Crystal structure of μ_2-hydridododecacarbonyltriosmium dioxooctafluoro-μ_2-fluoroditungsten

Martin C. Crossman, John Fawcett, Eric G. Hope *, David R. Russell

Department of Chemistry, University of Leicester, Leicester LE1 7RH, UK

Abstract

Protonation of $[Os_3(CO)_{12}]$ occurs readily in anhydrous HF; the addition of WF_6 gives a route to the title compound, $[HOs_3(CO)_{12}][W_2O_2F_9]$, which forms as triclinic crystals. The anion is a fluoride-bridged dimer, whilst the bridging hydride ligand in the carbonyl cluster cation has been located by difference Fourier techniques and the geometry of the carbonyl ligands.

Keywords: Osmium; Tungsten; Hydrido; Carbonyl; Cluster; Crystal structure

1. Introduction

We have been investigating the fluorination of zero valent metal complexes and have found that anhydrous HF (AHF) is a convenient solvent [1,2]. However, our investigations indicated that AHF was not an innocent solvent in these reactions, and protonation readily occurs in this very strong acid to afford species like $[HOs_3(CO)_{12}]^+$ and $[H_2Ir_4(CO)_{12}]^{2+}$, which have been characterised by a combination of ^1H and ^{13}C NMR spectroscopic experiments [3]. Similar protonations with other strong acids have been reported previously [4–7]. However, all previous attempts to confirm the structures of any of these cationic carbonyl species by an X-ray structure determination have been unsuccessful. Here we report the structural characterisation of the title compound; suitable crystals were obtained serendipitously from a sample of $[Os_3(CO)_{12}]$ dissolved in AHF after treatment with tungsten hexafluoride.
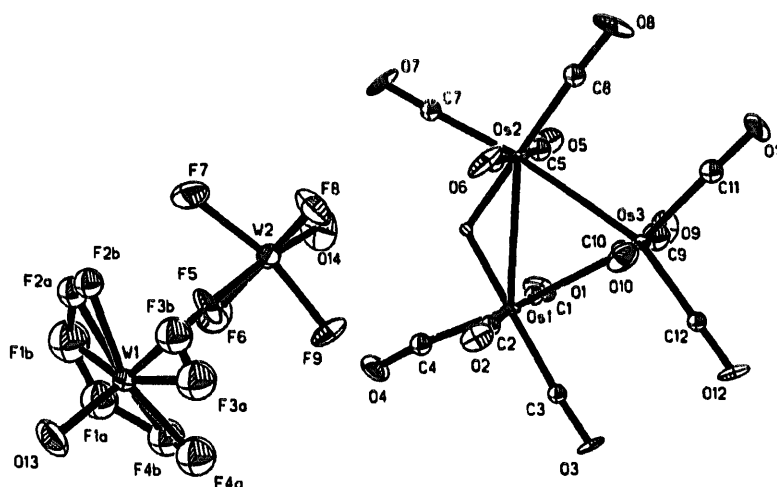

Fig. 1. The molecular structure of the title compound. Displacement ellipsoids are shown at the 30% probability level.

* Corresponding author.

Table 1

Selected intramolecular distances (Å) and angles (°) with estimated standard deviations in parentheses

Distances			
Os(1)–C(3)	1.86(3)	Os(1)–C(2)	1.96(3)
Os(1)–C(4)	1.96(3)	Os(1)–C(1)	1.97(3)
Os(1)–Os(3)	2.893(2)	Os(1)–Os(2)	3.043(2)
Os(2)–Os(3)	2.891(2)	C(1)–O(1)	1.14(4)
C(2)–O(2)	1.14(3)	C(3)–O(3)	1.19(3)
C(4)–O(4)	1.10(4)	W(1)–O(13)	1.66(3)
W(1)–F(2A)	1.75(4)	W(1)–F(4B)	1.81(7)
W(1)–F(1A)	1.84(5)	W(1)–F(4A)	1.85(5)
W(1)–F(3A)	1.86(5)	W(1)–F(3B)	1.86(6)
W(1)–F(1B)	1.89(8)	W(1)–F(2B)	1.91(5)
W(1)–F(5)	2.08(2)	W(2)–O(14)	1.69(3)
W(2)–F(7)	1.81(3)	W(2)–F(9)	1.83(2)
W(2)–F(8)	1.83(3)	W(2)–F(6)	1.83(3)
W(2)–F(5)	2.10(2)		
Angles			
C(3)–Os(1)–C(2)	88.7(12)	C(3)–Os(1)–C(4)	97.0(12)
C(2)–Os(1)–C(4)	90.1(12)	C(3)–Os(1)–C(1)	90.0(12)
C(2)–Os(1)–C(1)	176.5(11)	C(4)–Os(1)–C(1)	93.2(12)
C(3)–Os(1)–Os(3)	89.5(8)	C(2)–Os(1)–Os(3)	89.2(8)
C(4)–Os(1)–Os(3)	173.5(9)	C(1)–Os(1)–Os(3)	87.6(8)
C(3)–Os(1)–Os(2)	147.7(8)	C(2)–Os(1)–Os(2)	89.3(8)
C(4)–Os(1)–Os(2)	115.3(9)	C(1)–Os(1)–Os(2)	90.1(8)
Os(3)–Os(1)–Os(2)	58.23(3)	Os(3)–Os(2)–Os(1)	58.28(3)
Os(2)–Os(3)–Os(1)	63.48(4)	O(1)–C(1)–Os(1)	172(3)
O(2)–C(2)–Os(1)	177(3)	O(3)–C(3)–Os(1)	176(3)
O(4)–C(4)–Os(1)	173(3)	O(13)–W(1)–F(2A)	97(2)
O(13)–W(1)–F(4B)	104(2)	O(13)–W(1)–F(1A)	94(2)
F(2A)–W(1)–F(1A)	92(2)	O(13)–W(1)–F(4A)	98(2)
F(2A)–W(1)–F(4A)	163(2)	F(1A)–W(1)–F(2A)	80(2)
O(13)–W(1)–F(3A)	98(2)	F(2A)–W(1)–F(4A)	110(2)
F(1A)–W(1)–F(3A)	153(2)	F(4A)–W(1)–F(3A)	75(3)
O(13)–W(1)–F(3B)	102(2)	F(4B)–W(1)–F(3B)	129(3)
O(13)–W(1)–F(1B)	97(3)	F(4B)–W(1)–F(1B)	83(3)
F(3B)–W(1)–F(1B)	135(3)	O(13)–W(1)–F(2B)	95(2)
F(4B)–W(1)–F(2B)	157(3)	F(3B)–W(1)–F(2B)	57(3)
F(1B)–W(1)–F(2B)	82(3)	O(13)–W(1)–F(5)	176.9(13)
F(2A)–W(1)–F(5)	79.5(14)	F(4B)–W(1)–F(5)	78(2)
F(1A)–W(1)–F(5)	86(2)	F(4A)–W(1)–F(5)	85(2)
F(3A)–W(1)–F(5)	83(2)	F(3B)–W(1)–F(5)	78(2)
F(1B)–W(1)–F(5)	81(3)	F(2B)–W(1)–F(5)	83(2)
O(14)–W(2)–F(7)	105(2)	O(14)–W(2)–F(9)	93(2)
F(7)–W(2)–F(9)	162.2(12)	O(14)–W(2)–F(8)	99(2)
F(7)–W(2)–F(8)	90.1(13)	F(9)–W(2)–F(8)	89.2(13)
O(14)–W(2)–F(6)	96(2)	F(7)–W(2)–F(6)	88.7(12)
F(9)–W(2)–F(6)	87.3(12)	F(8)–W(2)–F(6)	164.5(13)
O(14)–W(2)–F(5)	173(2)	F(7)–W(2)–F(5)	81.4(11)
F(9)–W(2)–F(5)	80.9(10)	F(8)–W(2)–F(5)	81.3(10)
F(6)–W(2)–F(5)	83.3(11)	W(1)–F(5)–W(2)	159.5(12)

2. Results and discussion

Even though AHF is notorious as a poor solvent from which to grow crystals suitable for X-ray structure determinations, single crystals of $[HOs_3(CO)_{12}][W_2O_2F_9]$ formed overnight from a saturated solution of $[Os_3(CO)_{12}]$ in AHF in the presence of WF_6. Although the anion may appear unusual, the difficulty in removing the last traces of water from anhydrous HF is well documented, as is the hydrolytic sensitivity of WF_6,

which has been shown to give a number of tungsten-oxide–fluoride anions (e.g. WOF_5^-, $W_2O_2F_9^-$) [8,9].

In the solid state, the title compound consists of discrete $[HOs_3(CO)_{12}]^+$ cations and $[W_2O_2F_9]^-$ anions (Fig. 1). Selected intramolecular bond lengths and angles and fractional coordinates are listed in Tables 1 and 2 respectively.

The structure of the anion, particularly the *trans*-arrangement of O(13) and O(14), agrees with the solution ^{19}F NMR data (the bridging fluoride ligand is a

Table 2
Fractional atomic coordinates [×10⁴] and equivalent isotropic displacement parameters

Atom	x	y	z	U_{eq} [a]
Os(1)	2030(1)	2830(1)	3578(1)	21(1)
Os(2)	2860(1)	2960(1)	1232(1)	24(1)
Os(3)	2430(1)	5137(1)	2502(1)	24(1)
C(1)	4093(33)	2657(26)	3909(22)	28(6)
O(1)	5268(28)	2418(26)	4134(19)	57(7)
C(2)	−23(32)	3109(25)	3237(21)	25(6)
O(2)	−1228(22)	3248(23)	3074(18)	45(6)
C(3)	1538(30)	3676(25)	4823(22)	25(6)
O(3)	1288(29)	4270(22)	5595(16)	52(7)
C(4)	1789(34)	1180(29)	4148(25)	35(7)
O(4)	1688(32)	295(23)	4554(19)	60(7)
C(5)	4913(39)	2753(30)	1561(26)	38(7)
O(5)	6115(29)	2580(27)	1681(21)	59(7)
C(6)	866(35)	3149(27)	863(23)	30(7)
O(6)	−296(32)	3380(25)	625(20)	64(8)
C(7)	3100(33)	1390(27)	546(23)	30(7)
O(7)	3269(33)	481(22)	141(18)	64(8)
C(8)	3344(33)	3927(27)	43(24)	31(7)
O(8)	3647(31)	4592(28)	−667(19)	70(9)
C(9)	4481(50)	4916(39)	2927(34)	62(11)
O(9)	5668(26)	4806(25)	3074(2)	65(8)
C(10)	363(35)	5313(27)	2118(24)	30(7)
O(10)	−779(26)	5612(24)	1906(20)	54(7)
C(11)	2787(35)	6346(29)	1429(25)	36(7)
O(11)	3056(29)	7081(21)	787(18)	51(6)
C(12)	1961(30)	6142(24)	3662(21)	23(6)
O(12)	1760(29)	6761(24)	4421(17)	57(7)
H(1) [b]	2697	1955	2411	50
W(1)	−4535(1)	−1356(1)	2865(1)	32(1)
W(2)	−427(2)	−532(1)	2107(1)	40(1)
F(1A)	−3331(54)	−2511(47)	3601(41)	91(17)
F(2A)	−4179(43)	−2170(37)	1698(30)	56(12)
F(3A)	−5370(52)	246(45)	2551(44)	80(15)
F(4A)	−4310(57)	−488(48)	4056(39)	88(16)
F(1B)	−3325(87)	−2872(73)	2701(67)	108(28)
F(2B)	−4773(55)	−1555(47)	1394(38)	49(15)
F(3B)	−5244(64)	−62(55)	1965(54)	69(18)
F(4B)	−3558(74)	−1309(64)	4060(51)	83(22)
O(13)	−6032(31)	−1933(27)	3256(26)	75(9)
F(5)	−2644(21)	−696(20)	2304(19)	63(6)
F(6)	−252(33)	−1746(24)	3137(22)	92(9)
F(7)	−513(33)	−1709(25)	1145(20)	90(9)
F(8)	−1123(33)	661(27)	1147(21)	93(9)
F(9)	−919(29)	566(23)	3160(16)	76(7)
O(14)	1326(31)	−295(38)	2072(36)	122(16)

[a] U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

[b] Located by difference Fourier techniques (see text).

nonet as a result of coupling to the eight equivalent equatorial fluorine atoms) and compares well with that reported previously [9], in which the anion was co-crystallized with the $[WF_4(bipy)_2]^{2+}$ cation, also in a triclinic system with space group P1. All the lengths of comparable bonds are identical, within experimental error, and the W-F(5)-W bond angles show only a slight difference; 156(2)° compared with 159.5(12)°.

Unfortunately, there is slight disorder in the equatorial plane around W(1).

Despite the difficulty of locating hydrogen atoms using X-ray data, particularly in the presence of heavy metal atoms, the highest residual electron density in a non-hydrogen difference Fourier map was consistent with a hydride ligand bridging one Os–Os bond in the cation (Fig. 1). This hydride position was also consistent with differences in the geometry of the carbonyl ligands in the neutral parent carbonyl [10] and the cationic cluster found here. The cation may be compared with the structures of the closely related, neutral $[Os_3(CO)_{12}]$ and $[H_2Os_3(CO)_{11}]$ (Table 3) [10]. For $[Os_3(CO)_{12}]$, the Os–Os bond lengths vary between 2.8824(5) and 2.8738(5) Å, and the angles within the Os_3 triangle fall in the range 59.88(1) to 60.18(1)°. For $[HOs_3(CO)_{12}]^+$, two Os–Os bond lengths are very similar to those for $[Os_3(CO)_{12}]$ at 2.893(2) and 2.891(2) Å, but the third at 3.042(2) Å is considerably longer. Similarly, two angles within the Os_3 triangle are very similar, 58.23(3) and 58.27(3)°, whilst the third is significantly wider at 63.48(4)°. Comparable lengthening of one Os–Os bond, and a widening of one angle in the Os_3 triangle, are seen in the structure of $[H_2Os_3(CO)_{11}]$, where the bridging hydride ligand was placed between osmium atoms at a distance of 2.9886(9) Å.

The bridging hydride ligand also influences the Os–CO bonding within the equatorial plane; the equatorial carbonyl ligands are bent away from the hydride, i.e. for $[Os_3(CO)_{12}]$ the six equatorial Os–Os–C angles range from 96.1(3) to 99.9(3)°, whilst those for $[HOs_3 (CO)_{12}]^+$ range from 89.5(8) to 115.3(9)°. These changes correspond with those seen in the structure of $[H_2Os_3(CO)_{11}]$ (Table 3). These structural dissimilarities between $[Os_3(CO)_{12}]$ and both $[HOs_3(CO)_{12}]^+$ and $[H_2Os_3(CO)_{11}]$ are restricted to the equatorial plane, and no other significant structural changes are noted in the remaining osmium–carbonyl bond distances and angles.

3. Experimental details

Triosmium dodecacarbonyl was dissolved in AHF (1 cm³) in a 6 mm O.D. FEP (fluoroethylene–propylene copolymer; Production Techniques, Fleet, Hampshire, UK) tube fitted with a PTFE valve and exposed to WF_6 in the gas-phase. Yellow single crystals of the title compound were formed overnight at room temperature. The crystals were isolated by decanting away the majority of the solvent, before removing the last traces of AHF under dynamic vacuum.

Crystal data and details of measurements and refinement are summarised in Table 4. The program systems XSCANS [11], SHELXTL-PC [12] and SHELXL93 [13] were

Table 3
Selected bond lengths (Å) and angles (°) for [Os₃(CO)₁₂] [10]; [H₂Os₃(CO)₁₁] [10] and [HOs₃(CO)₁₂][W₂O₂F₉]

	Os₃(CO)₁₂	H₂Os₃(CO)₁₁	[HOs₃(CO)₁₂]⁺
Bond lengths			
Os(1)–Os(2)	2.8824(5)	2.9886(9)	3.043(2)
Os(1)–Os(3)	2.8752(5)	2.9097(7)	2.893(2)
Os(2)–Os(3)	2.8737(5)	2.8574(7)	2.891(2)
Bond angles			
Os(2)–Os(1)–Os(3)	57.93(2)	59.88(1)	58.23(3)
Os(1)–Os(2)–Os(3)	59.93(1)	59.65(1)	58.23(3)
Os(1)–Os(3)–Os(2)	60.18(1)	62.42(2)	63.48(4)
Os(1)–Os(2)–C(7)	99.7(3)	112.0(5)	114.5(9)
Os(2)–Os(1)–C(4)	99.5(4)	113.8(6)	115.3(9)
Os(3)–Os(1)–C(3)	97.8(3)	89.4(4)	89.5(8)
Os(3)–Os(2)–C(8)	96.1(3)	92.0(4)	90.0(9)
C(3)–Os(1)–C(4)	102.8(5)	98.9(7)	97.0(12)
C(7)–Os(2)–C(8)	104.2(4)	96.3(6)	97.3(12)
C(11)–Os(3)–C(12)	103.6(4)	99.4(5)	100.6(12)

Table 4
Crystal structure determination details

Formula	$C_{12}HF_9O_{14}Os_3W_2$
Formula weight	1478.42
Crystal system	Triclinic
Space group	P1̄
Cell dimensions	
a (Å)	9.317(2)
b (Å)	10.945(2)
c (Å)	12.684(3)
α (°)	88.20
β (°)	87.28
γ (°)	82.23
Cell volume (Å³)	1279.7(5)
Z	2
D_{calc} (Mg m⁻³)	3.837
F(000)	1284
Monochromated Mo K α radiation	
λ (Å)	0.7107
μ (mm⁻¹)	23.920
T (K)	293(2)
Crystal size (mm³)	0.46×0.44×0.30
Diffractometer	Siemens P4 diffractometer
Reflections for calculating cell number, θ_{min}, θ_{max}	36, 4.76, 12.48
Scan mode for data collection	θ–2θ
Index ranges	$-1 \le h \le 10$, $-12 \le k \le 12$, $-14 \le l \le 14$
Total reflections measured	4069
Unique reflections	3889
R_{int}	0.0731
Significant reflections	3038
Intensity decay	Insignificant
Absorption correction, max, min	Empirical, 0.806, 0.594
R_1	0.0742
wR_2 all data	0.2101
Goodness of fit(s)	1.056

used throughout. All non-hydrogen atoms were refined anisotropically. The position of the hydride ligand was clearly indicated by the cation geometry, and a major residual electron density peak consistent with this position was assigned to a hydrogen atom, which was included in the final least-squares refinement. The terminal fluorine atoms bonded to W(1) all exhibited high displacement parameters, suggesting disorder. These atoms were subsequently each refined on two distinct sites (atoms labelled A or B), with isotropic displacement parameters. The final population ratio of A:B atoms was 58:42. A list of structure factors has been deposited with the Inorganic Chemistry Structure Database.

Acknowledgement

References

[1] S.A. Brewer, J.H. Holloway and E.G. Hope, J. Chem. Soc., Dalton Trans., (1994) 1067.

[2] S.A. Brewer, A.K. Brisdon, J.H. Holloway, E.G. Hope, L.A. Peck and P.G. Watson, J. Chem. Soc., Dalton Trans., (1995) 2945.

[3] S.A. Brewer, A.K. Brisdon, J.H. Holloway and E.G. Hope, J. Fluorine Chem., 70 (1994) 167.

[4] J. Knight and M.J. Mays, J. Chem. Soc. A., (1970) 711.

[5] A.J. Deeming, B.F.G. Johnson and J. Lewis, J. Chem. Soc. A., (1970) 2967.

[6] A.A. Koridze, O.A. Kizas, N.M. Astakhova, P.V. Petrovskii and Y.K. Grishin, *J. Chem. Soc., Chem. Commun.*, (1981) 853.

[7] P. Yarrow and P.C. Ford, *J. Organomet. Chem.*, *214* (1981) 115.

[8] H. Selig, W.A. Sunder, F. Schilling and W.E. Falconer, *J. Fluorine Chem.*, *11* (1978) 629; A.M. Bond, I. Irvine and T.A. O'Donnell, *Inorg. Chem.*, *14* (1975) 2408; W.W. Dukat, J.H. Holloway and J. Rook, *Proc. 12th Int. Symp. on Fluorine Chemistry*, Santa Cruz, 1988, p. 402.

[9] L. Arnaudet, R. Bougon, Buu Ban, M. Lance, A. Navaza, M. Nielich and J. Vigner, *J. Fluorine Chem.*, *59* (1992) 141.

[10] M.R. Churchill and B.G. DeBoer, *Inorg. Chem.*, *16* (1977) 878.

[11] J. Fait, *XSCANS Users Manual*, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1991.

[12] G.M. Sheldrick, *SHELXTL-PC Users Manual*, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1991.

[13] G.M. Sheldrick, *SHELXL93, Program for the refinement of crystal structures*, University of Göttingen, Germany, 1993.