

Preliminary communication

OSMIUM CLUSTER RADICAL ANIONS *

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Summary

Several radical anions of decaosmium carbonyl clusters have been generated both electrochemically and chemically and their ESR spectra investigated.

In contrast to finely divided metal surfaces, high nuclearity metal clusters may be obtained in high purity and are easily structurally characterised by single crystal X-ray crystallography (see Fig. 1) [1,2].

In this communication we report an investigation into the oxidative redox chemistry of the two anionic clusters $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{2-}$ (**1**) and $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{2-}$ (**2**) by both electrochemical and chemical methods. The addition or removal of an electron from a closed shell configuration of polynuclear metal carbonyl clusters is known to cause structural distortion [3]. In this way the new radical anions $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{\cdot -}$ (**3**) and $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{\cdot -}$ (**5**), and the neutral clusters $[\text{Os}_{10}\text{C}(\text{CO})_{24}]$ (**4**) and $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]$ (**6**), have been prepared from their respective dianions **1** and **2** (Scheme 1) [4]. Electrochemical studies in dichloromethane solution at a platinum electrode show that the dianionic clusters **1** and **2** undergo two oxidation steps (Fig. 2). The first is fully reversible ($\Delta E_p = 56$ mV for **3** and 58 mV for **5**), and corresponds to a single one-electron oxidation. Plots of i_p /vs. μ are linear through the origin, and $i_a/i_c = 1$ ($E_{1/2} = +0.78$ V for **1** and $+0.39$ V for **2** vs. Ag/AgCl). The second oxidations are irreversible ($\Delta E_p = +1.21$ V vs. Ag/AgCl for **1**), and associated with this step is a consequent reduction at $+0.35$ V vs. Ag/AgCl. Likewise for **2** the second oxidation is irreversible ($\Delta E_p = +0.70$ V vs. Ag/AgCl), and associated with this are consequent reductions at $+0.13$ and -0.27 V (both vs. Ag/AgCl) [4].

Controlled potential electrolysis of **1** at $+1.0$ V or **2** at $+0.5$ V yield the new radical anions $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{\cdot -}$ (**3**) and $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{\cdot -}$ (**5**). The radical species **3** is highly air sensitive, on exposure to moist air conversion back to the dianion **1** is

* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday.

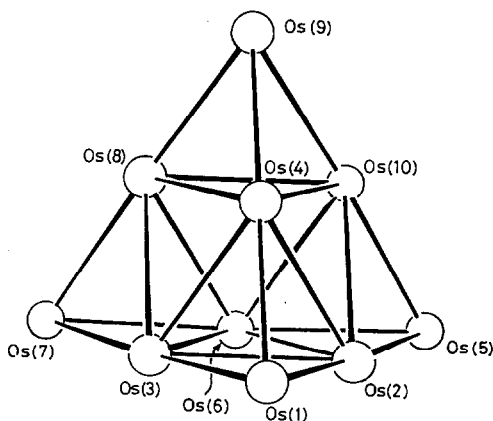
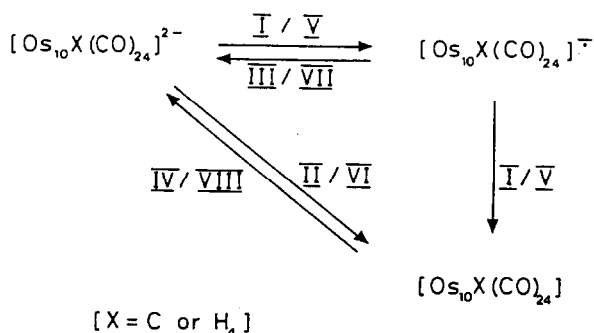
Os₁₀ metal core.

Fig. 1. The metal cluster structure on which $[\text{Os}_{10}\text{X}(\text{CO})_{24}]^{2-}$ (1: X = C, 2: X = H₄) and its derivatives are based. The carbon atom in 1 occupies an octahedral site, whilst the hydrogen atoms in 2 occupy three tetrahedral sites and the octahedral site.



SCHEME 1. I: X = C, 1 equiv. AgBF₄ or FeCl₃ or 1.0 V at a Pt electrode; II: X = C, 2 equiv. AgBF₄ or FeCl₃ or 1.40 V at a Pt electrode; III: X = C, air exposure for 2–3 min; IV: X = C, donor solvents, acetone, CH₃CN or Δ; V: X = H₄, 1 equiv. AgBF₄ or FeCl₃ or 0.50 V at a Pt electrode; VI: X = H₄, 2 equiv. AgBF₄ or FeCl₃ or 0.70 V at a Pt electrode; VII: X = H₄, air exposure up to 12 h; VIII: X = H₄, donor solvents, acetone, CH₃CN or Δ.

instantaneous. Whereas 5 was found to be stable in air for up to 12 h, slowly reverting back to 2 after this period (Scheme 1) *.

This reflects the greater oxidising power of 3 than of 5, and 3 is hence more readily reduced by atmospheric moisture. Chemical oxidation of 1 or 2 with either one equivalent of AgBF₄ in CH₂Cl₂ or FeCl₃ in THF produces the same radical

* IR (CH₂Cl₂, cm⁻¹) at room temperature: 1 2033s, 1988s; 2 2076w, 2034s, 1994ssh, 1986s; 3 2054s, 2010s; 4 2078s, 2034s; 5 2092w, 2056s, 2050sh, 2016ssh, 2009s; 6 2106w, 2080s, 2068ssh, 2050msh, 2035s, 2014msh.

Fast atom bombardment spectroscopy (negative ion mode): 3 *m/z* 2604 corresponds to Os₁₀C(CO)₂₄ using ¹⁹²Os; 4 *m/z* 2604 corresponds to Os₁₀C(CO)₂₄ using ¹⁹²Os; 5 *m/z* 2596 corresponds to H₄Os₁₀(CO)₂₄ using ¹⁹²Os; 6 *m/z* 2596 corresponds to H₄Os₁₀(CO)₂₄ using ¹⁹²Os.

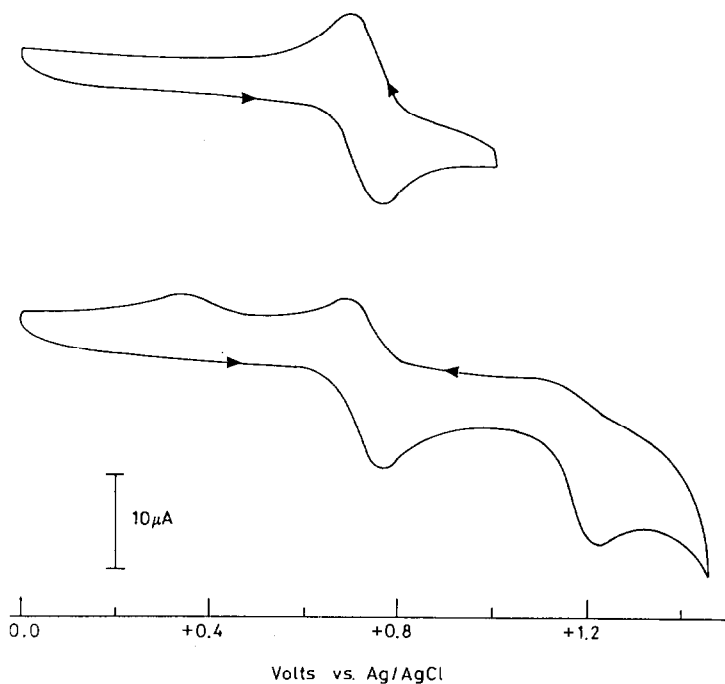


Fig. 2. Cyclic voltammogram of $5.5 \times 10^{-6} M$ [PPN] $[\text{Os}_{10}\text{C}(\text{CO})_{24}]$ in $\text{CH}_2\text{Cl}_2/0.2 M \text{Bu}_4\text{NBF}_4$ at a platinum electrode. Scan rate 100 mV/s (at room temperature).

anions **3** and **5**. No metal-hydride signals were observed in the ^1H NMR spectrum of **5** in CD_2Cl_2 between $\delta +20$ and -50 ppm over the temperature range 198–293 K.

Controlled potential electrolysis of **1** at +1.4 V or **2** at +0.70 V, yield the neutral species $[\text{Os}_{10}\text{C}(\text{CO})_{24}]$ (**4**) and $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]$ (**6**) as diamagnetic solids. The neutral clusters **4** and **6** are also the products of the chemical oxidation of **1** and **2**, respectively, with either AgBF_4 in CH_2Cl_2 or FeCl_3 in tetrahydrofuran (Scheme 1). These two clusters have been characterised on the basis of their spectroscopic and analytical data, but in donor solvents such as acetone slow conversion back to their respective dianions occurs.

As expected, the radical species **3** and **5** are paramagnetic. In Fig. 3a and 3b are shown the ESR spectra of these compounds in frozen CH_2Cl_2 solutions at 6 and 9.4 K, respectively. For **3** an isotropic value of g of 2.295 is taken as indicative of spin-orbit coupling between various states in the monoanion, while the lineshape of **3** is Lorentzian. The spectrum of a polycrystalline sample of **3** at 7.7 K is nearly identical to that of the frozen solution, being asymmetrical in lineshape with a value of $g = 2.298$. For **5** the g value of 2.277, is also taken as an indication of spin-orbit coupling. The curve fit is Gaussian with a large linewidth (100 Gauss at 9.4 K) due to unresolved hyperfine couplings from the four hydrogen interstitial atoms. To the left of the main ESR signal for **5** are two weak signals, possibly arising from a certain degree of anisotropy in the radical wavefunction. Previous ESR studies on **1** and $[\text{H}_2\text{Os}_{10}\text{C}(\text{CO})_{24}]$ [6] have shown that the latter is intrinsically paramagnetic at temperatures below 100 K and gives rise to broad linewidths and values of g close

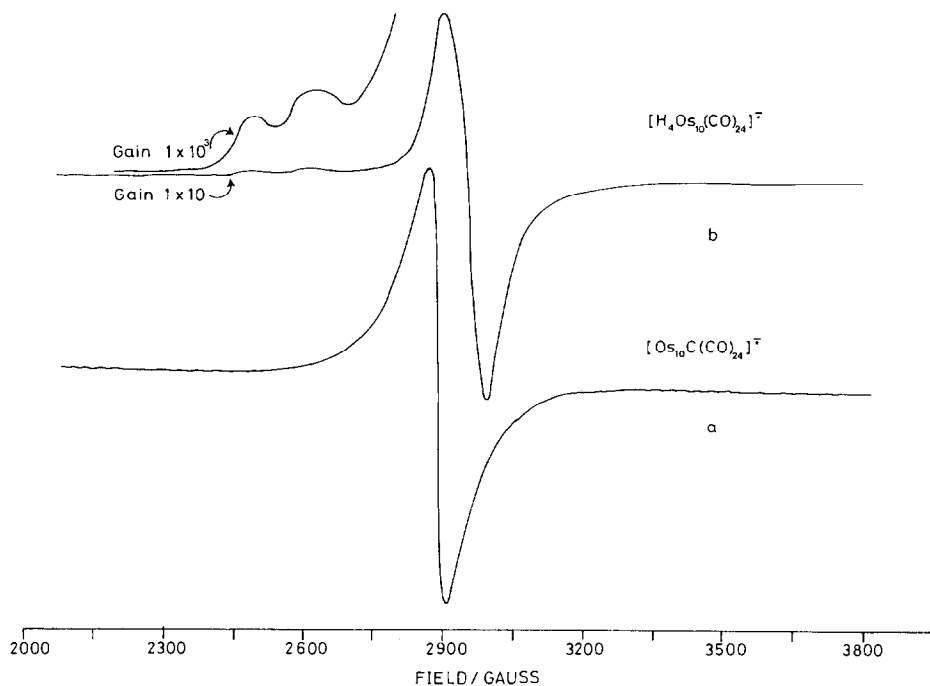


Fig. 3. ESR spectra of the radical species $[\text{Os}_{10}\text{C}(\text{CO})_{24}]^{\bullet -}$ (**3**) and $[\text{H}_4\text{Os}_{10}(\text{CO})_{24}]^{\bullet -}$ (**5**) recorded at 6 and 9.4 K respectively as frozen CH_2Cl_2 solutions. Modulation 10 Gauss, Gain 1×10^1 , ΔH_{pp} (**3**) 62 Gauss, ΔH_{pp} (**5**) 100 Gauss and A/B 1.0.

to free spin. Paramagnetic osmium clusters are rare [7,8], and other high nuclearity cluster radicals have also been little studied [9,10]. Magnetic moment studies on **3**, have shown that this radical species has a moment μ of 1.68 ± 0.05 BM at 293 K, which is in accord with the presence of one unpaired electron. (This value (μ) is per cluster; diamagnetic corrections for the sample container, Os, CO and $[\text{PPN}]^+$ were applied [11]) The two radical species **3** and **5** exhibit paramagnetic behaviour up to 293 K in the solid state, as expected for genuine odd-electron clusters.

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