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Isolation and structural characterisation of the allyl complexes $Os_4H(CO)_{11}(C_4H_5)$ and $Os_3H(CO)_9(C_4H_5)$

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Abstract

A new tetraosmium cluster, $[Os_4H(CO)_{11}(C_4H_5)]$, has been isolated from the products of pyrolysis of $[Os_3(CO)_{10}(Me_2C_2)]$, and shown by a single crystal X-ray study to have a tetrahedral metal framework with the allyl ligand bonding to one of the faces in a μ_3-η^3 mode. The structure of $Os_3H(CO)_9(C_4H_5)$ is also discussed.

Introduction

The interactions of alkynes and metal clusters have attracted attention over many years, and many interesting results were summarised in a recent review [1]. In order to investigate the reactions of triosmium-alkyne species under vigorous conditions, the pyrolysis of $[Os_3(CO)_{10}(Me_2C_2)]$ was carried out at 210 °C. The new tetraosmium allyl complex, $[Os_4H(CO)_{11}(C_4H_5)]$ (**2**) was isolated from the product mixture and characterised, together with the previously reported complex $[Os_3H(CO)_9(C_4H_5)]$ (**1**), for which two isomers have been identified [2], and two isomers of $[Os_4(CO)_{12}(C_4H_6)]$ (**3**) [3].

Results and discussion

The pyrolysis of $[Os_3(CO)_{10}(Me_2C_2)]$ at 210 °C produced as the major product $[Os_3H(CO)_9(C_4H_5)]$ (**1**, 60%), together with $[Os_4(CO)_{12}(C_4H_6)]$ (**3**, two isomers, ca. 15%) and $[Os_4H(CO)_{11}(C_4H_5)]$ (**2**, ca. 15%). These were identified from spectroscopic data (Table 1).

The ^1H NMR data for cluster **3** indicates that in addition to the previously reported $[Os_4(CO)_{12}(HCCEt)]$ (**3a**) [3], there is present a new isomer

Table 1

Spectroscopic data for **1–3**

Compound	IR (ν(CO), cm^{-1})[a]	MS[b]	^{1}H NMR[c]	
$[Os_3H(CO)_9(C_4H_5)]$	2099m, 2077s, 2049s,	882	8.68d[d]	1H: $J = 6.9$
(**1**)	2020s, 2008s, 2002s,		8.17dd	1H: $J_1 = 6.9$, $J_2 = 0.9$
	1991m, 1964vw.		2.95s	3H
			−19.25d	1H: $J = 0.9$
$[Os_4H(CO)_{11}(C_4H_5)]$	2100w, 2072s, 2055s,	1130	1.037d[e]	1H: $J = 5.9$
(**2**)	2026s, 2002w, 1985w,		8.05dd	1H: $J_1 = 5.9$, $J_2 = 0.5$
	1973vw, 1949w.		2.84s	3H
			−21.13d	1H: $J = 0.5$
$[Os_4(CO)_{12}(C_4H_6)]$	2099vw, 2071vs,	1158	10.96s[e]	1H
(**3**)	2045s,sh, 2039vs, 2017s,		3.67q	2H: $J = 7.4$
	2000s, 1974w.		1.27t	3H: $J = 7.4$
			3.56s	

[a] Recorded in hexane solution. [b] Based on ^{192}Os. [c] Recorded in $CDCl_3$ at room temperature; all J values in Hz. [d] Recorded on a Bruker WP 80MHz spectrometer. [e] Recorded on a Bruker WM 250MHz spectrometer.

$[Os_4(CO)_{12}(MeCCMe)]$ (**3b**) which accounts for the singlet at δ 3.56. These are inseparable by chromatographic techniques, and both may have the same butterfly structure.

Complex **1** gives an IR spectrum and a coupling pattern in the ^{1}H NMR spectrum identical to those of a previously reported cluster [2], but the ^{1}H NMR spectrum of $[Os_3H(CO)_9(C_4H_5)]$ (**1**) from our preparation shows different chemical shifts (0.4–0.8 ppm greater in our case). As no crystal structure of $[Os_3H(CO)_9(C_4$-

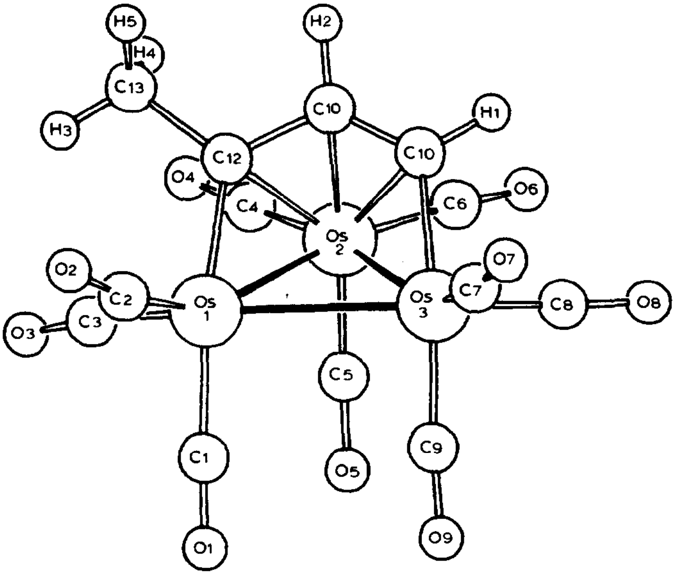

Fig. 1. The molecular structure of $Os_3H(CO)_9(\mu\text{-}\eta^3\text{-}C_4H_5)$ (**1**) showing the atom labelling.

Table 2

Selected bond lengths (Å) and angles (°) in $[Os_3H(CO)_9(C_4H_5)]$ (1) with estimated standard deviations in parenthesis

Os(1)–Os(2)	2.801(1)	Os(1)–Os(3)	2.952(1)
Os(2)–Os(3)	2.823(1)	Os(1)–C(12)	2.07(2)
Os(3)–C(10)	2.08(2)	Os(2)–C(10)	2.27(1)
Os(2)–C(11)	2.28(1)	Os(2)–C(12)	2.29(1)
C(10)–C(11)	1.43(2)	C(11)–C(12)	1.40(2)
C(12)–C(13)	1.60(2)		
C(10)–C(11)–C(12)	124(2)	C(11)–C(12)–C(13)	113(2)

$H_5)]$ (1) has been reported, and there was the possibility that we had a new isomeric form, an X-ray diffraction analysis of 1 was carried out. We found that 1 has the structure proposed by Deeming [2], i.e. the allyl ligand is σ-bonded to two osmium atoms and η^3-π-bonded to the third (Fig. 1). The origin of the differences in the chemical shift values between 1 and those previously reported is not clear.

Complex 2 is a 60-electron species, thus according to PSEP theory a tetrahedral structure would be expected. However, since it is isoelectronic with a cluster such as $[(\eta-C_5H_5)NiRu_3(CO)_8C_5H_7]$ [4], a butterfly structure was not impossible [4], and a single crystal X-ray diffraction study was carried out. This revealed a tetrahedral structure (Fig. 2), in which the allyl moiety, C_4H_5, is bonded to one of the tetrahedral faces in a manner similar to that observed in $[Os_3H(CO)_9(C_4H_5)]$ (1), i.e. in a μ_3-η^3-bonding mode. Complex 2 is the first example of a tetranuclear cluster in which this bonding mode has been observed. Tetranuclear allyl species previously

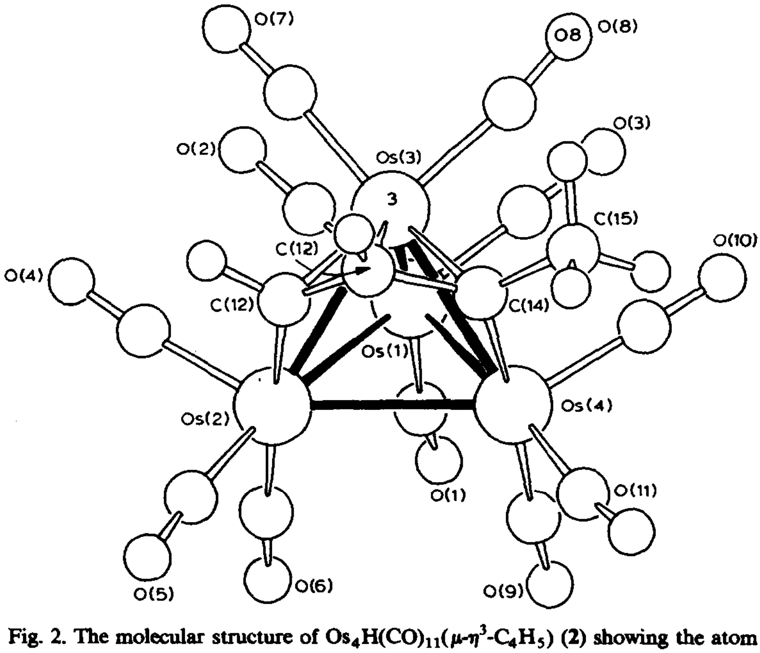

Fig. 2. The molecular structure of $Os_4H(CO)_{11}(\mu-\eta^3-C_4H_5)$ (2) showing the atom labelling.

Table 3

Selected bond lengths (Å) and angles (°) in $[Os_4H(CO)_{11}(C_4H_5)]$ (**2**) with estimated standard deviations in parenthesis

Os(1)–Os(2)	2.879(2)	Os(1)–Os(3)	2.596(2)
Os(1)–Os(4)	2.868(2)	Os(2)–Os(3)	2.789(2)
Os(2)–Os(4)	2.904(2)	Os(3)–Os(4)	2.777(2)
Os(2)–C(12)	2.08(4)	Os(3)–C(12)	2.09(4)
Os(3)–C(13)	2.21(4)	Os(3)–C(14)	2.15(3)
Os(4)–C(14)	2.15(3)	C(12)–C(13)	1.35(5)
C(13)–C(14)	1.47(5)	C(14)–C(15)	1.47(5)
C(12)–C(13)–C(14)	115(3)	C(13)–C(14)–C(15)	116(3)

reported have either a 'butterfly' structure with a μ_4-η^3 interaction [4,5] or a tetrahedral structure with the allyl ligand interacting with only two osmium atoms, i.e. σ-bonding to one metal atom and η^3-π-bonding to the other [6].

In both **1** and **2**, the hydride atom is probably bound to the Os–Os bonds spanned by the C_3-system, since this bond is the longest (2.952(1) Å in **1** and 2.904(2) Å in **2**) and the CO-ligands appear to be forced away from the middle of the bond. One interesting feature of the molecular structure of **2** is the remarkably short Os–Os distance (Os(1)–Os(3) 2.596(2) Å) for the bond *trans* to the π-interac-

Table 4

Fractional atomic coordinates for **1**

Atom	*x*	*y*	*z*
Os(1)	0.28873(5)	0.45604(3)	0.00292(5)
Os(2)	0.20990(5)	0.32273(3)	0.06267(4)
Os(3)	0.36701(4)	0.31263(3)	−0.05535(4)
C(1)	0.3914(13)	0.4821(9)	0.0810(13)
O(1)	0.4541(10)	0.4976(7)	0.1292(11)
C(2)	0.3024(12)	0.5330(9)	−0.0894(14)
O(2)	0.3057(8)	0.5819(6)	−0.1513(10)
C(3)	0.2202(11)	0.5111(8)	0.0995(12)
O(3)	0.1827(9)	0.5426(6)	0.1620(9)
C(4)	0.1071(13)	0.3557(9)	0.1371(12)
O(4)	0.0465(9)	0.3758(8)	0.1788(9)
C(5)	0.2915(12)	0.3368(8)	0.1721(13)
O(5)	0.3425(8)	0.3412(6)	0.2393(8)
C(6)	0.1832(14)	0.2237(9)	0.0894(12)
O(6)	0.1672(9)	0.1629(7)	0.1084(10)
C(7)	0.4294(11)	0.3110(8)	−0.1822(15)
O(7)	0.4631(8)	0.3088(7)	−0.2645(9)
C(8)	0.3793(14)	0.2106(10)	−0.0299(11)
O(8)	0.3852(10)	0.1486(6)	−0.0190(9)
C(9)	0.4726(15)	0.3339(12)	0.0275(14)
O(9)	0.5292(11)	0.3400(8)	0.0808(10)
C(10)	0.2401(12)	0.2871(9)	−0.1044(10)
C(11)	0.1708(11)	0.3407(8)	−0.1083(10)
C(12)	0.1764(12)	0.4102(9)	−0.0616(11)
C(13)	0.0867(14)	0.4563(9)	−0.0693(13)

tion, and this may be due to poor back-donation to the organic ligand resulting in a slight multiple-bond character of the metal–metal bond.

Experimental

Pyrolysis for [$Os_3(CO)_{10}(Me_2C_2)$]

In a typical reaction, a 63 cm^3 Carius tube containing 61 mg $Os_3(CO)_{10}(Me_2C_2)$ was evacuated for 3 h then sealed and heated at 210 °C for 60 h. The product mixture was extracted with ethyl acetate at 80 °C and the extracts subjected to thin layer chromatography on silica plates. Repeated elution with 30% CH_2Cl_2 in hexane gave five bands. The product in the first, yellow, band was identified as [$Os_3H(CO)_9(C_4H_5)$] (**1**) (~ 60%) from spectroscopic data [2]. The second, orange, band was found to contain a mixture of two orange compounds which were separated by chromatography on alumina with hexane as eluent. They were characterised as [$Os_4(CO)_{12}(C_4H_6)$] (**3**, two isomers, ~ 15%) [3], and [$Os_4H(CO)_{11}(C_4H_5)$] (**2**, ~ 15%). The other minor products were not identified.

Table 5

Fractional atomic coordinates for **2**

Atom	*x*	*y*	*z*
Os(1)	0.26340(10)	0.10206(15)	0.03901(8)
Os(2)	0.26097(10)	0.32176(14)	0.16070(8)
Os(3)	0.35276(9)	0.06125(15)	0.18445(8)
Os(4)	0.14471(9)	0.06801(14)	0.17890(8)
C(1)	0.1684(35)	0.1680(54)	−0.0514(30)
O(1)	0.1159(24)	0.1847(37)	−0.1096(21)
C(2)	0.3787(26)	0.1467(37)	−0.0126(22)
O(2)	0.4551(22)	0.1751(34)	−0.0426(19)
C(3)	0.2695(29)	−0.0776(43)	0.0040(25)
O(3)	0.2745(24)	−0.2028(37)	−0.0139(21)
C(4)	0.3791(49)	0.4050(73)	0.1179(40)
O(4)	0.4513(31)	0.4455(44)	0.0962(26)
C(5)	0.2377(33)	0.4709(48)	0.2323(28)
O(5)	0.2174(21)	0.5589(31)	0.2797(18)
C(6)	0.1771(26)	0.4032(39)	0.0736(22)
O(6)	0.1210(23)	0.4485(34)	0.0188(20)
C(7)	0.4912(33)	0.0859(48)	0.1633(28)
O(7)	0.5687(21)	0.1081(31)	0.1471(17)
C(8)	0.3737(28)	−0.1376(43)	0.1771(24)
O(8)	0.3942(19)	−0.2462(30)	0.1732(17)
C(9)	0.0429(30)	0.1260(46)	0.0938(26)
O(9)	−0.0200(24)	0.1554(36)	0.0498(20)
C(10)	0.1359(27)	−0.1251(40)	0.1504(23)
O(10)	0.1324(19)	−0.2414(29)	0.1312(17)
C(11)	0.0492(23)	0.0566(36)	0.2637(21)
O(11)	0.0004(29)	0.0324(42)	0.3141(24)
C(12)	0.3441(28)	0.2360(42)	0.2618(24)
C(13)	0.3285(28)	0.1268(41)	0.3126(24)
C(14)	0.2526(24)	0.0251(35)	0.2805(21)
C(15)	0.2428(26)	−0.1031(37)	0.3299(22)

Crystal structure determinations

Intensity data were collected at room temperature on an Enraf-Nonius CAD4 diffractometer by the ω–2θ scan method. An absorption correction was applied by the Walker and Stuart method [7] (correction range 0.56–1.00 and 0.48–1.00 for **1** and **2**, respectively). H-atoms were added in calculated positions (C–H 1.08 Å). All non-hydrogen atoms in **1**, and only Os-atoms in **2** were treated anisotropically. Isotropic values were refined for H-atoms in **1** (0.12 $Å^2$) and in **2** (0.09 $Å^2$). Fractional atomic coordinates for **1** and **2** are listed in Tables 4 and 5, respectively.

For all calculations the SHELX76 package of crystallographic programs was used [8].

Crystal structure data for $[Os_3H(CO)_9(C_4H_5)]$ *(1).* $C_{13}H_6O_9Os_3$, $M = 876.77$, orthorhombic, space group *Pbca*, $a = 15.175(3)$, $b = 18.12(1)$, $c = 12.709(5)$ Å, $U = 3494.6$ $Å^3$, $Z = 8$, $D_c = 3.33$ g. cm^{-3}, $F(000) = 3072$, $\mu(\text{Mo-}K_\alpha) = 209.5$ cm^{-1}, θ-range 2.5–25° final R-value 0.030, $R_w = 0.028$ for 1809 observed independent reflections ($I_o > 2\sigma(I_o)$).

Crystal structure data for $[Os_4H(CO)_{11}(C_4H_5)]$ *(2).* $C_{15}H_6O_{11}Os_4$, $M = 1123.01$, monoclinic, $P2_1/c$, $a = 13.367(4)$, $b = 9.549(3)$, $c = 16.178(1)$ Å, $\beta = 93.82(3)°$, $U = 2060.4$ $Å^3$, $Z = 4$, $D_c = 3.62$ g cm^{-3}, θ-range 2.5–25°, final R-value 0.056, $R_w = 0.060$ for 2032 observed independent reflections ($I_o > 2\sigma(I_o)$).

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