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Synthesis and structural characterization of $[HOs_3(CO)_9(OEt)(R_2C_2)]$ (R = Me or Ph)

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Abstract

The compound $[Os_3(CO)_{10}(R_2C_2)]$ (R = Me or Ph) reacts smoothly with ethanol at 80°C to give the ethoxy-bridged cluster $[(\mu\text{-H})Os_3(CO)_9(\mu_3\text{-}\eta^2\text{-}R_2C_2)(\mu\text{-OEt})]$. An X-ray diffraction study shows that the structure of this compound is closely related to other bridged ethoxy species and confirms that addition of EtOH has occurred across an Os–Os bond and not across the alkyne.

Introduction

Deeming and coworkers [1] have shown that the μ_3-ethynyl compound $[HOs_3(C{\equiv}CH)(CO)_9]$ reacts smoothly with ethanol to give two isomeric adducts $[H_2Os_3(CCHOEt)(CO)_9]$ (**1**) and $[H_2Os_3(CHCOEt)(CO)_9]$ (**2**) which are derived by the addition of the ethoxy group to the β and α carbon atoms, respectively. These observations led us to consider the possibility of the addition of EtOH across the alkyne link in the derivatives $[HOs_3(CO)_{10}(R_2C_2)]$ (**3a**, R = Me; **3b**, R = Ph).

Results and discussion

We have now established that $[Os_3(CO)_{10}(R_2C_2)]$ (**3a**, R = Me; **3b**, R = Ph) react with EtOH at 80°C to generate the new clusters $[HOs_3(CO)_9(OEt)(R_2C_2)]$ (**4a**, R = Me; **4b**, R = Ph). In this reaction, the ethoxy group attacks the triosmium

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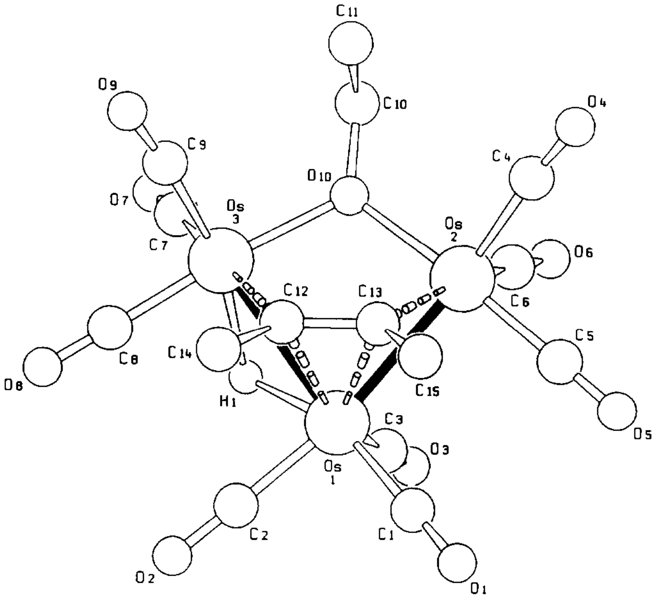

Fig. 1. Molecular structure of $HOs_3(CO)_9(\mu\text{-}OEt)(\mu_3\text{-}\eta^2\text{-}C_2Me_2)$.

core and not, as expected, a carbon atom of the alkyne. The overall reaction corresponds to the replacement of one μ-CO group and the opening of an Os–Os bond by H and OEt, and may be considered to occur by loss of CO to generate an unsaturated 46-electron cluster followed by oxidative addition of EtOH. The spectroscopic data for the new compounds **4a** and **4b** are recorded in the Experimental section. In their IR spectra, bands in the region 1950–2110 cm^{-1} are consistent with the presence of only terminal bonded CO. The ^1H NMR spectra are also consistent with the established structures. Thus, for example, compound **4a** in $CDCl_3$ exhibits a triplet at δ 0.75 and a quartet at δ 3.61 assigned to the OEt group. In addition the singlet at δ -14.15 must arise from the hydrido ligand and the singlet at δ 3.26 from the C_2Me_2. Finally, the appearance of a parent ion at *m/e* 873 agrees with the established molecular formula.

The molecular structure of **4a** has been established by single crystal X-ray analysis. Crystals of **4a** were grown by slow evaporation of a CH_2Cl_2/*n*-hexane solution at -5°C over a period of 5 days. The structure is shown in Fig. 1; some important bonding parameters are reported in Table 1.

The three Os atoms form a triangle, the "open edge" of which is occupied by the symmetrically bridging OEt group. The two Os–Os bonds have very different lengths: Os(1)–Os(2) 2.786(1) and Os(1)–Os(3) 2.896(1) Å, indicating that the hydride atom is very likely to be bridging the "long" Os–Os bond. The final difference Fourier map showed a residual peak which could be attributed to a hydrogen atom in a quasi-symmetrical bridging mode [Os(1)–H(1) 1.88, Os(3)–H(1) 1.99 Å], with an Os(1)–H(1)–Os(3) angle of 96°, similar to that found in $[(\mu\text{-}H)(\mu\text{-}OMe)Os_3(CO)_{10}]$ [2]. The oxygen atom of the OEt group lies almost coplanar with the three Os atoms, the dihedral angle between the planes defined by Os(1), Os(2) and Os(3) and by Os(2), O(10) and Os(3) being 20.2°. The plane containing the

Table 1

Bond distances (Å) and angles (deg) of **4a**

Os(1)–Os(2)	2.786(1)	Os(1)–Os(3)	2.896(1)
Os(2) ··· Os(3)	3.537	Os(2)–O(10)	2.11(1)
Os(3)–O(10)	2.11(1)	O(10)–C(10)	1.38(2)
C(10)–C(11)	1.52(1)	Os(1)–C(12)	2.29(1)
Os(1)–C(13)	2.31(1)	Os(2)–C(13)	2.09(1)
Os(3)–C(12)	2.13(1)	Os(1)–H(1)	1.88
Os(3)–H(1)	1.99	C(12)–C(13)	1.39(2)
C(12)–C(14)	1.53(1)	C(13)–C(15)	1.53(1)
Os(2)–O(10)–Os(3)	113.9(3)	Os(2)–Os(1)–Os(3)	77.0(1)
Os(3)–C(12)–C(13)	120.5(6)	Os(2)–C(13)–C(12)	120.5(6)
C(13)–C(12)–C(14)	121.1(5)	C(12)–C(13)–C(15)	118.9(5)
Os(2)–O(10)–C(10)	123.5(8)	Os(3)–O(10)–C(10)	122.2(8)

O–C_2H_5 group is almost perpendicular [92.8°] to the osmium atom triangle. Whereas the Os–O bond lengths, 2.11(1) Å, are comparable with those in $[Os_3(CO)_{10}(\mu\text{-}OCH_3)_2]$, ave. 2.08_1 Å [3], the Os–O–Os angle is considerably wider [113.9(3) in **4a** compared with 95_1° in the second species]. The O-bridged atoms, Os(2) and Os(3), are separated by a distance of 3.537 Å. The methyl ethyne ligand is μ_3-η^2-coordinated to the core and forms σ-bonds with Os(2) and Os(3) and one π-bond with Os(1), formally donating a total of four electrons. Considering the μ-OC_2H_5 group as a three-electron donor [4], the 50-electron requirement for an "open edge" triangular cluster is formally satisfied.

The distances involved in the π-interaction are, as expected, appreciably longer than those involved in the σ-interactions [2.29(1) and 2.31(1) *cf.* 2.09(1) and 2.13(1) Å, this second longer bond being directed towards the edge bearing the bridging hydride]. The ethyne carbon atoms have sp^2 character, as inferred from the alkyne carbon–carbon bond length [1.39(2) Å] and the C–C–C angles [121.1(5) and 118.9(5)°, respectively]. The plane of the alkyne is approximately orthogonal to the plane formed by the three Os atoms, the dihedral angle between the two planes being 109.3°.

Experimental

All reactions were carried out under dry dinitrogen using standard Schlenk and vacuum-line techniques. The solvents were distilled under dinitrogen from the appropriate drying agents.

Routine separation of products was performed by thin-layer chromatography (TLC), using commercially prepared glass plates, precoated to 0.25 mm thickness with Merck Kieselgel 60 F_{254}, or using laboratory prepared glass plates coated to 1 mm thickness with Merck Kieselgel 60 PF_{254}.

The IR spectra were recorded on Perkin Elmer PE 983 and PE 1710 FT IR spectrometers. Electron impact (EI) mass spectra of the neutral low nuclearity clusters were recorded on Kratos MS 902 and Kratos MS 890 spectrometers. The calibrant used for FAB MS was CsI. The ^1H NMR spectra were recorded on a Bruker WM 250 NMR spectrometer. $[Os_3(CO)_{12}]$ [5] was prepared by the literature method. Other chemicals were used as obtained from Aldrich.

Preparation of $[HOs_3(CO)_9(\mu\text{-}OEt)(R_2C_2)][R = Me \text{ or } Ph]$

A solution of $[Os_3(CO)_{10}(R_2C_2)]$ [R = Me or Ph] (50 mg) in EtOH (20 cm^3) was heated in an autoclave at 80°C under an atmosphere of CO for 15 h. The excess of solvent was removed *in vacuo* and the residue redissolved in 5 cm^3 of dichloromethane; the mixture was subjected to TLC using dichloromethane/hexane (40/60) as eluant. Pale yellow products $[HOs_3(CO)_9(OEt)(Me_2C_2)]$, **4a** (40%), and $[HOs_3(CO)_9(OEt)(Ph_2C_2)]$, **4b** (30%), were isolated from $[Os_3(CO)_{10}(Me_2C_2)]$ and $[Os_3(CO)_{10}(Ph_2C_2)]$, respectively.

Spectroscopic data for **4a**: IR (CH_2Cl_2) ν(CO): 2101(w), 2072(vs), 2043(s), 2035(sh), 2022(w), 2000(s), 1957(w) cm^{-1}. ^{1}H NMR: δ −14.15(s), 0.75 (t, J(H–H) = 7.6 Hz), 3.61 (q, J(H–H) = 7.6 Hz), 3.26 (s) ppm; electron impact mass spectrum (CH_2Cl_2): 873 m/e.

Spectroscopic data for **4b**: IR (CH_2Cl_2) ν(CO): 2110(w), 2069(vs), 2059(s), 2020(sh) cm^{-1}. ^{1}H NMR: δ −12.56 (s), 1.08 (t, J(H–H) = 5.9 Hz), 3.57 (q, J(H–H) = 6.9 Hz), 7.32–7.39 (m), 7.50–7.56 (m) ppm; electron impact mass spectrum (CH_2Cl_2): 996 m/e.

Crystal data for 4a

$C_{15}H_{12}O_{10}Os_3$, monoclinic, space group $P2_1/n$, $a = 9.173(5)$, $b = 12.937(4)$, $c = 17.173(4)$ Å, $\beta = 97.94(4)$°, $U = 2018.4$ Å^3, $Z = 4$, $F(000) = 1639$, crystal size

Table 2

Fractional atomic coordinates for **4a**

Os(1)	0.09595(5)	0.21608(3)	0.66476(3)
Os(2)	−0.15614(5)	0.22643(4)	0.55413(3)
Os(3)	−0.08055(5)	0.37102(3)	0.72987(3)
O(1)	0.2967(14)	0.1379(9)	0.5506(7)
O(2)	0.3619(12)	0.2497(10)	0.7918(7)
O(3)	−0.0015(13)	0.0017(7)	0.7121(6)
O(4)	−0.3606(14)	0.3117(9)	0.4140(6)
O(5)	−0.0126(12)	0.0954(8)	0.4420(6)
O(6)	−0.3492(13)	0.0392(9)	0.5889(8)
O(7)	−0.2661(14)	0.3061(9)	0.8600(7)
O(8)	0.1624(13)	0.4363(8)	0.8558(6)
O(9)	−0.1727(15)	0.5956(8)	0.7204(8)
O(10)	−0.2421(8)	0.3136(7)	0.6411(5)
C(1)	0.2193(14)	0.1662(10)	0.5946(8)
C(2)	0.2613(15)	0.2370(10)	0.7442(8)
C(3)	0.0369(13)	0.0819(10)	0.6925(7)
C(4)	−0.2922(18)	0.2795(10)	0.4703(8)
C(5)	−0.0677(15)	0.1439(9)	0.4841(8)
C(6)	−0.2751(17)	0.1095(11)	0.5782(9)
C(7)	−0.2039(19)	0.3318(11)	0.8134(9)
C(8)	0.0692(15)	0.4107(9)	0.8078(8)
C(9)	−0.1434(16)	0.5120(11)	0.7223(8)
C(10)	−0.3885(17)	0.3413(13)	0.6362(9)
C(11)	−0.4138(17)	0.4440(13)	0.5938(9)
C(12)	0.0511(11)	0.3873(7)	0.6379(7)
C(13)	0.0150(11)	0.3344(8)	0.5673(6)
C(14)	0.1701(11)	0.4713(7)	0.6470(7)
C(15)	0.0996(11)	0.3588(8)	0.4989(6)

$0.25 \times 0.30 \times 0.015$ mm, $\mu(\text{Mo-}K_\alpha) = 200.8\ \text{cm}^{-1}$, θ range 2.5–25°, final R 0.038, $R_w = 0.040$ for 2877 out of 3359 independent reflections $[I_0 > 2\sigma(I_0)]$, electron density residual < 0.4 e Å^{-3} in proximity of Os atoms. Absorption correction was applied by the Walker and Stuart method [6] (min. and max. values in the range 0.63–1.0). Intensity data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer by the $\omega/2\theta$ method. All non-H atoms were allowed to vibrate anisotropically. Two isotropic thermal parameters were refined for the methylene (0.066 Å^2) and the methyl (0.101 Å^2) H atoms, which were included in calculated positions and refined riding on their respective C atoms. The H (bridging hydride) atom was located in a difference Fourier map and refined with its distances from Os(1) and Os(3) fixed at the values found [1.88 and 1.99 Å, respectively]. The structure was solved by direct methods; for all calculations SHELX-86 and SHELX-76 programs were used [7,8]. Fractional atomic coordinates are reported in Table 2. Full listings of bond lengths and angles and anisotropic thermal parameters are available on request from the Cambridge Crystallographic Data Centre.

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