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The site selectivity of hydride ligand in tungsten-triosmium clusters: the crystal structure and the solution dynamics of $(C_5Me_5)W Os_3(CO)_{12}H$

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Abstract

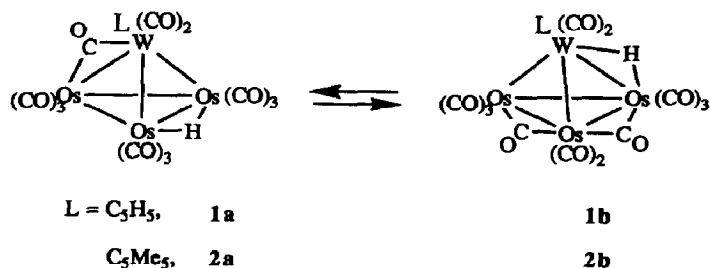
The solid-state structure of a tetranuclear mixed-metal cluster $(C_5Me_5)W Os_3(CO)_{12}H$ (**2b**) which has hydride ligand bridging across a W–Os bond is presented. In solution, the isomer adopting the solid-state structure is in equilibrium with a second isomer (**2a**) in which the hydride is associated with an Os–Os edge. Complex **2** crystallizes in the orthorhombic space group $Pna2_1$, with a 21.598(6), b 8.973(4), c 14.121(4) Å, $Z = 4$; 2260 observed reflections with $I > 3\sigma(I)$ were used in the refinement. The R values converged to $R_F = 0.023$, $R_w = 0.018$ and $GOF = 1.500$.

Introduction

The chemistry of the mixed-metal clusters of transition metals has been the subject of much research [1], because the reactivities of the various metals present in mixed metal clusters can show reactivity patterns and/or structures very different from those of their homometallic analogues. Owing to the high thermal stability of the osmium containing compounds, many papers dealing with the synthesis of mixed-metal clusters containing a triosmium unit have appeared [2].

A decade ago, Shapley and coworkers [3] reported the synthesis of a tungsten-triosmium cluster, $CpW Os_3(CO)_{12}H$ (**1**) by a condensation of $Os_3(CO)_{10}(CH_3CN)_2$ with $CpW(CO)_3H$. The structure of **1** is shown in Scheme 1. Starting from this complex, our group has successfully prepared a polynuclear cluster oxide complex, $CpW Os_3(CO)_9(\mu-O)_2H$ [4]. During our investigation of this interesting oxidation

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Scheme 1.

reaction, we noticed that complex **1** displays two hydride resonances at $\delta -18.63$ and -21.82 ($J_{W-H} = 43$ Hz) with relative intensities 3 : 1 (400 MHz, CD_2Cl_2 , RT), suggesting the presence of two interconvertible isomers in solution. The downfield resonance is clearly attributable to the isomer adopting a solid-state structure, but the structure of the second isomer, which possesses a W–H–Os interaction, is at present unknown. In order to examine the structure of the unknown isomer, we decided to prepare the relevant pentamethylcyclopentadienyl analogue, $Cp^*WOs_3(CO)_{12}H$ (**2**, $Cp^* = C_5Me_5$).

Results and discussion

Complex **2** can be prepared by the condensation of $Os_3(CO)_{10}(CH_3CN)_2$ with $Cp^*W(CO)_3H$. The 1H NMR spectrum exhibits two hydride resonances at $\delta -18.22$ and -20.93 ($J_{W-H} = 41$ Hz) with relative intensities 1 : 2.1 at room temperature, suggesting that the structurally uncharacterized isomer becomes the dominant species in solution. Encouraged by this discovery, we then carried out a single crystal X-ray diffraction study.

The molecular structure of **2b** is shown in Figure 1 while interatomic distances and angles are listed in Table 1. The tungsten atom and the three osmium atoms define a distorted tetrahedral core framework which is associated with the expected 60 outer valence electrons. The tungsten atom is coordinated to a cyclopentadienyl ligand and two CO ligands and the three basal osmium atoms are associated with eight terminal and two semi-bridging CO ligands. The three basal Os–Os bond distances are almost identical, but the W–Os(1) distance (3.0734 Å) is substantially longer than the other two W–Os bonding interactions, W–Os(2) = 2.9038 Å and W–Os(3) = 2.9074 Å. The hydride ligand, which bridges the longest W–Os(1) bond, was located on the difference electron-density map. The observed W–H distance (1.966 Å) is approximately 0.3 Å greater than the corresponding Os(1)–H (1.679 Å) distance, suggesting that the bonding mode of the hydride ligand involves a unique, asymmetric, three-center two-electron W–H–Os interaction.

An additional feature of interest is the presence of three semi bridging carbonyl ligands [5]. The first C(12)–O(12), coordinates to the W atom while also interacting very weakly with the Os(2) atom (W–C(12) = 1.983(18) Å; Os(2)–C(12) = 2.844(17) Å). The bond angle, W–C(12)–O(12) = 167.5(14)°, suggests that this CO ligand can almost be classified as a semi-bridging ligand. The second, C(7)–O(7), spans the Os(3)–Os(1) linkage with Os(3)–C(7) = 1.982 Å and Os(1)–C(7) = 2.583 Å; the third, C(10)–O(10), associates with the Os(3)–Os(2) edge, with Os(3)–C(10)

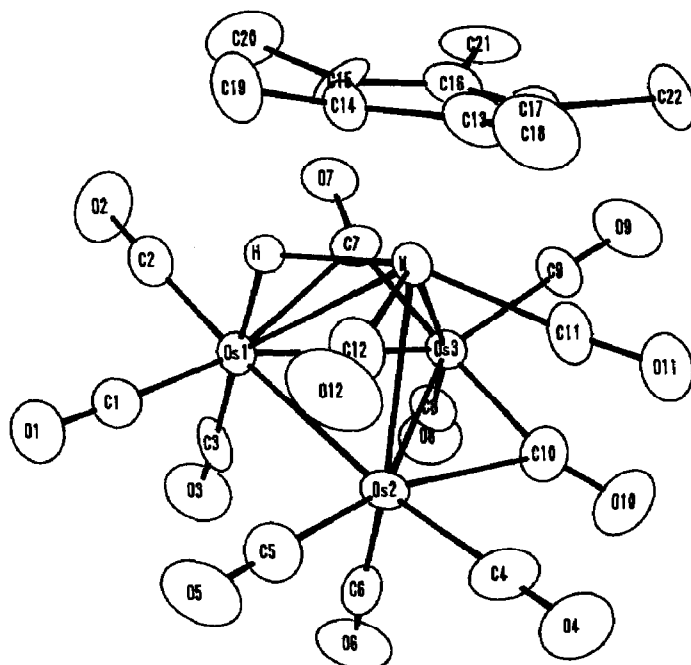


Fig. 1. The molecular structure of $(C_5Me_5)WOs_3(CO)_{12}H$ (**2b**) showing the atom numbering scheme.

Table 1

Selected bond distances and bond angles for complex **2**

| <i>Bond distances (Å)</i> | | | |
|---------------------------|------------|-------------------|------------|
| Os(1)–Os(2) | 2.8128(12) | Os(1)–Os(3) | 2.8231(13) |
| Os(2)–Os(3) | 2.8228(14) | W–Os(1) | 3.0734(11) |
| W–Os(2) | 2.9038(11) | W–Os(3) | 2.9074(11) |
| W–H | 1.966(15) | Os(1)–H | 1.679(13) |
| Os(1)–C(1) | 1.889(18) | Os(1)–C(2) | 1.895(20) |
| Os(1)–C(3) | 1.887(19) | Os(2)–C(4) | 1.910(20) |
| Os(1)–C(7) | 2.583(17) | Os(2)–C(5) | 1.872(19) |
| Os(2)–C(6) | 1.906(12) | Os(2)–C(10) | 2.510(16) |
| Os(2)–C(12) | 2.844(17) | Os(3)–C(7) | 1.982(18) |
| Os(3)–C(10) | 1.947(17) | Os(3)–C(8) | 1.897(20) |
| Os(3)–C(9) | 1.896(16) | W–C(11) | 2.000(17) |
| W–C(12) | 1.983(18) | W–C(13) | 2.297(14) |
| W–C(14) | 2.311(15) | W–C(15) | 2.403(14) |
| W–C(16) | 2.406(15) | W–C(17) | 2.306(15) |
| <i>Bond angles (°)</i> | | | |
| W–H–Os(1) | 114.7(8) | Os(1)–C(1)–O(1) | 177.5(16) |
| Os(1)–C(2)–O(2) | 177.8(14) | Os(1)–C(3)–O(3) | 176.2(16) |
| Os(1)–C(7)–O(7) | 123.9(13) | Os(2)–C(4)–O(4) | 176.2(20) |
| Os(2)–C(5)–O(5) | 176.5(15) | Os(2)–C(6)–O(6) | 176.4(15) |
| Os(2)–C(10)–O(10) | 123.3(13) | Os(3)–C(10)–O(10) | 159.2(15) |
| Os(3)–C(7)–O(7) | 160.9(13) | Os(3)–C(8)–O(8) | 176.0(15) |
| Os(3)–C(9)–O(9) | 178.0(17) | W–C(11)–O(11) | 174.9(14) |
| W–C(12)–O(12) | 167.5(14) | Os(2)–C(12)–O(12) | 118.9(12) |

= 1.947 Å and Os(2)–C(10) = 2.510 Å. The presence of the last two semi-bridging CO ligands reduces the charge imbalance between the three basal osmium atoms. The formal electron counts for the Os(1), Os(2), and Os(3) atoms are 18.5, 18, and 17 e⁻, respectively.

There is much steric crowding around the pentamethylcyclopentadienyl rings as indicated by the out-of-plane displacement of the methyl groups. The methyl groups of the pentamethylcyclopentadienyl ring have been pushed away from the WOs₃ core, and the average displacement from the plane defined by the five center carbons is 0.26(3) Å. We propose that this steric effect is responsible not only for the lengthening of the W–H distance of the W–H–Os three-center two-electron bond, but also for the reduction of the **2a/2b** ratio in comparison with the **1a/1b** ratio. As suggested by the structure of **1a**, isomer **2a** possesses a bridging CO ligand associated with an Os–W edge. Because the CO ligand is larger than the hydride ligand, this CO ligand would experience an even greater steric repulsion from the Cp* group in **2a**. Thus, because of the bridging CO–Cp* repulsion in **2a**, the **2a/2b** ratio is decreased in solution.

Isomers **2a** and **2b** interconvert rapidly in solution on the NMR time scale above ambient temperature: saturation [6] of the hydride resonance at δ –18.22 results in a 43% and a 65% decrease of the intensity of the second resonance at δ –20.93 at 293 K and 298 K, respectively. The activation parameter was calculated from the variable-temperature ¹H NMR data, and the Gibbs energy of activation (ΔG^\ddagger) calculated from the coalescence of the Cp* signals is approximately 17.4 kcal/mole ($T_c = 355$ K). Furthermore, both the temperature and the solvent polarity have little effect on the equilibration constant. The ratio of **2a/2b** recorded in THF-*d*₈ is 1 : 2.2, identical with that recorded in either CD₂Cl₂ or toluene-*d*₈.

In an attempt to monitor the exchange of CO ligands we carried out a variable-temperature ¹³C NMR study on complex **2**. The ¹³C NMR spectrum (CD₂Cl₂, 294 K) of a ¹³CO enriched sample exhibits a W–CO signal, attributable to isomer **2a**, at δ 224.2 with a characteristic J_{W-C} coupling ($J_{W-C} = 78$ Hz), and shows several uncharacterized Os–CO signals in the area between δ 193.4 and 170.7 emanating from both isomers **2a** and **2b**. This J_{W-C} coupling constant is very small compared with those of the regular, terminal W–CO ligands which are in the range 140–165 Hz, suggesting that the W–CO ligands undergo rapid exchange with the Os–CO ligands. In accord with this assignment, the signal at δ 224.2 broadened and split into a broad signal at δ 226.7 and a sharp signal at δ 221.6 at 173K. The W–CO signals of isomer **2b** were not observed at room temperature because of the rapid chemical exchange by the CO ligands. However, when the temperature was decreased to 173K, two signals of equal intensity at δ 212.6 ($J_{W-C} = 130$ Hz) and 207.8 ($J_{W-C} = 115$ Hz), from isomer **2b**, appeared.

Finally, we have also extended the synthesis to the related tungsten-triruthenium complexes, CpWRu₃(CO)₁₂H and Cp*WRu₃(CO)₁₂H and have determined their solid state structure. Interestingly, these ruthenium complexes adopted a butterfly framework possessing a quadruply bonded CO ligand [7].

Experimental

Infrared spectra were recorded on a Perkin–Elmer 580 spectrometer calibrated to the absorption of cyclohexane at 2138.5 cm⁻¹ and the absorption of polystyrene

film at 1944.5 cm^{-1} . ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-400 (400.13 MHz) instrument. Mass spectra were recorded on a JEOL-HX110 instrument operating in electron impact, field desorption, or fast atom bombardment modes. All reactions were performed under nitrogen in deoxygenated solvents dried with suitable reagents. $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$ [8] and $\text{Cp}^*\text{W}(\text{CO})_3\text{H}$ [9] were prepared by published procedures.

Preparation of $\text{C}_5\text{Me}_5\text{W}(\text{CO})_3\text{H}$. To solution of $\text{Os}_3(\text{CO})_{10}(\text{CH}_3\text{CN})_2$, prepared from $\text{Os}_3(\text{CO})_{12}$ (500 mg, 0.55 mmol) and anhydrous Me_3NO (91 mg, 1.21 mmol) in toluene (40 ml), was added a solution of $\text{C}_5\text{Me}_5\text{W}(\text{CO})_3\text{H}$ (600 mg, 1.48 mmol) in toluene (15 ml) dropwise during five minutes. The mixture was then refluxed for 20 minutes until the color had changed from yellow-orange to redbrown. The solvent was then evaporated under vacuum and the residue was separated by thin layer chromatography (silica gel, dichloromethane : hexane = 1 : 2). Recrystallization gave 155 mg of **2** as a red crystalline solid (0.13 mmol, 24%). Crystals suitable for X-ray diffraction study were obtained from a layered solution of methanol on dichloromethane at room temperature.

Spectroscopic data: MS (EI, ^{192}Os , ^{184}W), m/z 1232 (M^+); IR (C_6H_{12}) $\nu(\text{CO})$ 2087(m), 2086(sh,m), 2069(w), 2053(m), 2047(vs), 2033(vs), 2010(s), 2002(w), 1988(m), 1982(sh, w), 1956(br, vw), 1901(br, vw), 1885(br, vw), 1760(vw) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3 , RT) δ 2.07 (s, 10.2H), 2.01 (s, 4.8H), -18.22 (s, 0.32H), -20.93 (s, 0.68H, $J_{\text{W-H}} = 41$ Hz).

Elemental analysis: Found: C, 21.53; H, 1.34. $\text{C}_{22}\text{H}_{16}\text{O}_{12}\text{W}_1\text{Os}_3$ calcd.: C, 21.54; H, 1.31%.

Structural determination of complex (2). Crystals suitable for diffraction analysis were obtained from dichloromethane-methanol solution. A crystal was mounted on

Table 2

Data for the X-ray diffraction study of complex **2**

| Crystal data | | | |
|--|------------------------|--------------------------------------|--|
| <i>a</i> | 21.598(6) Å | Laue symmetry | orthorhombic |
| <i>b</i> | 8.973(4) Å | space group | <i>Pna</i> ₂ ₁ |
| <i>c</i> | 14.121(4) Å | <i>Z</i> | 4 |
| <i>V</i> | 2736.46 Å ³ | Formula | $\text{C}_{22}\text{H}_{16}\text{O}_{12}\text{W}_1\text{Os}_3$ |
| mol.wt. | 1226.39 | density (calcd) | 2.978 mg cm^{-3} |
| Data collection, reduction, solution and refinement | | | |
| data collection instrument | | Nonius CAD-4 | |
| radiation (monochromated in incident beam) | | Mo- K_α (λ 0.7093 Å) | |
| scan method | | $\theta/2\theta$ scan mode | |
| scan parameter | | 0.7 + 0.35 tan θ | |
| crystal size, mm | | 0.12 × 0.22 × 0.28 | |
| linear absorption coefficient, mm^{-1} | | 18.24 | |
| transmission factors: max, min | | 0.998800, 0.352100 | |
| no. of unique data, total with $I > 3\sigma(I)$ | | 2507, 2260 | |
| no. of atoms and parameters refined | | 54, 343 | |
| R ; R_w ^a | | 0.029; 0.018 | |
| GOF ^b | | 1.500 | |
| residue electron density, $e \text{ \AA}^{-3}$: max | | 0.87 | |

^a $w = 1/\sigma^2(F_o)$. ^b $s = [\sum w |F_o - F_c|^2 / (N_o - N_v)]^{1/2}$ (N_o = number of observations; N_v = number of variables).

a glass fiber. Diffraction measurements were carried out by use of an Enraf–Nonius CAD-4 fully automated four circle diffractometer. Unit cells were determined and refined from 25 randomly selected reflections, with 2θ in the range of 15.58 – 20.52° , obtained by using the CAD-4 automatic search, center, index and least-squares routines. All data reductions and structure refinements were performed by use of the NRCC-SDP-PDP-11 and NRCC-SDP-VAX packages. The structure was solved by the Patterson method and refined by least squares recycle; all non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms of the

Table 3

Positions and thermal parameters for complex 2

| Atom | <i>x</i> | <i>y</i> | <i>z</i> | <i>B</i> (iso) ^a , Å ² |
|-------|------------|-------------|------------|--|
| Os(1) | 0.45873(3) | 0.53711(7) | 0.75000 | 2.45(3) |
| Os(2) | 0.41687(3) | 0.29875(7) | 0.63759(6) | 2.51(3) |
| Os(3) | 0.43152(3) | 0.25973(7) | 0.83468(6) | 2.245(24) |
| W | 0.32482(3) | 0.42374(6) | 0.76496(6) | 2.002(24) |
| C1 | 0.4608(7) | 0.6658(20) | 0.6433(13) | 3.6(8) |
| C2 | 0.4797(8) | 0.6992(20) | 0.8298(13) | 3.6(8) |
| C3 | 0.5420(9) | 0.4796(19) | 0.7323(13) | 3.9(8) |
| C4 | 0.3752(10) | 0.146(3) | 0.5678(12) | 4.2(9) |
| C5 | 0.4154(8) | 0.4175(21) | 0.5286(13) | 3.7(9) |
| C6 | 0.4974(10) | 0.2249(19) | 0.6084(11) | 3.8(10) |
| C7 | 0.4435(8) | 0.4338(20) | 0.9192(20) | 3.5(8) |
| C8 | 0.5124(9) | 0.1874(22) | 0.8598(10) | 3.6(8) |
| C9 | 0.3899(9) | 0.1588(21) | 0.9340(11) | 3.8(8) |
| C10 | 0.4168(7) | 0.0874(18) | 0.7540(13) | 3.5(8) |
| C11 | 0.2941(7) | 0.2196(19) | 0.7326(12) | 3.3(7) |
| C12 | 0.3060(7) | 0.4694(20) | 0.6303(12) | 3.4(8) |
| C13 | 0.2218(7) | 0.4755(18) | 0.7887(9) | 2.9(7) |
| C14 | 0.2549(7) | 0.6153(17) | 0.7880(11) | 2.7(7) |
| C15 | 0.2926(7) | 0.6145(17) | 0.8735(11) | 2.9(7) |
| C16 | 0.2827(8) | 0.4766(22) | 0.9188(11) | 3.2(8) |
| C17 | 0.2430(8) | 0.3931(17) | 0.8679(10) | 3.2(7) |
| C18 | 0.1711(8) | 0.4428(22) | 0.7203(11) | 4.6(9) |
| C19 | 0.2421(9) | 0.7491(20) | 0.7311(16) | 6.0(10) |
| C20 | 0.3242(9) | 0.7447(24) | 0.9153(13) | 5.4(10) |
| C21 | 0.3045(9) | 0.4432(22) | 1.0207(10) | 4.4(9) |
| C22 | 0.2113(8) | 0.2467(21) | 0.9056(12) | 3.9(8) |
| O1 | 0.4621(8) | 0.7469(15) | 0.5819(9) | 6.9(9) |
| O2 | 0.4930(7) | 0.7951(15) | 0.8809(9) | 5.8(7) |
| O3 | 0.5934(6) | 0.4529(17) | 0.7220(9) | 6.5(8) |
| O4 | 0.3490(8) | 0.0640(19) | 0.5259(10) | 6.8(8) |
| O5 | 0.4112(6) | 0.4889(16) | 0.4610(8) | 5.6(7) |
| O6 | 0.5455(7) | 0.1742(19) | 0.5940(9) | 5.6(8) |
| O7 | 0.4456(5) | 0.5062(15) | 0.9869(7) | 3.9(6) |
| O8 | 0.5594(6) | 0.1389(16) | 0.8787(9) | 5.1(7) |
| O9 | 0.3661(7) | 0.0944(18) | 0.9942(10) | 6.6(8) |
| O10 | 0.4071(7) | −0.0374(13) | 0.7324(10) | 6.0(8) |
| O11 | 0.2724(6) | 0.1064(14) | 0.7167(9) | 5.4(7) |
| O12 | 0.2841(6) | 0.4944(17) | 0.5579(8) | 5.4(8) |
| H | 0.368 | 0.583 | 0.781 | 3.2 |

^a *B*(iso) is the mean of the principle axes of the thermal ellipsoid.

methyl group were added at the idealized positions and were included in the structure factor calculations; the hydride hydrogen was located on the difference electron density map. The data collection parameters and the atomic coordinates are summarized in Tables 2 and 3. Tables of anisotropic thermal parameters, structure factor amplitudes, and non-essential bond distances and angles are available from the authors (S.M.P.).

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