

Preliminary communication

THE ELECTROCHEMICAL REDUCTION OF AN UNSATURATED MIXED-METAL CLUSTER ANION: SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF $[(\text{Ph}_3\text{P})_2\text{N}][\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]^-$

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Summary

The unsaturated mixed-metal cluster anion $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]^-$ has been prepared by the reaction of $[(\text{Ph}_3\text{P})_2\text{N}][\text{Os}_3\text{H}(\text{CO})_{11}]$ with $\text{Ag}[\text{PF}_6]$, and the anion has been shown by an X-ray analysis to consist of an Ag^{I} atom linking together two “ $\text{Os}_3\text{H}(\text{CO})_{10}$ ” fragments. The electrochemistry of this complex has been investigated and it has been shown to undergo two one-electron reductions.

A number of formally “unsaturated” mixed-metal clusters containing metals of Group Ib have been characterised [1,2,3]. These clusters contain fewer electrons than is required by the Effective Atomic Rule if the metal—metal links are to be considered to be composed of localised two-centre two-electron interactions. In the cases of the clusters $[\text{Os}_3\text{H}(\text{CO})_{10}(\text{AuPPh}_3)]$ [1] and $[\text{Os}_3(\text{CO})_{10}(\text{AuPEt}_3)_2]$ [3] there is a close analogy with the hydrido carbonyl $[\text{Os}_3\text{H}_2(\text{CO})_{10}]$ [4] which also contains two electrons fewer than the 48 electrons required for three two-centre two-electron bonds. In these three compounds, the “unsaturation” is considered to be localised in the Os—Os “double” bond which is doubly bridged by two one electron donor groups, either hydrido hydrogens or the Au^{I} atom of the AuPR_3 group. A similar explanation has been offered in the anion $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Au}]^-$ where the Au^{I} atom links two Os_3 units via bonding across two short Os—Os bonds [2]. All the bridged Os—Os bonds are significantly shorter by some 0.13 Å than the unbridged bonds which would be consistent with double bond character, but it is probably better to look at these systems in terms of four-centre four-electron bonds [4]. In view of the “unsaturation” in these clusters it should be possible to add electron pairs either chemically or electrochemically without causing cluster breakdown. In this communication, we re-

TABLE 1

 ^{13}C NMR SPECTRUM FOR $[(\text{Ph}_3\text{P})_2\text{N}][\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]$ (ppm)

δ	Intensity	Relative intensity
188.94	0.49	1
187.61	0.48	1
186.89	0.89	2
185.18	0.87	2
183.01	0.93	2
180.16	0.84	2
134.22	4.99	
132.64	8.31	
129.93	8.33	$[(\text{Ph}_3\text{P})_2\text{N}]^+$
128.12	0.67	
127.04	0.58	

port the synthesis of the anion $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]^-$, which is isostructural with the gold analogue [2], and its electrochemical reduction.

The reaction of $[(\text{Ph}_3\text{P})_2\text{N}][\text{Os}_3\text{H}(\text{CO})_{11}]$ with $\text{Ag}[\text{PF}_6]$ (2/1 molar ratio) in refluxing tetrahydrofuran, under a nitrogen atmosphere, affords the salt $[(\text{Ph}_3\text{P})_2\text{N}][\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]$. The infrared spectrum of the complex in the carbonyl region exhibits bands at 2076(m), 2040(vs), 1988(s), 1975(s, sh), and 1955(s, sh) $[\text{CH}_2\text{Cl}_2]$, which are analogous to the bands reported for the gold anion [2]. Similarly, the ^1H NMR spectrum of the silver anion, in the hydride region, displays a single resonance at τ 22.61 (CD_2Cl_2 solution), which compares well with the value of τ 21.26 reported for $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Au}]^-$ [2].

The ^{13}C NMR spectra of both the Ag and Au anions are characterised by six resonances in the ratio 1/1/2/2/2/2 which correspond to a molecular structure with identical "Os₃" units having a carbonyl distribution as shown in the solid state structure. The ^{13}C chemical shifts are presented in Table 1.

The solid state structure* of the $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]^-$ anion, as determined by a single-crystal X-ray analysis, is shown in Fig. 1 which includes some important bond parameters. This complex is isostructural with the analogous Au containing salt $[(\text{Ph}_3\text{P})_2\text{N}][\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Au}]$ [2], with, in this case, the two independent Ag atoms lying on crystallographic centres of symmetry. These atoms are bonded to symmetry related isosceles triangles, bridging the short Os—Os bonds. The central $\text{Ag}(1)\text{Os}(1)\text{Os}(2)\text{Os}(1')\text{Os}(2')$ unit is necessarily planar, and the dihedral angle between the $\text{Ag}(1)\text{Os}(1)\text{Os}(2)$ and $\text{Os}(1)\text{Os}(2)\text{Os}(3)$ plane is 114.8° (115.4° in the second molecule) which compares to 112.2° (113.8°) in the gold analogue [2]. The Os—Ag distances are ca. 0.06 Å longer than the equivalent Os—Au distances in the $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Au}]^-$ anion, while the bridged Os—Os bonds are ca. 0.02 Å shorter than the equivalent bonds (2.698(1) and 2.689(1) Å) in the Au complex [2]. The bonding in the system should probably be considered as an *sp* hybridized Ag^{I} atom with the lobes of the hybrid orbital pointing at the mid-point of the "unsaturated" Os—Os bonds

* $\text{C}_{36}\text{H}_{32}\text{AgNO}_{10}\text{Os}_6\text{P}_2$, $M = 2849.59$, monoclinic, space group $C2/c$, a 27.851(4), b 18.218(2), c 26.830(4) Å, β 112.10(1)°, U 12519 Å³, D_c 2.49 g cm⁻³, $Z = 8$, $F(000) = 8526$, $\lambda(\text{Mo-K}\alpha)$ 0.71089 Å, $\mu(\text{Mo-K}\alpha)$ 125.36 cm⁻¹. 8179 reflections measured on a Stoe-Siemens 4-circle diffractometer. Structure solved by a combination of direct methods and Fourier difference techniques, and refined by blocked cascade least squares to $R = 0.061$ and $R_w = 0.059$ for 5632 observed reflections [$F > 4\sigma(F)$].

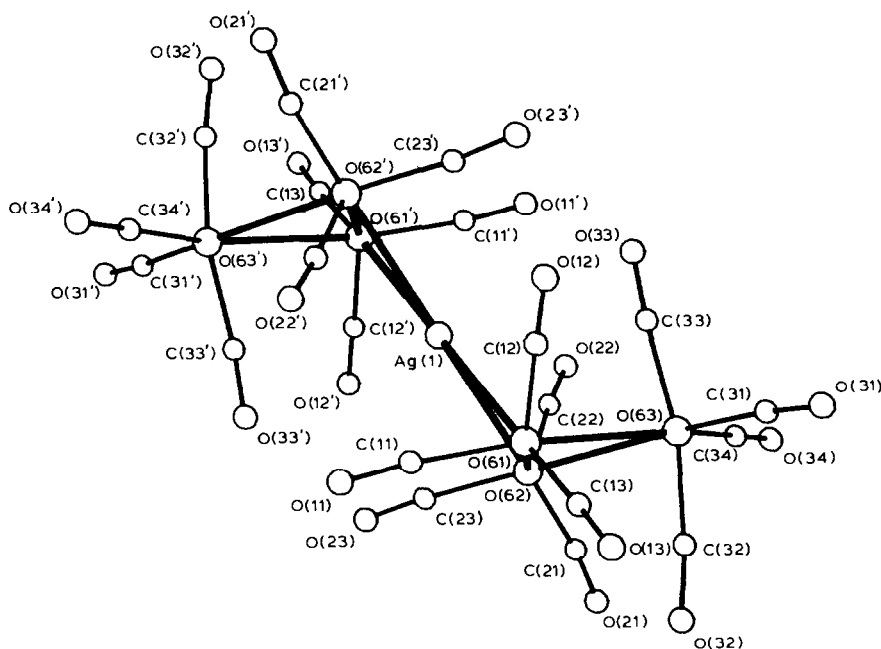


Fig. 1. The molecular structure of the $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]^-$ anion. Bond lengths: Ag(1)—Os(1), 2.865(1) (2.874(1)); Ag(1)—Os(2), 2.852(1) (2.865(1)); Os(1)—Os(2), 2.876(1) (2.666(1)); Os(1)—Os(3), 2.830(1) (2.827(1)); Os(2)—Os(3), 2.827(1) (2.839(1)) Å; bond angles: Os(1)—Ag(1)—Os(2), 55.8(1) (55.4(1))°. The values in square brackets denote the bond parameters for the second anion.

resulting in a delocalised bonding system. The Os—Os unbridged distances are similar to the average value for the equivalent Os—Os bonds (2.831(3) Å) in the gold salt [2]. All the carbonyl groups are essentially linear. Although the hydride ligands were not located directly the carbonyl groups adjacent to the short Os—Os edge bend away from it with an average *cis*-Os—Os—C(carbonyl) angle of 132(2)°. This is consistent with the location of the hydride ligands along these edges.

In view of the established “unsaturation” of the $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]^-$ anion it is expected that it might be readily reduced. Voltammetric studies were, therefore, undertaken and Fig. 2a shows the cyclic voltammogram of $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]^-$ anion in acetonitrile solution at 20°C. Under these conditions a single irreversible reduction step (E_p -1.35 V) is observed. On cooling the solution to -25°C the reduced species are stabilised, and two quasi-reversible reduction steps ($E_{1/2}$ -1.29 V (ΔE_p 90 mV) and $E_{1/2}$ 1.38 V (ΔE_p 80 mV)) are shown in Fig. 2b. This indicates that the anion can accept an electron pair without losing cluster integrity.

Atomic coordinates and bond parameter data for $[(\text{Ph}_3\text{P})_2\text{N}][\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]$ have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. They may be obtained on request from the Director if the full literature citation for the communication is given.

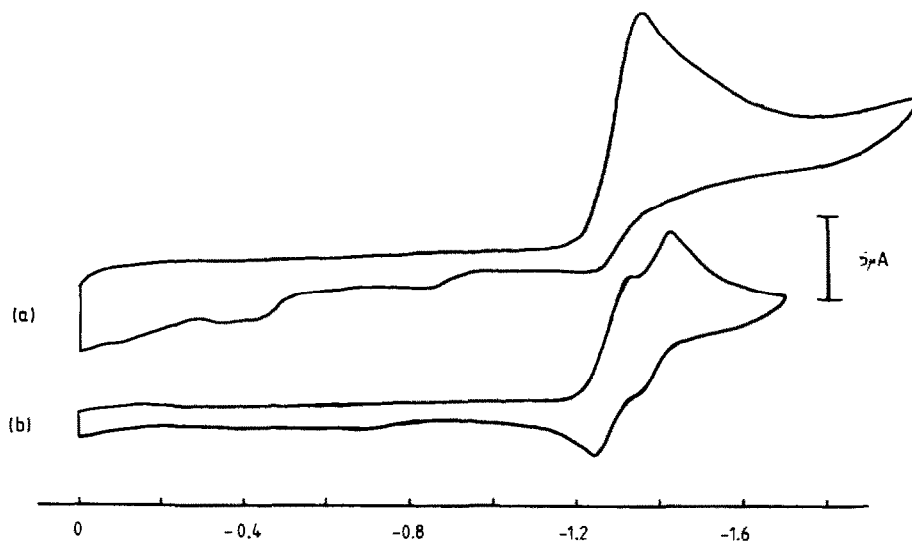


Fig. 2. (a) Cyclic voltammogram of $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]^-$ at 20°C ; (b) Cyclic voltammogram of $[\{\text{Os}_3\text{H}(\text{CO})_{10}\}_2\text{Ag}]^-$ at -25°C .

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