

A zwitterionic triosmium cluster bearing a metallated azulene ligand coordinated perpendicularly as an alkylidene bridge

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Abstract

The cluster $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ reacts readily with azulene in refluxing cyclohexane to give the oxidative addition product $[\text{Os}_3(\mu\text{-H})(\mu_2\text{-}\eta^1\text{-C}_{10}\text{H}_7)(\text{CO})_{10}]$ **1** which was shown by its X-ray crystal structure to contain the C_5 ring of the azulenyl ligand bonded through a single carbon atom at the 1-position. We propose that the compound is zwitterionic, with the 7-membered ring a tropylium cation and the 5-membered ring coordinated as a μ -alkylidene to the metal cluster, which carries a formal negative charge. Thermal loss of one CO ligand leads by further oxidative addition to the known cluster $[\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-}\eta^1:\eta^1:\eta^1\text{-C}_{10}\text{H}_6)(\text{CO})_9]$ **2**. © 2004 Elsevier B.V. All rights reserved.

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1. Introduction

The co-ordination of aromatic rings to transition-metal clusters has been extensively studied by several research groups [1]. Apart from a wish to form novel ligand systems, there has been a drive to produce molecular models for the chemisorption of aromatics on metal surfaces and for the catalytic transformations of these compounds. Commonly, arene complexation reduces the electron density of the π -electrons, thereby enhancing unusual nucleophilic addition and substitution reactions. In this communication we report an addition to our earlier report on azulene in which the double oxidative addition product $[\text{Os}_3(\mu\text{-H})_2(\mu_3\text{-}\eta^1:\eta^1:\eta^1\text{-C}_{10}\text{H}_6)(\text{CO})_9]$ **2** was obtained from $[\text{Os}_3(\text{CO})_{11}(\text{MeCN})]$ [2]. The Os_3 triangle was coordinated to a bridging alkylidene in the 5-membered ring and to a

terminal alkylidene in the 7-membered ring with the planar azulene system perpendicular to the Os_3 plane. Overall there has been a double oxidative addition with cleavage of C–H bonds at the 1- and 8-positions. The reactivity of azulene with triosmium is in contrast with that of iron and ruthenium where the azulene is parallel to the metal plane as in $[\text{Ru}_3(\mu_3\text{-}\eta^5:\eta^5:\eta^3\text{-C}_{10}\text{H}_8)(\mu\text{-CO})(\text{CO})_6]$ [3] or parallel to the metal–metal axis as in the dinuclear compound $[\text{Ru}_2(\mu\text{-}\eta^5:\eta^3\text{-C}_{10}\text{H}_8)(\text{CO})_5]$ [4].

In light of the double oxidative addition of azulene in refluxing octane (125 °C), we wished to establish whether the single oxidative addition product could be obtained at lower temperatures and, if so, whether the initial C–H activation was at the 5- or 7-membered ring. In free azulene there is a significant dipole moment with positive charge at the 7-membered ring and negative charge at the 5-membered ring, and therefore which ring is activated might depend upon the electrophilic or nucleophilic nature of the oxidative addition. This paper will show that it is the 5-membered ring which is activated first.

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2. Experimental

2.1. Synthesis of cluster $[\text{Os}_3(\mu\text{-H})(\mu_2\text{-}\eta^1\text{-C}_{10}\text{H}_7)(\text{CO})_{10}] \mathbf{1}$

A solution of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ (0.050 g, 0.054 mmol) and azulene (0.013 g, 0.101 mmol) in cyclohexane (50 cm³) was refluxed under nitrogen. By following the colour change from yellow to green, the changes in the IR spectrum, and using analytical TLC, we stopped the reaction after 40 min when it appeared that the starting cluster had been consumed. TLC work-up (silica, eluent petroleum spirit, b.p. 40–60 °C) gave unreacted azulene, the known deep yellow-orange cluster **2** (10% yield) and a green band, which yielded compound **1** (15%). Cluster **2** was characterized by comparison of its spectroscopic data with those published [2] and spectral data for **1** are: $\nu(\text{CO})/\text{cm}^{-1}$ (cyclohexane): 2095 m, 2074 s, 2061 s, 2054 ms, 2037 m, 2012 ms, 2000 s, 1974 w; ¹H NMR (CDCl_3 , 20 °C, J in Hz): δ 9.34 (d, H², $J_{2,3} = 4.1$), 8.54 (ddd, H⁴, $J_{4,5} = 9.7$, $J_{4,6} = 0.9$, $J_{3,4} = 0.8$), 8.25 (dd, H⁸, $J_{7,8} = 9.2$, $J_{6,8} = 0.9$), 8.11 (ddd, H⁷, $J_{6,7} = 9.7$, $J_{7,8} = 9.2$, $J_{5,7} = 0.9$), 7.99 (ddd, H⁵, $J_{4,5} = 9.7$, $J_{5,6} = 9.7$, $J_{5,7} = 0.9$), 7.88 (dddd, H⁶, $J_{6,7} = 9.7$, $J_{5,6} = 9.7$, $J_{4,6} = 0.9$, $J_{6,8} = 0.9$), 7.46 (dd, H³, $J_{2,3} = 4.1$, $J_{3,4} = 0.8$), –14.40 (s, OsHOs); ¹³C NMR (CDCl_3 , 20 °C): δ 29.7 (C¹), 72.0 (C⁹), 122.6 (C³), 128.9 (C⁷), 132.4 (C⁵), 138.4 (C⁴), 141.1 (C⁶), 151.1 (C⁸), 154.0 (C¹⁰), 178.5 (C²). Crystals of **1** suitable for X-ray structure determination were obtained by slow evaporation of a hexane solution at room temperature.

2.2. Thermolysis of cluster $[\text{Os}_3(\mu\text{-H})(\mu_2\text{-}\eta^1\text{-C}_{10}\text{H}_7)(\text{CO})_{10}] \mathbf{1}$

A solution of cluster **1** (0.030 g) in cyclohexane (50 cm³) was refluxed under nitrogen for 4 h by which time the green solution had become yellow-orange. TLC work-up gave $[\text{Os}_3(\text{CO})_{12}]$ (3%), unreacted cluster **1** (10%) and cluster **2** (80%), which was characterized by comparison of its spectra with those reported [2].

2.3. Crystal structure determination for cluster **1**

The structure was determined using a Rigaku AFC7S diffractometer (graphite-monochromated Mo K α radiation, 0.71073 Å) at 298(2) K. Corrections for L_p effects and semi-empirical absorption corrections [5] were applied. Structure solution was by direct methods [6] and expanded using Fourier techniques [7]. All non-H atoms were refined anisotropically, using a riding model for H-atoms with thermal parameters $1.2 \times U_{\text{eq}}$ of the corresponding C atoms. The final cycle of full-matrix least-squares was based on F^2 . teXsan crystallographic software package for data reduction and graphical representations was used [8], with refinement using

SHELXTL-PLUS [7]. Crystal data: $\text{C}_{20}\text{H}_8\text{O}_{10}\text{Os}_3$, formula weight = 977.86, monoclinic, space group $P2_1/c$, $a = 9.740(7)$ Å, $b = 8.936(3)$ Å, $c = 25.963(12)$ Å, $\beta = 100.39(4)^\circ$, $V = 2223(2)$ Å³, $Z = 4$, green prisms, $0.60 \times 0.30 \times 0.20$ mm. 4176 measured reflections ($h = 0$ to 11, $k = 0$ to 10, $l = -30$ to 30), 3927 independent reflections, $R_{\text{int}} = 0.0754$, $R = 0.0482$, $wR(F^2) = 0.1259$ for 3067 reflections with $I_0 \geq 2\sigma(I_0)$, 298 parameters.

3. Results and discussion

Azulene was added to a suspension of $[\text{Os}_3(\text{CO})_{10}(\text{MeCN})_2]$ in cyclohexane and the mixture refluxed during which time the color of the solution changed from yellow to green. The green azulene derivative $[\text{Os}_3(\mu\text{-H})(\mu_2\text{-}\eta^1\text{-C}_{10}\text{H}_7)(\text{CO})_{10}] \mathbf{1}$ was isolated in 15% yield. The ¹H NMR spectrum confirmed the presence of a hydride (δ –14.40) and there were seven multiplets for the remaining seven hydrogen atoms on the ligand. Two signals coupled by 4.1 Hz for the 5-membered ring and analysis of the remainder of the spectrum, showed that there were still five hydrogens on the 7-membered ring, confirming that the metallation had occurred at the 1-position on the 5-membered ring. An analysis of the ¹³C NMR spectrum, including ¹H–¹³C COSY spectra confirmed these findings.

The molecular structure of **1** (Fig. 1) confirmed the site of metallation but also that the 1-azulenyl ligand is attached to the cluster through the 1-position alone. The organic ligand is planar and orientated perpendicularly to the metal triangle (dihedral angle between the azulene and the Os₃ planes = 85.9°, See Table 1 for selected bond lengths and angles). The metal triangle has three Os–Os bonds with the shortest [Os(1)–Os(2) = 2.7638(11) Å] associated with the bridging C(1) atom of the azulenyl. The other two Os–Os bonds are similar but longer

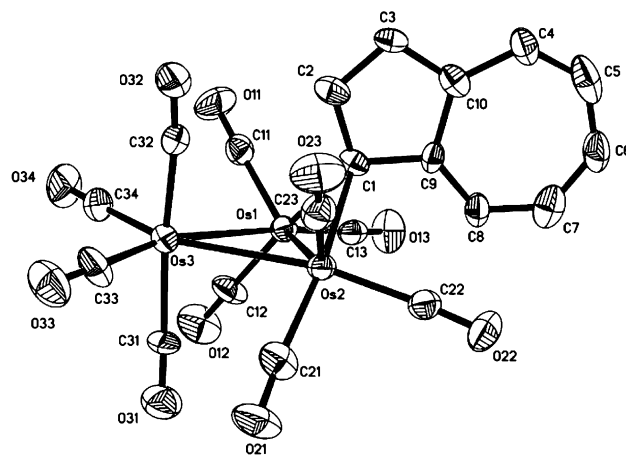


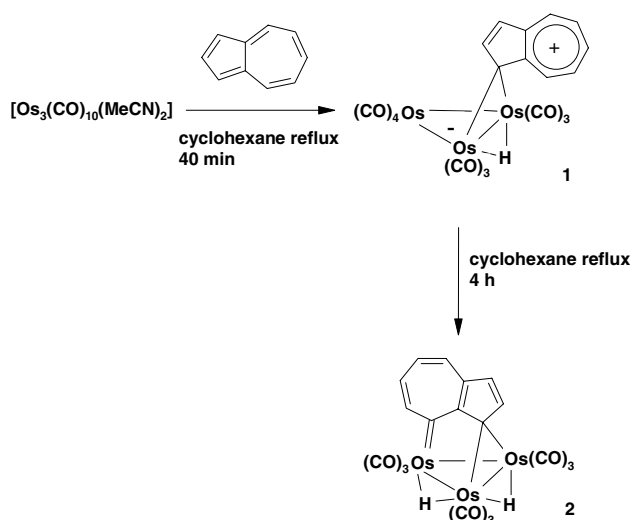
Fig. 1. ORTEP view (35% probability ellipsoids, H atoms omitted for clarity) of the molecular structure of **1** in the crystal.

Table 1
Selected bond lengths (Å) and angles (°) for $[\text{Os}_3(\mu\text{-H})(\mu_2\text{-}\eta^1\text{-C}_{10}\text{H}_7)(\text{CO})_{10}]$ **1**

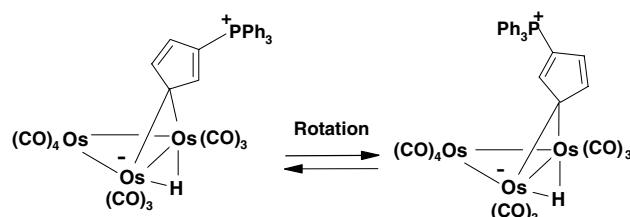
Os(1)–Os(2)	2.7638(11)	C(5)–C(6)	1.35(3)
Os(1)–Os(3)	2.895(2)	C(6)–C(7)	1.41(2)
Os(2)–Os(3)	2.8626(13)	C(7)–C(8)	1.40(2)
Os(1)–C(1)	2.235(14)	C(8)–C(9)	1.38(2)
Os(2)–C(1)	2.301(13)	C(9)–C(10)	1.45(2)
C(1)–C(2)	1.459(19)	Os(3)–Os(1)–C(1)	90.9(30)
C(1)–C(9)	1.38(2)	Os(3)–Os(2)–C(1)	90.4(4)
C(2)–C(3)	1.36(2)	Os(1)–C(1)–Os(2)	75.1(4)
C(3)–C(10)	1.38(2)	Os(1)–C(1)–C(2)	121.2(10)
C(4)–C(5)	1.40(3)	Os(1)–C(1)–C(9)	120.3(11)
C(4)–C(10)	1.34(3)	Os(2)–C(1)–C(2)	112.9(9)
		Os(2)–C(1)–C(9)	120.1(9)

$[\text{Os}(1)\text{--Os}(3) = 2.895(2) \text{ \AA}$, $\text{Os}(2)\text{--Os}(3) = 2.8626(13) \text{ \AA}$], which is consistent with an approximate mirror plane through the azulenyl ligand bisecting Os(1) and Os(2). We interpret the bonding as involving an alkylidene bridge between Os(1) and Os(2), and a charge distribution tending towards a cationic tropylium arrangement for the 7-membered ring and a negative charge at the metal atoms. The $\nu(\text{CO})$ values lend support to some build-up of negative charge at the metal atoms. The C–C distances in the ligand are similar but their uncertainties do not allow us to discuss any differences in bond order in the carbon–carbon bonds around the two rings.

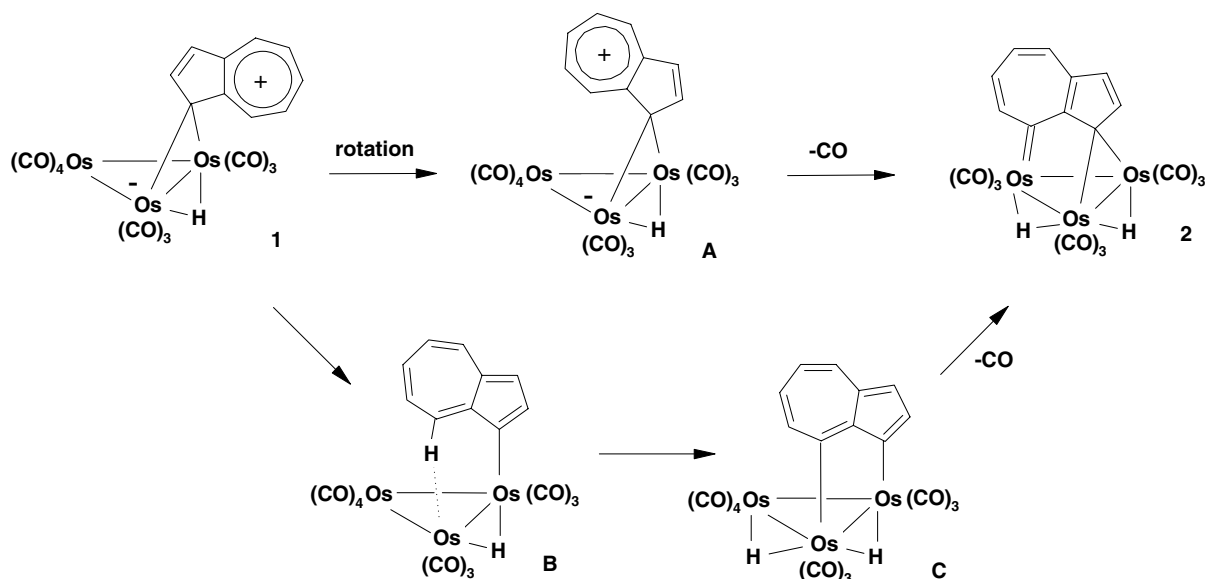
The green cluster **1** converts in good yield by loss of a CO ligand to the previously reported yellow-orange cluster **2** on heating a cyclohexane solution for 4 h (Scheme 1). This conversion requires a rotation of the alkylidene bridge so that the 7-membered ring can approach the third Os atom at which it is metallated, rather than away from it as in **1**. Scheme 2 shows two possible mechanisms. The alkylidene could rotate by 180° to give **A** followed by loss of CO and C–H activation. Alternatively the ligand could convert from bridging to terminal, rotate by 90° to form **B** so that the



Scheme 1.



Scheme 3.



Scheme 2.

8-H can approach an osmium atom with an agostic interaction, followed by C–H bond activation to give **C**, all occurring before the loss of CO which occurs in the final step. There is precedence for the rotation of a bridging alkylidene as in the phosphonium zwitterionic species shown in Scheme 3 [9]. There appears to be no tendency for triosmium clusters to form π -interactions with azulene and it is likely that the greater tendency for osmium to undergo C–H bond activation than ruthenium and iron and its ability to form stronger M–C σ -bonds accounts for the differences.

4. Supporting material

Complete crystallographic data for the structure of **1** have been deposited at the Cambridge Crystallographic Data Centre, No. 229940.

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