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The reactions of $[HOs_3(CO)_{11}]^-$ with disubstituted acetylenes. Synthesis and structural characterisation of the novel pentanuclear species $[H_2Os_5(CO)_{13}(Ph_2C_2)(PhC_2(H)C_6H_4)]$

Brian F.G. Johnson, Jack Lewis *, J. Lunniss
University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (UK)

Dario Braga and Fabrizia Grepioni *
Università degli Studi di Bologna, Dipartimento di Chimica "G. Ciamician", Via F. Selmi, 2, 40126 Bologna (Italy)

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Abstract

The reaction of the trinuclear anion $[HOs_3(CO)_{11}]^-$ with Ph_2C_2 unexpectedly leads to the pentanuclear species $[H_2Os_5(CO)_{13}(Ph_2C_2)(PhC_2(H)(C_6H_4)]$, which has been shown by an X-ray crystal structure determination to have a twisted bow-tie arrangement of metal atoms bearing a μ_3-η^1-PhCCPh and an orthometallated μ_2-η^2-Ph–CC(H)–C_6H_4 ligands, this ligand being formed by an intramolecular H-transfer reaction from a phenyl group to the acetylene group.

Introduction

The dihydrido cluster $[H_2Os_3(CO)_{10}]$ (1) is remarkably reactive, readily undergoing reactions with donor ligands (L) to afford species of the type $[H_2Os_3(CO)_{10}L]$, in which one bridging hydrido ligand has opened out to generate a terminally-bonded hydridospecies. This observation gives a clear indication of the probable reaction pathway, which may be envisaged as proceeding via an initial bridge-opening by one μ_2-H to generate a vacant coordination site and a μ_1-H bonded atom. Given that the structure of the anion $[HOs_3(CO)_{11}]^-$ (2) is related to that of $[H_2Os_3(CO)_{10}]$ [1] with one μ_2-H-ligand replaced by a μ_2-CO-group, it seemed reasonable to suppose that their chemistries might be related, even though 1 is a 46 electron species whereas 2 is a 48 electron species. Thus, the primary objective of this work was to examine this possibility and to compare the chemistries of these two closely related species and that of $[HFe_3(CO)_{11}]$ [2].

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Results and discussion

We found that, in contrast to **1**, the reaction of the salt $[PPN][HOs_3(CO)_{11}]$ (**2a**) with donor ligands occurs only under fairly vigorous conditions. Thus, whereas **1** reacts readily with Ph_2C_2 under ambient conditions, the corresponding reaction with the salt **2a** occurs only at elevated temperatures.

Reaction of **2a** with Ph_2C_2 in MeCN at 80 °C for 2 h, followed by protonation with $HBF_4 \cdot Et_2O$, yields three products: **3** (yellow), **4** (yellow-orange) and **5** (orange). Products **3** and **4** were identified on the basis of mass spectrometry as $[H_2Os_3(CO)_{10}(Ph_2C_2)]$ ($m/e = 1256$ amu) and $[H_2Os_4(CO)_{11}(Ph_2C_2)]$ ($m/e = 1256$ amu) respectively, and were not examined further. However, the major product **5** (which was obtained in ca 30% yield) exhibited the highest molecular peak in the electron impact mass spectrum at $m/e = 1682$ amu, and apparently corresponded with the formulation $[H_2Os_5(CO)_{13}(Ph_2C_2)_2]$. The analytical data were also consistent with this formulation. However, the ^1H NMR spectrum of **5** in CD_2Cl_2 exhibits a broad multiplet centred at ca 7.55 ppm and two strongly-coupled hydridoresonances at -14.97 and -15.17 ppm ($J = 4.1$ Hz), respectively, suggesting the presence of metallated dihydrido-species of the type $[H_2Os_5(CO)_{12}(Ph_2C_2)(PhC_2C_6H_4)]$. A single crystal X-ray structural analysis allowed unambiguous characterisation of **5** as $[H_2Os_5(CO)_{12}(Ph_2C_2)(PhC_2(H)C_6H_4)]$.

Species **5** has the structure shown in Fig. 1. The metal atom unit consists of two Os-triangles sharing a corner (Os(1)). Because of the presence of two independent molecules in the asymmetric unit all structural parameters discussed hereafter are reported as pairs of corresponding mean values for the two molecules. The two triangles form a dihedral angle of approximately 95° describing a sort of twisted bow-tie. The Os–Os bond lengths (range 2.737(1)–3.033(1); 2.738(1)–3.054(1) Å) belong to three distinct sets: two short outer edges (mean 2.740(1); 2.745(1) Å), and two sets of medium (mean 2.867(1); 2.862(1) Å) and long (mean 3.000(1); 3.015(1) Å) bond distances from the central Os-atom. The two longest bonds are believed to be bridged by the H (hydride) atoms in view of the metal–metal bond-lengthening effect which is usually found to accompany the presence of μ_2-H atoms. However, no further support for this location can be obtained from the examination of the CO-ligand distribution around the two sites because of the very irregular molecular shape. It is noteworthy that the central Os atom (Os(1)) is involved not only in four Os–Os bonds but also in two Os-μ_2-H (hydride) interactions and in bonding to two terminal CO ligands. Interestingly, one of these carbonyl ligands shows an incipient bridging interaction with a neighbouring Os-atom (Os(4)) as indicated by the short Os(4)–C(2) contact (2.72(2); 2.71(2) Å) and by the slight Os(1)–C(2)–O(2) bending (168(1); 166(1)°). Each Os-atom bears three terminal CO-ligands with the exception of Os(3) which bears only two.

The main outcome of the structural determination of **5** is the stereogeometry of the two organic ligands, which show two completely different coordination modes with the Os_5 system. The PhCCPh ligand lies on one of the two Os-triangles, and adopts a $\mu_3\eta$ coordination with the three metal atoms Os(1), Os(4) and Os(5). The phenyl groups are bent away from the metal triangle with typical sp^2-angles (CPh–C–C 121(1) and 126(1); 121(1) and 123(1)°) and C=C bond length (1.40(2); 1.41(2) Å). The ligand bonds via two σ-interactions (Os(1)–C(15) 2.16(1); 2.15(1), Os(5)–C(14) 2.09(1); 2.08(1) Å) and one π-interaction (Os(4)–C(14) 2.29(1); 2.31(1),

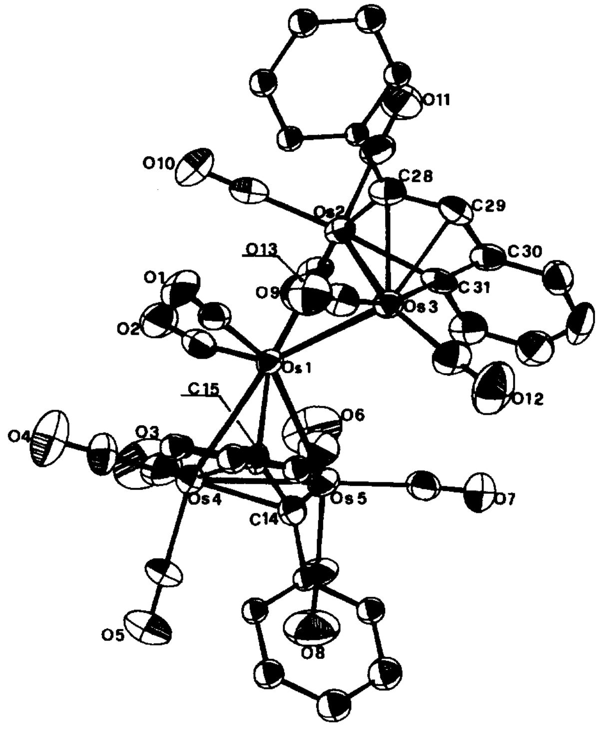

Fig. 1. ORTEP diagram of 5, showing 50% probability thermal ellipsoid. H-atoms are omitted for clarity. Bond lengths (Å) for the two independent molecules are: Os(1)–Os(2) 2.967(1); 2.975(1), Os(1)–Os(3) 2.885(1); 2.881(1), Os(1)–Os(4) 2.849(1); 2.842(1), Os(1)–Os(5), 3.033(1); 3.054(1), Os(2)–Os(3) 2.743(1); 2.738(1), Os(4)–Os(5) 2.737(1); 2.751(1). Average Os–C and C–O distances are 1.90(1); 1.90(1) and 1.14(2); 1.13(2) Å respectively. Other relevant structural parameters are discussed in the text.

Os(4)–C(15) 2.18(1); 2.17(1) Å) altogether acting as a four-electron donor. Similar structural parameters were found for other Os-clusters containing μ-alkylidene ligands such as $Os_3(CO)_9(CH_2)(C_2Ph_2)$ [3] (Os–C(σ) 2.13 (2), Os–C(π) 2.27(2) Å) and $Os_3(CO)_{10}(C_2Ph_2)$ [4] (Os–C(σ) 2.13(1), Os–C(π) 2.24(1) Å).

Less usual is the bonding mode adopted by the second organic ligand, which is found to form a μ_2-bridging system along the outer cluster edge Os(2)–Os(3) which is not involved in bonding with the PhCCPh group (see Fig. 1). The Ph–C–C–(C_6H_4) system adopts a *trans* configuration (C(Ph)–C–C 120(1), 119(1); 118(1), 117(1)°) with one *ortho* phenyl carbon atom participating to the bonding. The resulting planar system comprises the chelated Os-atom (Os(2)), the C_2 moiety, and the *ortho*-metallated phenyl ring. Such bonding fashion is, to our knowledge, unprecedented, and implies migration of the *ortho* H-atom from the phenyl group to the C_2 system. A formal six-electron contribution is achieved via two π-interactions from the C_2 and phenyl groups towards Os(3) and two σ-interactions from the *ortho* C(Ph) and C(C_2) atoms towards Os(2). This partitioning of the electron donation between the two Os-atoms is supported by the presence of only two CO-ligands on Os(3) compared with the three CO-ligands on Os(2). Os–C bond distances show a pattern similar to that observed for the PhCCPh ligand with shorter σ-interactions (mean 2.14(1); 2.13(1) Å) and longer π-ones (mean Os(3)–C(C_2) 2.23(1); 2.23(1),

Table 1

Fractional atomic coordinates

Atom	*x*	*y*	*z*
Os(1)	0.64756(2)	0.19108(2)	0.45942(3)
Os(2)	0.53147(2)	0.17798(3)	0.57577(3)
Os(3)	0.67952(2)	0.20666(3)	0.65220(3)
Os(4)	0.68021(3)	0.22652(3)	0.30776(3)
Os(5)	0.61037(3)	0.35918(3)	0.45938(3)
C(1)	0.7038(7)	0.0815(7)	0.4262(8)
O(1)	0.7355(5)	0.0161(5)	0.4053(6)
C(2)	0.5793(7)	0.1577(7)	0.3523(8)
O(2)	0.5320(5)	0.1312(5)	0.2951(6)
C(3)	0.5767(11)	0.2478(9)	0.2416(10)
O(3)	0.5188(7)	0.2592(8)	0.2017(9)
C(4)	0.7236(8)	0.1194(8)	0.2204(8)
O(4)	0.7436(7)	0.0579(6)	0.1656(7)
C(5)	0.7277(9)	0.2703(8)	0.2444(9)
O(5)	0.7513(8)	0.2975(8)	0.2048(8)
C(6)	0.4935(8)	0.3826(7)	0.4303(10)
O(6)	0.4264(6)	0.3939(7)	0.4089(9)
C(7)	0.6129(9)	0.4318(8)	0.5885(10)
O(7)	0.6211(8)	0.4741(7)	0.6621(7)
C(8)	0.6221(8)	0.4324(7)	0.4112(10)
O(8)	0.6307(7)	0.4745(7)	0.3803(9)
C(9)	0.4624(7)	0.2314(7)	0.5020(9)
O(9)	0.4170(5)	0.2650(6)	0.4594(6)
C(10)	0.5402(7)	0.0717(8)	0.4786(9)
O(10)	0.5458(5)	0.0085(5)	0.4199(6)
C(11)	0.4408(7)	0.1751(7)	0.6337(8)
O(11)	0.3885(6)	0.1742(6)	0.6702(7)
C(12)	0.7472(7)	0.2674(8)	0.7322(9)
O(12)	0.7857(6)	0.3059(7)	0.7847(8)
C(13)	0.7699(6)	0.1237(7)	0.6217(8)
O(13)	0.8275(6)	0.0682(6)	0.6037(7)
C(14)	0.7353(7)	0.3012(7)	0.4462(7)
C(15)	0.7535(6)	0.2197(6)	0.4314(6)
C(28)	0.6041(6)	0.1395(7)	0.6802(8)
C(29)	0.6139(6)	0.2007(7)	0.7638(7)
C(30)	0.5788(6)	0.2840(7)	0.7719(8)
C(31)	0.5420(6)	0.2894(7)	0.6843(8)
C(32)	0.5086(6)	0.3703(7)	0.6885(9)
C(33)	0.5101(7)	0.4352(8)	0.7669(9)
C(34)	0.5472(7)	0.4271(8)	0.8513(9)
C(35)	0.5801(7)	0.3521(8)	0.8540(8)
Os(6)	0.16741(2)	0.20628(3)	−0.00989(3)
Os(7)	0.04247(3)	0.18240(3)	0.08604(3)
Os(8)	−0.00439(3)	0.28510(3)	−0.00681(3)
Os(9)	0.33168(3)	0.19659(3)	−0.04056(3)
Os(10)	0.26591(3)	0.32390(3)	0.11942(3)
C(51)	0.1411(7)	0.1307(7)	−0.1237(8)
O(51)	0.1275(5)	0.0806(5)	−0.1931(6)
C(52)	0.2433(7)	0.1225(7)	0.0135(8)
O(52)	0.2780(5)	0.0663(5)	0.0338(7)
C(53)	0.4023(9)	0.1471(11)	0.407(13)
O(53)	0.4413(7)	0.1184(9)	0.0860(10)

Table 1 (continued)

Atom	x	y	z
C(54)	0.3500(8)	0.0997(9)	−0.1541(11)
O(54)	0.3643(7)	0.0437(7)	−0.2177(8)
C(55)	0.4227(8)	0.2268(8)	−0.0629(10)
O(55)	0.4766(6)	0.2444(7)	−0.0743(9)
C(56)	0.3030(10)	0.2863(10)	0.2172(10)
O(56)	0.3267(9)	0.2644(9)	0.2764(9)
C(57)	0.1934(8)	0.4238(8)	0.1874(9)
O(57)	0.1527(8)	0.4874(7)	0.2249(8)
C(58)	0.3565(8)	0.3693(7)	0.1401(8)
O(58)	0.4128(5)	0.3941(6)	0.1493(6)
C(59)	0.1339(7)	0.1819(7)	0.1714(8)
O(59)	0.1853(6)	0.1821(6)	0.2249(6)
C(60)	0.0760(7)	0.0718(8)	0.0040(8)
O(60)	0.0972(6)	0.0046(6)	−0.0432(7)
C(61)	−0.0202(8)	0.1601(8)	0.1609(8)
O(61)	−0.0592(6)	0.1449(6)	0.2014(7)
C(62)	−0.0414(7)	0.3845(8)	−0.0157(9)
O(62)	−0.0637(6)	0.4463(7)	−0.0224(8)
C(63)	−0.0155(6)	0.2399(7)	−0.1364(8)
O(63)	−0.0234(6)	0.2110(7)	−0.2158(6)
C(64)	0.2510(6)	0.3245(7)	−0.0155(7)
C(65)	0.2160(6)	0.2625(6)	−0.0798(7)
C(78)	−0.0716(7)	0.2071(7)	0.0141(7)
C(79)	−0.1176(7)	0.2881(7)	0.0530(8)
C(80)	−0.0815(7)	0.3431(7)	0.1353(8)
C(81)	0.0006(6)	0.3085(7)	0.1558(7)
C(82)	0.0395(7)	0.3642(7)	0.2287(8)
C(83)	−0.0018(8)	0.4416(8)	0.2775(9)
C(84)	−0.0816(8)	0.4711(8)	0.2541(10)
C(85)	−0.1237(7)	0.4248(7)	0.1862(8)
C(92)	0.2340(14)	0.3827(17)	0.5294(20)
Cl(1)	0.1573(6)	0.3389(6)	0.4614(7)
Cl(2)	0.2650(4)	0.3479(6)	0.6148(5)
C(17)	0.8714(4)	0.0953(4)	0.3752(4)
C(18)	0.9491(4)	0.0523(4)	0.3915(4)
C(19)	0.9906(4)	0.0836(4)	0.4763(4)
C(20)	0.9544(4)	0.1581(4)	0.5446(4)
C(21)	0.8767(4)	0.2011(4)	0.5283(4)
C(16)	0.8352(4)	0.1697(4)	0.4435(4)
C(23)	0.7979(5)	0.4172(5)	0.5208(5)
C(24)	0.8609(5)	0.4541(5)	0.5298(5)
C(25)	0.9275(5)	0.4141(5)	0.4701(5)
C(26)	0.9311(5)	0.3372(5)	0.4013(5)
C(27)	0.8681(5)	0.3003(5)	0.3922(5)
C(22)	0.8015(5)	0.3403(5)	0.4520(5)
C(37)	0.6674(5)	−0.0096(5)	0.5994(4)
C(38)	0.6836(5)	−0.0878(5)	0.5964(4)
C(39)	0.6577(5)	−0.1012(5)	0.6689(4)
C(40)	0.6155(5)	−0.0364(5)	0.7443(4)
C(41)	0.5993(5)	0.0418(5)	0.7473(4)
C(36)	0.6252(5)	0.0552(5)	0.6748(4)
C(67)	0.1952(4)	0.1982(4)	−0.2580(5)
C(68)	0.1549(4)	0.2034(4)	−0.3402(5)
C(69)	0.0966(4)	0.2737(4)	−0.3365(5)
C(70)	0.0785(4)	0.3388(4)	−0.2507(5)
C(71)	0.1187(4)	0.3336(4)	−0.1685(5)
C(66)	0.1771(4)	0.2633(4)	−0.1722(5)

Table 1 (continued)

Atom	*x*	*y*	*z*
C(73)	0.3122(4)	0.3563(3)	−0.1301(5)
C(74)	0.3375(4)	0.4106(3)	−0.1537(5)
C(75)	0.3234(4)	0.4914(3)	−0.0927(5)
C(76)	0.2840(4)	0.5179(3)	−0.0080(5)
C(77)	0.2586(4)	0.4636(3)	0.0156(5)
C(72)	0.2727(4)	0.3827(3)	−0.0454(5)
C(87)	−0.0739(4)	0.0865(5)	−0.1353(5)
C(88)	−0.1135(4)	0.0282(5)	−0.1955(5)
C(89)	−0.1915(4)	0.0302(5)	−0.1746(5)
C(90)	−0.2300(4)	0.0906(5)	−0.0935(5)
C(91)	−0.1904(4)	0.1489(5)	−0.0333(5)
C(86)	−0.1124(4)	0.1468(5)	−0.0542(5)

Os(3)–C(Ph) 2.40(1); 2.40(1) Å. Overall (5) possesses 78 valence electrons, and is thus isoelectronic with other "bow-tie" Os_5-clusters such as $Os_5(CO)_{19}$ and $Os_5(CO)_{17}(HC_2H)$ [5].

Experimental

The complex $[PPn][HOs_3(CO)_{11}]$ 100 mg (0.07 mmol) and a three-fold excess of PhC_2Ph were dissolved in 25 ml of THF. The solution was stirred for several days at room temperature but no reaction occurred. The solution was thus heated under reflux for ca 2 h, during which the colour changed from red to orange. The mixture was cooled to room temperature and a two-fold excess of HBF_4 added. Separation of the mixture by TLC, with 10% CH_2Cl_2/90% hexane as eluant, gave three main products: $H_2Os_4(CO)_{10}(Ph_2C_2)$ (**3**, yellow, yield 20%); $H_2Os_4(CO)_{11}(Ph_2C_2)$ (**4**, yellow-orange) and **5** (orange, yield 30%). Elementary analysis: Found: C, 29.29%, H, 1.32. $C_{37}H_{11}O_{13}Os_5$, calc.: C, 29.42; H, 1.42%.

X-ray quality crystals of **5** were obtained by slow evaporation of a solution of **5** in CH_2Cl_2/hexane at 0 °C.

Structural characterisation

Crystal data: $C_{41}H_{22}O_{13}Os_5$, $M_v = 1673.6$, triclinic, space group $P\bar{1}$, $a = 17.031(5)$, $b = 18.729(4)$, $c = 15.545(4)$ Å, $\alpha = 113.79(2)°$, $\beta = 97.48(2)°$, $\gamma = 73.72(2)°$, $U = 4354.3$ Å^3, $F(000) = 1546$, $Z = 4$, $D_{calcd} = 2.55$ g · cm^{-3}, Mo-$K_\alpha = 70.39$ cm^{-1}, $R = 0.033$ ($R_w = 0.036$) for 10441 independent reflections ($I > 2\sigma(I_o)$) collected in the range $2.5 < \theta < 25°$. Absorption correction was applied by azimuthal scanning of 15 reflections ($\chi > 80°$) at intervals of 10° (min and max transmission factor 71–100). The structure was solved by direct methods and light atoms were located by subsequent difference Fourier syntheses. All atoms were allowed to vibrate anisotropically except for the phenyl C-atoms and the H-atoms. The H-atoms were placed in calculated positions and refined 'riding' on their corresponding C-atoms. Geometrical constraints (C–C–C 120°, C–C 1.395 Å) were also used for the phenyl groups. No constraints and full anisotropy was used for the *ortho*-metallated phenyl groups. The SHELX package of crystallographic programs was used for the calculations [6]. Fractional atomic coordinates are reported in Table 1. Lists of hydrogen atom coordinates, bond distances and angles, thermal parameters and structure factors are available from the authors.

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