os}_3(\text{CO})_9(\text{trans}\text{-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})]$  (**4**).

TABLE 6  
FRACTIONAL COORDINATES FOR 2

Atom	x	y	z
Os(1)	0.2648(1)	0.1983(1)	0.1367(1)
Os(2)	0.1424(1)	0.1098(1)	0.1105(1)
Os(3)	0.1541(1)	0.2341(1)	0.0706(1)
Br	0.1264(2)	0.1711(1)	0.1801(1)
C(1)	0.2279(21)	0.3362(15)	0.1809(10)
C(2)	0.2911(15)	0.2905(10)	0.1637(7)
C(3)	0.3243(14)	0.2418(10)	0.1900(7)
C(4)	0.4178(19)	0.2382(14)	0.1937(9)
F(1)	0.2699(13)	0.3850(8)	0.2062(5)
F(2)	0.1918(11)	0.3766(7)	0.1534(5)
F(3)	0.1686(12)	0.3125(7)	0.2049(5)
F(4)	0.4658(9)	0.2552(8)	0.1601(5)
F(5)	0.4510(12)	0.2755(11)	0.2226(6)
F(6)	0.4488(11)	0.1802(8)	0.2052(5)
C(11)	0.3496(13)	0.2077(10)	0.1006(6)
O(11)	0.4042(11)	0.2122(8)	0.0767(5)
C(12)	0.3028(13)	0.1123(9)	0.1468(7)
O(12)	0.3354(11)	0.0621(7)	0.1539(5)
C(21)	0.1845(15)	0.0645(10)	0.0651(6)
O(21)	0.2138(10)	0.0335(7)	0.0386(5)
C(22)	0.1371(13)	0.0331(9)	0.1420(6)
O(22)	0.1358(11)	-0.0170(8)	0.1594(6)
C(23)	0.0288(11)	0.1102(9)	0.0896(6)
O(23)	-0.0393(10)	0.1094(7)	0.0759(5)
C(31)	0.2166(11)	0.3144(8)	0.0644(6)
O(31)	0.2532(10)	0.3628(7)	0.0571(5)
C(32)	0.2233(12)	0.1917(8)	0.0357(5)
O(32)	0.2670(10)	0.1672(7)	0.0113(5)
C(33)	0.0657(14)	0.2372(11)	0.0305(7)
O(33)	0.0094(12)	0.2383(8)	0.0075(6)
C(34)	0.0801(15)	0.2708(11)	0.1122(7)
O(34)	0.0270(13)	0.2937(8)	0.1325(6)
N	0.7769(9)	0.4485(6)	0.1029(4)
P(1)	0.7004(3)	0.4221(2)	0.1294(1)
P(2)	0.8583(3)	0.4937(2)	0.1088(1)
C(101)	0.6703(7)	0.4732(5)	0.1719(4)
C(102)	0.7029(7)	0.4620(5)	0.2115(4)
C(103)	0.6849(7)	0.5063(5)	0.2434(4)
C(104)	0.6344(7)	0.5618(5)	0.2358(4)
C(105)	0.6018(7)	0.5729(5)	0.1962(4)
C(106)	0.6198(7)	0.5286(5)	0.1643(4)
C(111)	0.7218(7)	0.3412(6)	0.1498(4)
C(112)	0.6641(7)	0.3109(6)	0.1766(4)
C(113)	0.6824(7)	0.2489(6)	0.1933(4)
C(114)	0.7585(7)	0.2171(6)	0.1833(4)
C(115)	0.8162(7)	0.2474(6)	0.1566(4)
C(116)	0.7979(7)	0.3095(6)	0.1398(4)
C(121)	0.6098(7)	0.4173(6)	0.0953(4)
C(122)	0.6187(7)	0.4291(6)	0.0530(4)
C(123)	0.5484(7)	0.4237(6)	0.0268(4)
C(124)	0.4692(7)	0.4064(6)	0.0430(4)
C(125)	0.4603(7)	0.3945(6)	0.0853(4)

TABLE 6 (continued)

Atom	x	y	z
C(126)	0.5306(7)	0.4000(6)	0.1115(4)
C(201)	0.9004(8)	0.4943(5)	0.1602(4)
C(202)	0.8824(8)	0.5447(5)	0.1884(4)
C(203)	0.9060(8)	0.5378(5)	0.2298(4)
C(204)	0.9475(8)	0.4805(5)	0.2430(4)
C(205)	0.9654(8)	0.4301(5)	0.2148(4)
C(206)	0.9419(8)	0.4370(5)	0.1734(4)
C(211)	0.8382(7)	0.5774(6)	0.0927(4)
C(212)	0.7611(7)	0.5918(6)	0.0734(4)
C(213)	0.7460(7)	0.6552(6)	0.0579(4)
C(214)	0.8080(7)	0.7042(6)	0.0617(4)
C(215)	0.8852(7)	0.6898(6)	0.0810(4)
C(216)	0.9003(7)	0.6263(6)	0.0965(4)
C(221)	0.9390(6)	0.4627(6)	0.0752(4)
C(222)	0.9169(6)	0.4247(6)	0.0408(4)
C(223)	0.9794(6)	0.4045(6)	0.0129(4)
C(224)	1.0641(6)	0.4222(6)	0.0195(4)
C(225)	1.0862(6)	0.4602(6)	0.0539(4)
C(226)	1.0237(6)	0.4805(6)	0.0818(4)

Os(2) in **2** and across Os(2) and Os(3) in **4** acting as a three-electron donor. In the  $\mu$ -Br structures **2** and **4** the carbonyl has therefore presumably been lost from different Os atoms. It is impossible to determine whether this results from steric, and kinetic control during the decarbonylation reaction or whether it reflects the relative thermodynamic stability of the products. Certainly neither **2** or **4** showed any tendency to isomerise during the work-up procedures.

The bridging Br–Os bond lengths found for **2** are significantly different from each other (2.646 and 2.577 Å) with one distance longer than the terminal Br–Os bond in **1** (2.628 Å) and one distance shorter than the  $\mu$ -Br–Os distances in **4**. The Os–Os bromo bridged distance in **2** is short (2.757 Å) and may be associated with the progressive shortening of the C–C alkene bond in going from **1**  $\rightarrow$  **4**  $\rightarrow$  **2** of 1.489(21), 1.46(6) and 1.40(3) Å, respectively, where in compound (**2**) the alkene appears to possess the most double bond character. Also there is a corresponding increase in the twist of the plane of the Os(1)C(2)C(3) atoms with respect to the plane of the Os<sub>3</sub> core atoms from 4.0 to 9.5 to 13.6° for molecules **1**, **4** and **2**, respectively.

The metal hydrido ligand in the structure of **4** was not located but the disposition of the carbonyl ligands in the molecule suggest that it bridges the Os(2)–Os(3) edge, on the opposite side of the metal atom triangle from the bromine atom. For the closely related structure  $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-Br})]$  [18] the hydride atom was located across the Os–Os bond bridged by the Br atom. The average Os–Br distance in **4** of 2.585 Å is identical to the corresponding value found in  $[(\mu\text{-H})\text{Os}_3(\text{CO})_{10}(\mu\text{-Br})]$ , however the bromo-bridged Os–Os bond in **4** (2.820 Å) is shorter than the other two Os–Os distances (2.868, 2.914 Å) which is the reverse pattern to that found for  $[\text{HOs}_3(\text{CO})_{10}\text{Br}]$  where the bridge distance (2.863 Å) was longer than the unbridged values (mean 2.839 Å).

The Os–C(alkene) distances in the three complexes are, on average shorter than

TABLE 7  
FRACTIONAL ATOMIC COORDINATES FOR 4

Atom	x	y	z
Os(1)	0.1218(1)	0.2745(1)	-0.1329(1)
Os(2)	0.1890(1)	0.0313(1)	-0.1267(1)
Os(3)	0.1137(1)	0.0457(1)	-0.0187(1)
Br	0.2035(1)	0.0903(4)	0.0226(2)
C(1)	0.0089(15)	0.3572(42)	-0.0951(23)
C(2)	0.0591(14)	0.4081(36)	-0.0954(20)
C(3)	0.0785(15)	0.4599(39)	-0.1697(35)
C(4)	0.0986(23)	0.6102(58)	-0.1644(35)
F(1)	-0.0045(9)	0.2769(26)	-0.1655(16)
F(2)	-0.0220(9)	0.4683(25)	-0.0999(20)
F(3)	-0.0026(9)	0.2757(27)	-0.0297(16)
F(4)	0.1224(13)	0.6445(31)	-0.0909(25)
F(5)	0.0645(12)	0.7138(24)	-0.1744(21)
F(6)	0.1294(13)	0.6337(32)	-0.2259(29)
C(11)	0.0813(16)	0.1511(39)	-0.2011(21)
O(11)	0.0608(10)	0.0747(29)	-0.2474(17)
C(12)	0.1583(25)	0.3155(45)	-0.2072(26)
O(12)	0.1903(14)	0.3635(33)	-0.2630(25)
C(13)	0.1589(17)	0.3701(53)	-0.0533(34)
O(13)	0.1758(11)	0.4301(30)	0.0061(19)
C(21)	0.1712(15)	-0.0157(38)	-0.2251(22)
O(21)	0.1598(12)	-0.0447(32)	-0.3000(16)
C(22)	0.2449(16)	0.1291(42)	-0.1622(23)
O(22)	0.2783(12)	0.1838(37)	-0.1831(25)
C(23)	0.2200(17)	-0.1534(38)	-0.1117(20)
O(23)	0.2414(13)	-0.2585(34)	-0.1036(23)
C(31)	0.0931(17)	0.1958(29)	0.0541(21)
O(31)	0.0740(12)	0.2429(35)	0.1034(18)
C(32)	0.0528(13)	-0.0010(37)	-0.0614(18)
O(32)	0.0158(11)	-0.0336(27)	-0.0881(15)
C(33)	0.1133(16)	-0.1246(48)	0.0500(38)
O(33)	0.1173(12)	-0.2262(36)	0.0894(15)

" The structure showed a small degree of disorder and the site occupation factor for the main Os<sub>3</sub>Br core refined to 0.950(5). The coordinates of the minor Os<sub>3</sub>Br part with isotropic temperature factors were found to be:

Os(1a)	0.1086(23)	0.2772(61)	-0.0781(37)
Os(2a)	0.1957(19)	0.0392(49)	-0.1755(33)
Os(3a)	0.1245(22)	0.0418(53)	-0.0736(34)
Br(a)	0.1179(18)	0.0475(49)	-0.1915(28)

the  $\eta^2$ -Os-C distances observed previously for compounds in which the  $\eta^2$ -linkage is associated with additional shorter  $\sigma$ -Os-C bonding to other metal atoms [19]. With the alkene structure [Os<sub>3</sub>(CO)<sub>11</sub>{*cis*-CF<sub>3</sub>(H)C=C(H)CF<sub>3</sub>}] [8], where there are no extra substituents, the C-C alkene distance of 1.509(35) Å is close to that of a single bond and is coupled with near equal Os- $\eta^2$ -C distances of 2.19 and 2.18(2) Å. In the three structures discussed here there is a significant twist of the alkene out of a symmetrical arrangement, with unequal Os-C(alkene) bonding as a result.

All the carbonyls in the structures of **2** and **4** are terminal and there are no close contacts between the C(carbonyl) atoms and neighbouring Os atoms.

## Experimental

All experiments were carried out in an atmosphere of dry nitrogen using freshly degassed solvents. Infrared spectra were recorded on Perkin–Elmer 257 or 577 spectrophotometers in 0.5 mm sodium chloride cells and were calibrated with CO gas.  $^1\text{H}$  NMR spectra were recorded on a Varian XL-100-12 instrument in the Fourier Transform mode and solvent resonances were used as secondary standards to calibrate spectra. All chromatography was carried out on commercial Merck TLC plates coated with a 0.25 mm layer of silica.  $[\text{Os}_3(\text{CO})_{10}(\text{trans-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)\text{Br}][\text{PPN}]$  (**1**) was prepared from  $[\text{HOs}_3(\text{CO})_{10}(\text{CF}_3\text{C}=\text{C}(\text{H})\text{CF}_3)]$  as described previously [11].

(i) *Thermolysis of (1)*. A solution of **1** (0.200 g, 0.12 mmol) in dichloromethane (18 cm<sup>3</sup>) was refluxed with stirring for 23 h. The colour changed from amber to amber-red during this time and the resulting solution was blown to dryness under a stream of nitrogen. The oily residue obtained was crystallised from a hot, saturated methanol solution to give scarlet needles of  $[\text{Os}_3(\text{CO})_9(\text{trans-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})][\text{PPN}]$  (**2**) in 40% yield.

(ii) *Reaction of 1 with  $[\text{Me}_3\text{O}]\text{BF}_4$* . A large excess of  $[\text{Me}_3\text{O}]\text{BF}_4$  (0.023 g, 0.16 mmol) was added to a solution of **1** (0.050 g, 0.031 mmol) in dichloromethane (15 cm<sup>3</sup>). The mixture was stirred for 12 h at room temperature, filtered, and taken to dryness under reduced pressure. The residue was placed on TLC plates and eluted with dichloromethane/hexane (10/90) to give two neutral yellow products identified on the basis of infrared and mass spectrometry as  $[\text{HOs}_3(\text{CO})_{10}\text{Br}]$  (25%) [13] and  $[\text{Os}_3(\text{CO})_{11}(\text{trans-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)]$  (25%) [8].

(iii) *Reaction between 1 and  $\text{MeSO}_3\text{F}$* . An excess of  $\text{MeSO}_3\text{F}$  was added to a solution of **1** (0.100 g, 0.061 mmol) in dichloromethane (10 cm<sup>3</sup>). The mixture was stirred at room temperature overnight and then taken to dryness under reduced pressure. The residue was placed on TLC plates and eluted several times with dichloromethane/hexane (10/90). This gave two neutral yellow products identified as  $[\text{Os}_3(\text{CO})_{11}(\text{trans-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)]$  (30%) [8] and  $[\text{HOs}_3(\text{CO})_9(\text{trans-CF}_3(\text{H})\text{C}=\text{C}(\text{H})\text{CF}_3)(\mu\text{-Br})]$  (**4**) (20%).

(iv) *X-ray crystallographic determinations*. Data for the compounds **1**, **2** and **4** were collected on a four circle diffractometer using graphite monochromatised  $\text{Mo-K}_\alpha$  radiation ( $\lambda$  0.71069 Å) in the range  $3 < \theta < 25^\circ$ . The crystal data for each sample are summarised in Table 2. The methods of data collection for each compound were similar to that described previously in publications from the respective laboratories for compounds **1** [20], **2** [22], and **4** [21]. Intensities  $I$  and  $\sigma(I)$  were corrected for Lorentz and polarisation factors and semi-empirical absorption corrections based on a pseudo-ellipsoid model [23] were applied; relative transmission factors for the full data ranged from 1.0 to 0.575 for **1**; 1.0 to 0.362 for **4** and 1.0 to 0.4982 for **2**.

*Structure solution and refinement*. The Os atoms in each case were located from either a Patterson map or by multiresolution  $\Sigma$  sign expansion. For each complex subsequent difference Fourier syntheses revealed the positions of all the non-hydrogen atom. All three structures were refined by blocked full-matrix least squares. The

phenyl rings in **1** and **2** were treated as rigid bodies with C–C, 1.395 Å, C–C–C, 120°, C–H, 1.08 Å, and C–C–H 120° (assuming a common hydrogen isotropic thermal parameter). The hydridic H in **4** and the olefinic H's in the three compounds were not located. For compound **1** the non-hydrogen atoms in the anion and the P<sub>2</sub>N atoms of the cation were refined with anisotropic thermal parameters, while for **4** all the non-hydrogen atoms and for **2** only the Os, Br, F, P atoms were assigned anisotropic thermal values. For **4** the Os<sub>3</sub>Br core was found to be disordered and positions for the ~ 5% Os<sub>3</sub>Br atoms were included in the refinement with isotropic temperature factors. For **2** there was ~ 20% decomposition during data collection and as a result of the poor quality of the data the carbonyl C–O distances were constrained to be equal and refined to a common value of 1.158(26) Å.

Complex neutral atom scattering factors [24] were employed. In all cases the computing was carried out using a variety of programs written by Professor G.M. Sheldrick. The diagrams presented here were drawn using the ORTEP 2 program [25].

The refined atomic positional parameters and principal bond lengths and angles for **1**, **2** and **4** are presented in Tables 3–7. Hydrogen atom coordinates, additional bond lengths and angles, thermal parameters, equations of least squares planes, and observed and calculated structure factors may be obtained from the authors.

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