Journal of Organometallic Chemistry, 219 (1981) 251—257
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

NEUTRON DIFFRACTION STRUCTURE ANALYSIS OF $[(\mu\text{-H})(\mu\text{-NCHCF}_3)\text{Os}_3(\text{CO})_{10}]$ AT 20 K

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(Received April 9th, 1981)

Summary

The characterisation of $(\mu\text{-H})(\mu\text{-NCHCF}_3)\text{Os}_3(\text{CO})_{10}$ by neutron single crystal structure analysis at 20 K is reported. The 1,1,1-trifluoroethylidenimido ligand derived from the reaction of trifluoroacetonitrile with $H_2Os_3(CO)_{10}$ bonds as a three-electron donor, symmetrically bridging the same edge of the Os_3 cluster as the μ-hydride ligand.

Introduction

We have recently reported that $H_2Re_2(CO)_6(dpm)$ (dpm = $Ph_2PCH_2PPh_2$), which contains a formal Re—Re double bond shows a pattern of reactivity with small organic molecules which is in many ways similar to that exhibited by $H_2Os_3(CO)_{10}$ [1]. In some respects the rhenium complex is more reactive in that, for example, it reacts with MeCN under reflux to give two isomeric insertion products, $HRe_2(CO)_6$dpm(NCHMe) and $HRe_2(CO)_6$(dpm)(HNCMe) containing respectively an ethylideneimido and acetimidoyl ligand bridging the two rhenium atoms [1]. In contrast, under the same conditions $H_2Os_3(CO)_{10}$ does not undergo an insertion reaction with MeCN. In order to compare the reactions of the rhenium and osmium species more fully, the reaction of $H_2Os_3(CO)_{10}$ with the activated nitrile CF_3CN was studied, this reaction leading to two isomeric insertion reaction products, $HOs_3(CO)_{10}(NCHCF_3)$ and $HOs_3(CO)_{10}(HNCCF_3)$, which are analogous to the species formed by $H_2Re_2(CO)_6$(dpm) with MeCN. As is the case with the rhenium reactions already described, the major product of the reaction of $H_2Os_3(CO)_{10}$ with CF_3CN is the ethylideneimido product, $HOs_3(CO)_{10}(NCHCF_3)$ obtained in ca. 70% yield. This complex was first characterised by an X-ray diffraction study [3], which failed to locate

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the hydrogen atomic positions. In order to define the geometry of these and the other lighter atoms a neutron diffraction study was undertaken and the results of this study are reported here. The details of the reactions mentioned above will be reported in full elsewhere [2].

Experimental

A large (6 mg) crystal of $HOs_3(CO)_{10}(NCHCF_3)$ was grown by slow evaporation at room temperature of a seeded, saturated hexane solution of the complex.

Data were collected using an elongated cuboidal crystal of volume 1.99 mm^3 mounted on a vanadium pin in a DISPLEX ® Air products [4] closed-cycle helium refrigerator on a 4-circle diffractometer at the Bookhaven High Flux Beam Reactor. The crystal was cooled slowly to 20 K and the cell parameters derived from 32 automatically centred reflections. Marked anisotropy of mosaic spread was indicated, for example, by ω scan widths of between 0.4 and 0.8° for symmetry related reflections and unusually broad "tails" in the reflection profiles. A full quadrant of intensity data was measured by the θ—2θ step scan method for $5° < 2\theta < 83°$ and, in addition, ~800 unique data (calculated to be the most intense on the basis of preliminary refinements) were measured in the range $83° < 2\theta < 104°$: The scan data were integrated by a modified Lehmann-Larsen profile analysis method [7,8], and the intensities corrected for absorption using the analytical method of De Meulenaer and Tompa [9], transmission coefficients varied between 0.991 and 0.978 using $\mu = 0.174\ cm^{-1}$ calculated from the value 2.39 $mm^2\ mg^{-1}$ for chemically bound hydrogen [5].

Structure determination and refinement

A total of 4056 measured intensity data gave 3531 unique structure factors of which 2593 with $I > 4\sigma(I)$ were used in structure solution and refinement. Values for the coherent neutron scattering lengths were taken from ref. 6. A difference neutron scattering density map phased using coordinates for the non-hydrogen atoms from the X-ray analysis [3] revealed the locations of the hydridic and alkylidenimido hydrogen atoms. The structure solution was confirmed by application of direct methods to the 20 K neutron data: all non-hydrogen atoms being clearly indicated on the best E map. Refinement, with all atoms allocated isotropic thermal parameters, resulted in residual $R_F \sim 0.20$ at convergence. Full matrix least-squares refinement of scale, positional and anisotropic thermal parameters for all atoms converged smoothly to final indices $R_F = 0.124$, $R_{wF} = 0.100$ with weighting scheme $w = 4F_0^2/\sigma^2(F_0^2)$. The derived thermal parameters are highly anisotropic and much larger than might be expected for data collected at 20 K. These parameters are expected to be particularly sensitive to large crystal mosaic spreads should the acceptance angle of the detector be exceeded at high scattering angles. Refinement of an isotropic extinction parameter did not significantly improve the results of the analysis and hence no such correction was included in the final model. The molecular geometry (Fig. 1) appears little affected by these crystal defects; the coordinates, derived bond lengths and inter-bond angles are given in Tables

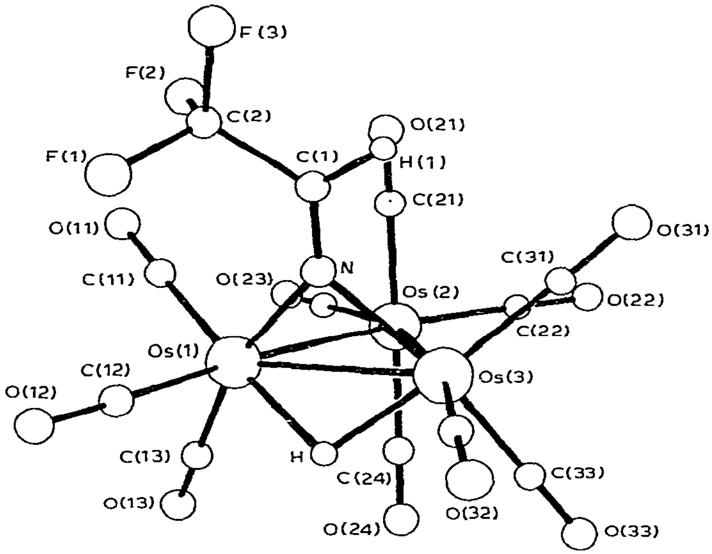

Fig. 1. Molecular diagram of $HOs_3(CO)_{10}(NCHCF_3)$ showing the atom labelling scheme (n.b. atoms C(23) and C(32) are not labelled for clarity).

TABLE 1

ATOMIC POSITIONAL COORDINATES [a] FOR $HOs_3(CO)_{10}NCHCF_3$

Atom	*x/a*	*y/b*	*z/c*
Os(1)	0.1958(5)	0.1372(1)	0.1100(3)
Os(2)	0.1227(6)	0.1759(1)	0.3783(4)
Os(3)	0.2746(5)	0.0845(1)	0.3703(3)
H	0.3928(16)	0.1096(5)	0.2304(12)
N	0.0706(6)	0.0786(1)	0.1872(4)
C(1)	—0.0615(10)	0.0493(3)	0.1520(6)
H(1)	—0.0932(28)	0.0207(6)	0.2212(14)
C(2)	—0.1913(12)	0.0536(5)	0.0072(7)
F(1)	—0.1005(13)	0.0516(4)	—0.1080(7)
F(2)	—0.2936(14)	0.0940(8)	—0.0045(9)
F(3)	—0.3121(22)	0.0154(7)	—0.0077(11)
C(11)	—0.0145(13)	0.1691(3)	0.0062(8)
O(11)	—0.1417(20)	0.1890(5)	—0.0518(13)
C(12)	0.2661(7)	0.1058(2)	—0.0586(5)
O(12)	0.3049(10)	0.0893(2)	—0.1617(6)
C(13)	0.3540(18)	0.1895(3)	0.0911(8)
O(13)	0.4488(33)	0.2206(5)	0.0823(12)
C(21)	—0.1143(11)	0.1440(3)	0.3329(7)
O(21)	—0.2536(14)	0.1265(7)	0.3075(10)
C(22)	0.0286(21)	0.2366(3)	0.3042(7)
O(22)	—0.0264(32)	0.2715(4)	0.2603(9)
C(23)	0.0996(13)	0.1804(2)	0.5829(6)
O(23)	0.0862(18)	0.1833(3)	0.7043(8)
C(24)	0.3808(15)	0.1979(3)	0.4112(7)
O(24)	0.5308(23)	0.2111(5)	0.4309(10)
C(31)	0.1313(10)	0.0604(2)	0.5098(6)
O(31)	0.0401(12)	0.0462(3)	0.5896(7)
C(32)	0.3967(15)	0.0261(3)	0.3351(7)
O(32)	0.4841(26)	—0.0071(5)	0.3197(10)
C(33)	0.4744(8)	0.1033(3)	0.5220(6)
O(33)	0.5952(12)	0.1150(5)	0.6114(8)

[a] The estimated standard deviation of the least significant digit is in parentheses, here and throughout this paper.

TABLE 2

BOND LENGTHS (Å) FOR $HOs_3(CO)_{10}NCHCF_3$

Os(1)—Os(2)	2.845(5)	Os(1)—Os(3)	2.813(4)
Os(2)—Os(3)	2.828(5)	Os(1)—H	1.838(12)
Os(3)—H	1.813(13)	Os(1)—N	2.078(5)
Os(3)—N	2.065(4)	Os(1)—C(11)	1.895(9)
Os(1)—C(12)	1.938(6)	Os(1)—C(13)	1.905(11)
Os(2)—C(21)	1.930(9)	Os(2)—C(22)	1.936(9)
Os(2)—C(23)	1.933(7)	Os(2)—C(24)	1.952(11)
Os(3)—C(31)	1.913(7)	Os(3)—C(32)	1.932(10)
Os(3)—C(33)	1.921(6)	N—C(1)	1.271(8)
C(1)—H(1)	1.083(18)	C(1)—C(2)	1.510(9)
C(2)—F(1)	1.345(11)	C(2)—F(2)	1.362(23)
C(2)—F(3)	1.385(22)	C(11)—O(11)	1.138(16)
C(12)—O(12)	1.139(8)	C(13)—O(13)	1.130(21)
C(21)—O(21)	1.116(15)	C(22)—O(22)	1.118(14)
C(23)—O(23)	1.147(10)	C(24)—O(24)	1.138(19)
C(31)—O(31)	1.145(10)	C(32)—O(32)	1.158(19)
C(33)—O(33)	1.150(10)		

TABLE 3

BOND ANGLES (°) FOR $HOs_3(CO)_{10}NCHCF_3$

Os(2)—Os(1)—Os(3)	60.0(1)	Os(1)—Os(2)—Os(3)	59.5(1)
Os(1)—Os(3)—Os(2)	60.6(1)	Os(1)—H—Os(3)	100.8(6)
Os(1)-N—Os(3)	85.5(2)	H—Os(1)—N	77.9(5)
H—Os(1)—C(11)	173.2(5)	H—Os(1)—C(12)	90.6(4)
H—Os(1)—C(13)	88.1(6)	H—Os(1)—Os(2)	82.8(4)
H—Os(1)—Os(3)	39.3(4)	N—Os(1)—C(11)	101.3(3)
N—Os(1)—C(12)	95.6(2)	N—Os(1)—C(13)	164.0(3)
N—Os(1)—Os(2)	81.6(2)	N—Os(1)—Os(3)	47.0(1)
C(11)—Os(1)—C(12)	96.3(3)	C(11)—Os(1)—C(13)	91.6(4)
C(11)—Os(1)—Os(2)	90.4(3)	C(11)—Os(1)—Os(3)	136.2(3)
C(12)—Os(1)—C(13)	92.4(3)	C(12)—Os(1)—Os(2)	173.2(2)
C(12)—Os(1)—Os(3)	113.7(2)	C(13)—Os(1)—Os(2)	88.9(3)
C(13)—Os(1)—Os(3)	116.9(3)	C(21)—Os(2)—C(22)	95.2(5)
C(21)—Os(1)—C(23)	91.5(4)	C(21)—Os(2)—C(24)	169.6(4)
C(21)—Os(2)—Os(1)	85.2(3)	C(21)—Os(2)—Os(3)	84.3(3)
C(22)—Os(2)—C(23)	101.9(4)	C(22)—Os(2)—C(24)	92.6(5)
C(22)—Os(2)—Os(1)	98.1(3)	C(22)—Os(2)—Os(3)	157.5(3)
C(23)—Os(2)—C(24)	93.6(4)	C(23)—Os(2)—Os(1)	160.0(3)
C(23)—Os(2)—Os(3)	100.6(3)	C(24)—Os(2)—Os(1)	86.9(3)
C(24)—Os(2)—Os(3)	85.9(3)	H—Os(3)—N	78.8(4)
H—Os(3)—C(31)	175.2(5)	H—Os(3)—C(32)	86.1(6)
H—Os(3)—C(33)	91.3(4)	H—Os(3)—Os(1)	39.9(4)
H—Os(3)—Os(2)	83.7(5)	N—Os(3)—C(31)	97.4(2)
N—Os(3)—C(32)	94.6(3)	N—Os(3)—C(33)	167.2(3)
N—Os(3)—Os(1)	47.4(1)	N—Os(3)—Os(2)	82.3(2)
C(31)—Os(3)—C(32)	97.1(3)	C(31)—Os(3)—C(33)	92.0(3)
C(31)—Os(3)—Os(1)	135.3(2)	C(31)—Os(3)—Os(2)	93.0(2)
C(32)—Os(3)—C(33)	92.9(4)	C(32)—Os(3)—Os(1)	110.2(2)
C(32)—Os(3)—Os(2)	169.7(3)	C(33)—Os(3)—Os(1)	120.0(3)
C(33)—Os(3)—Os(2)	88.6(3)	Os(1)—N—C(1)	142.2(4)
Os(3)—N—C(1)	132.3(4)	N—C(1)—C(2)	120.7(7)
N—C(1)—H(1)	124.4(10)	C(1)—C(2)—F(1)	112.6(7)
C(1)—C(2)—F(2)	112.9(8)	C(1)—C(2)—F(3)	108.5(9)
F(1)—C(2)—F(2)	107.8(9)	F(1)—C(2)—F(3)	105.9(9)
F(2)—C(2)—F(3)	108.8(11)	C(2)—C(1)—H(1)	115.0(11)
Os(1)—C(11)—O(11)	177.6(9)	Os(1)—C(12)—O(12)	176.6(5)
Os(1)—C(13)—O(13)	178.9(8)	Os(2)—C(21)—O(21)	178.2(12)
Os(2)—C(22)—O(22)	179.4(8)	Os(2)—C(23)—O(23)	179.8(3)
Os(2)—C(24)—O(24)	179.4(9)	Os(3)—C(31)—O(31)	177.6(6)
Os(3)—C(32)—O(32)	174.1(11)	Os(3)—C(33)—O(33)	179.1(7)

1—3. Tables of anisotropic thermal parameters and structure factors can be obtained from the authors.

Crystal data

$Os_3C_{12}H_2O_{10}NF_3$, $M = 947.6$, Monoclinic $a = 7.264(2)$, $b = 28.385(7)$, $c = 9.256(2)$ Å, $\beta = 99.52(2)°$, $U = 1881.9(8)$ Å^3 at 20 K. Space group $P2_1/n$, $\mu_N = 0.174$ cm^{-1}, $(\sin\theta/\lambda)_{max.} = 0.678$ Å^{-1}, $D_c = 3.345$ g cm^{-3}; Crystal volume 1.99 cm^3 bounded by faces {021} and {120}. $\lambda_N = 1.1621(5)$ Å based on KBr crystal ($a = 6.60000$ Å at 298 K).

Description and discussion of structure

At 20 K crystalline $HOs_3(CO)_{10}(NCHCF_3)$ consists of isolated molecules separated by normal Van der Waal's distances. The molecular structure shows a near equilateral Os_3 triangle with the shortest edge (Os(1)—Os(3) 2.813(4) Å) bridged symmetrically by the 1,1,1-trifluoroethylidenimido and hydride ligands (Os(1)—N 2.078(5) Å, Os(3)—N 2.065(4) Å, Os(1)—H 1.838(12) Å, Os(3)—H 1.813(13) Å). All ten carbonyl ligands are terminally bound, the unique osmium atom Os(2) is bonded to four and Os(1) and Os(3) are bonded to three carbonyls each. The cluster is a 48-electron species, formally having three metal—metal bonds; disregarding the Os(1)—Os(3) interaction all three metal atoms have approximately octahedral environments. The alkylidenimido ligand displays near exact planarity at N and C(1), the Os_2N and NC(1)H(1)C(2) planes being coplanar to within 0.5°. The C(1)—N distance (1.271(8) Å) is typical for a C=N bond length [10], cf. those observed in $Ru_3(CO)_{10}(\mu\text{-H})(\mu\text{-C=NMe}_2)$ [11a], 1.279(6); $Mn_2(CO)_7(N{=}C(CF_3)_2)_2$ [11b], 1.258(9), 1.259(9) Å; and $Fe_2(CO)_6$-$(N{=}C(p\text{-tolyl})_2)_2$ [12], 1.24(2), 1.29(2) Å and not significantly different from that in $HRe_2(CO)_6(dpm)(NCHMe)$ [1], 1.38(6) Å. These features are consistent with *sp* hybridisation at N and sp^2 at C(1), where one *p* orbital on N (p_x) overlaps with the b_1 combination of metal orbitals on Os(1) and Os(3) and the *sp* lone pair on N with the a_1 combination (Fig. 2). It should be noted that a bonding scheme using sp^2 hybridisation at N is entirely equivalent; we use *sp* to best illustrate the preferred geometry.

The observed planarity of the Os_2HCHC moiety is then forced in order to allow maximum overlap of the N p_x orbital with the metal orbitals. Similar behaviour has been noted in structural [13] and theoretical [14] analyses of bridging vinylidenes and related ligands. As discussed by Schultz et al. [15], the $(\mu\text{-H})(\mu\text{-N})Os_2$ system is best described as a 6*e*—4c moiety implying one metal—metal bond. When tested against currently used geometric criteria [16], the $(\mu\text{-H})Os_2$ and $(\mu\text{-N})Os_2$ groups are "open". That is, the angles between the extension of the Os—(CO) *trans* to the bridging ligands being 91.7 and 57.0° compared with Os(1)—H—Os(3) 100.8° and Os(1)—N—Os(3) 85.5°. Similar "open" M—H—M bonds have been noted previously, e.g. in $H_2Os_3(CO)_{10}$ [17]. This geometry for the Os_2N moiety presumably allows good overlap between the N and Os orbitals in the manner qualitatively described above (Fig. 2). The bond lengths and angles at the bridging atoms fall in the expected range for (μ-H) [15,17] and (μ-N) [1,11,12,18] ligands. Likewise Os—Os, Os—C, and C—O lengths are typical. As found for a range of $(\mu\text{-H})(\mu\text{-X})Os_3(CO)_{10}$ systems

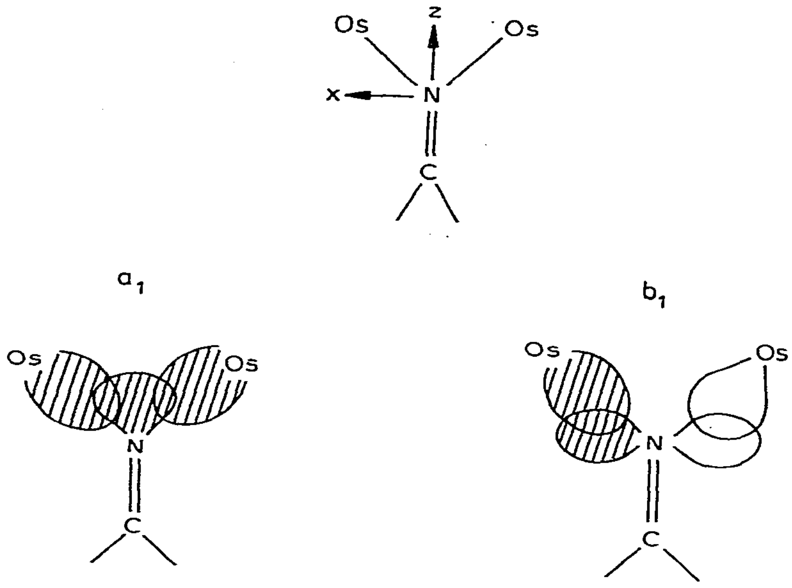

Fig. 2. Orbitals involved in binding of the ethylidenimido fragment to the cluster; C_{2v} local symmetry for the Os_2NC fragment is assumed.

the Os—Os distance is slightly shorter than the unbridged M—M bonds due to the contracting influence of the X ligand when the bridging atom is N, C or O [19].

The dihedral angles between the Os_3 and Os_2H and Os_2N planes are 61.4 and 72.1°, respectively, similar to those found in $HOs_3(CO)_{10}SEt$ [20] (76°) and $Os_3(CO)_{10}(OMe)_2$ [20] (63 and 70°). The $NCHCF_3$ fragment is slightly tilted with respect to the perpendicular to the Os(1)—Os(3) vector (Os(1)—N—C(1) 142.2(4)°; Os(3)—N—C(1) 132.3(4)°), presumably to relieve steric crowding in the ligand polyhedron caused by the bulky CF_3 group. The relevant short intramolecular contacts are between F(1) and F(2) and carbonyl groups on Os(1) (F(1)···C(12) 3.04 Å, F(2)···C(11) 2.93 Å, F(2)···O(11) 2.97 Å). If the Os(1)—N—C(1) angle were reduced these contacts would be still shorter. Similar angular distortion also without concomitant bond length asymmetry was noted for the isoelectronic $COCH_3$ fragment in $HRu_3(CO)_{10}(COMe)$ [21].

Acknowledgements

The neutron diffraction analysis in this research was carried out at Brookhaven National Laboratory under contract with the U.S. Department of Energy and was supported in part by its Office of Basic Energy. We thank Mr. Joseph Henriques for technical assistance in the neutron work. One of us (A.G.O.) would like to thank the W.C. Hamilton Scholarship Committee and Dr. T.F. Koetzle for suggesting and enabling the work at Brookhaven National Laboratory.

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