

Journal of Organometallic Chemistry, 423 (1992) 255–261
 Elsevier Sequoia S.A., Lausanne
 JOM 22219

Electrochemical behaviour of the electronically and coordinatively unsaturated cluster $[\text{Os}_3(\mu\text{-H})(\text{CO})_8\{\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4\}]$

Domenico Osella *, Mauro Ravera

Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica Materiali, Università di Torino, Via P. Giuria 7, 10125 Torino (Italy)

Anthony K. Smith, A. Jane Mathews

Department of Chemistry, University of Liverpool, P.O. Box 147, Liverpool L69 3BX (UK)

and Piero Zanello

Dipartimento di Chimica, Università di Siena Pian dei Mantellini, 44, 53100 Siena (Italy)

(Received June 11, 1991)

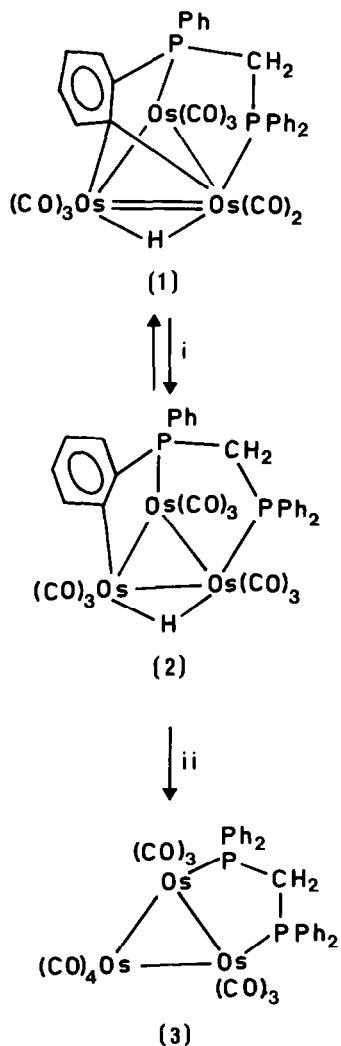
Abstract

The electrochemical behaviour of the unsaturated cluster $\text{Os}_3(\text{H})(\text{CO})_8[\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4]$ has been studied by electrochemical and spectroscopic methods. The transformations of the very reactive title compound into the saturated cluster $\text{Os}_3(\text{H})(\text{CO})_9[\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4]$ and $\text{Os}_3(\text{CO})_{10}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ by CO addition has been followed step-by-step by cyclic voltammetry.

Introduction

The ability to coordinate and then to activate small organic moieties is an essential requirement for the use of metal clusters in catalysis [1]. Addition of organic molecules to electronically and coordinatively unsaturated clusters is usually easy since ligand dissociation is not required. Few unsaturated clusters have been reported [1], the prototype being $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ [2]. We recently showed that the redox behaviour of the unsaturated (46e) $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9\text{L}$ clusters differs greatly from that of the saturated (48e) $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}\text{L}$ adducts (L = CO, PPh_3 , AsPh_3). The former series exhibits chemically reversible reduction processes, where the “Os–H₂–Os” core represents the reduction centre, whereas the latter series shows chemically irreversible steps [3].

Previously we described [4] the high yield synthesis of another unsaturated (46e) trimetallic cluster, namely $\text{Os}_3(\mu\text{-H})(\text{CO})_8[\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4]$ (1) by the thermolysis of $\text{Os}_3(\text{CO})_{10}(\text{Ph}_2\text{PCH}_2\text{PPh}_2)$ (3). The loss of two CO ligands results in



Scheme 1. Reaction sequence: $1 + \text{CO} \rightarrow 2 + \text{CO} \rightarrow 3$ in acetonitrile solution containing $[\text{Bu}_4\text{N}][\text{BF}_4]$ (0.1 M); i, CO, 25°C, 2 h; ii, CO, 25°C, 1 week.

metallation of one of the phenyl rings of the dppm ligand. Interestingly, the reaction can be reversed via the stable (48e) intermediate $\text{Os}_3(\text{H})(\text{CO})_9[\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4]$ (2) by bubbling CO through a solution of 1 (Scheme 1). We thought it of interest to investigate this reaction sequence by electrochemical methods.

Results and discussion

The cyclic voltammetric (CV) response of an acetonitrile solution of 1 at a Hg electrode is presented in Fig. 1. A reduction peak A, $E_p(\text{A}) = -1.18$ V, is observed, and a directly associated reoxidation peak B, $E_p(\text{B}) = -1.11$ V, is observed in the reverse scan. A small oxidation peak C is also present, at -0.96 V,

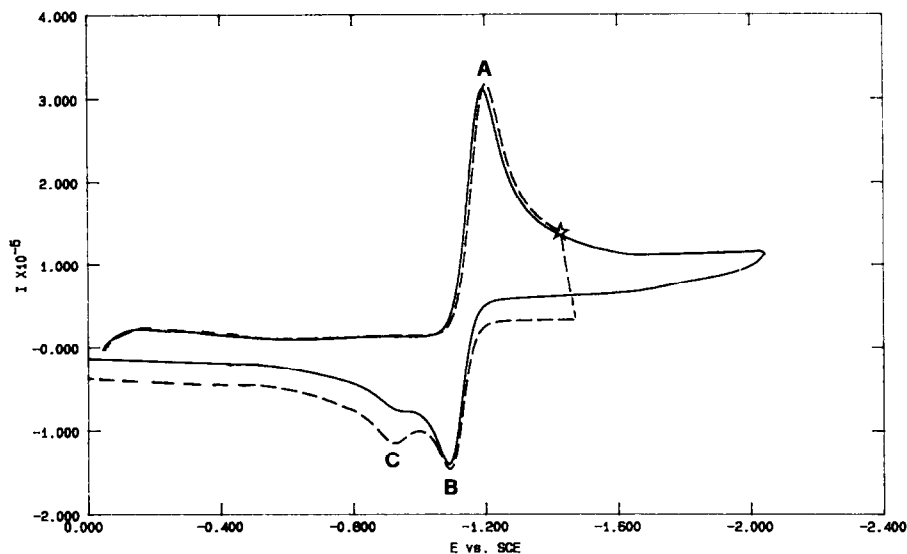


Fig. 1. Cyclic voltammograms of an acetonitrile solution of **1** (1 mM) and $[\text{Bu}_4\text{N}][\text{BF}_4]$ (0.1 M) at a Hg working electrode at 400 mV s^{-1} recorded without (bold line) and with (dotted line) a holding time (*) of 5 s.

in the reverse sweep owing to the oxidation of an electroactive by-product generated by reduction of **1** at the potential of peak A.

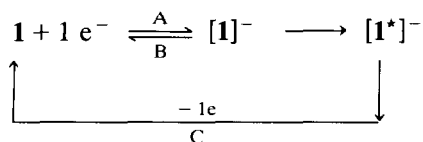
As expected, peak C decreases and eventually disappears as the scan rate is increased or the temperature lowered. Furthermore, a CV scan employing a short time delay after peak A has been traversed (Fig. 1) shows that peak C significantly increases in height in the reverse sweep.

Controlled potential coulometry at a mercury-pool working electrode ($E_w = -1.25 \text{ V}$) indicates the consumption of 1 Faraday/mol of **1**. D.C. polarography of an acetonitrile solution of **1** confirms the quasi-reversibility of the reduction process, the plot of E vs $\log(i_d - i/i)$ is linear with a slope of 78 mV, ($E_{1/2} = -1.13 \text{ V}$).

Analysis of the CV responses of the peak system A/B with scan rates varying from 0.02 to 10 V s^{-1} reveals the following features: (i) the anodic to cathodic peak current ratio, $ip(\text{B})/ip(\text{A})$, gradually increases from 0.6 to 0.9; (ii) the current function, $ip(\text{A})/v^{1/2}$, remains practically constant; (iii) the difference between the potential of the cathodic peak and that of the directly associated reoxidation peak, $E_p(\text{B}) - E_p(\text{A}) = \Delta E_p$, increases progressively from 70 to 320 mV. These features are diagnostic of a quasi-reversible one-electron transfer followed by a slow chemical change [5] (EC mechanism [6 *]). If a first order reaction is assumed to follow the electron transfer, and use is made of the Nicholson method [7], a half-life of ca. 10 s can be roughly estimated for the radical anion $[\text{I}]^-$.

This electrochemical behaviour does not substantially change when the solvent is changed from CH_3CN to CH_3COCH_3 or CH_2Cl_2 . Small shifts in the formal

* Reference number with asterisk indicates a note in the list of references.

Scheme 2. Proposed EC mechanism for the reduction of compound **1**.

electrode potentials, $E^\circ(0/1^-) = E_p(A) + E_p(B)/2$, are observed, namely: -1.14 (CH_3CN); -1.08 (CH_3COCH_3); -1.23 (CH_2Cl_2) V vs. SCE.

Controlled potential electrolysis at a Hg pool ($E_w = -1.25$ V) of an acetonitrile solution of **1** shows a change in colour from green to orange. *In situ* CV tests, carried out as the electrolysis proceeded, showed that peak B is progressively replaced by peak C in the oxidation scan. As expected from the CV results, in the electrolysis $[\mathbf{1}]^-$ was converted into a new species, $[\mathbf{1}^*]^-$, oxidizable at the potential of peak C. Nevertheless, exhaustive reoxidation of the electroreduced solution at $E_w = 0.0$ V regenerates **1** in ca. 75% yield, indicating that the transformation $[\mathbf{1}]^- \rightarrow [\mathbf{1}^*]^-$ is very readily reversible, and probably involves a simple geometrical reorganization.

The redox processes undergone by **1** are depicted in Scheme 2.

The X band EPR spectrum of an electroreduced solution of **1** in acetonitrile, recorded at liquid nitrogen temperature, shows an axial pattern with $g_\perp = 2.011$, $g_\parallel = 2.095 (\pm 0.005)$ and a peak-to-peak line width, $\Delta H_{pp} = 145 (\pm 0.5)$ G (Fig. 2).

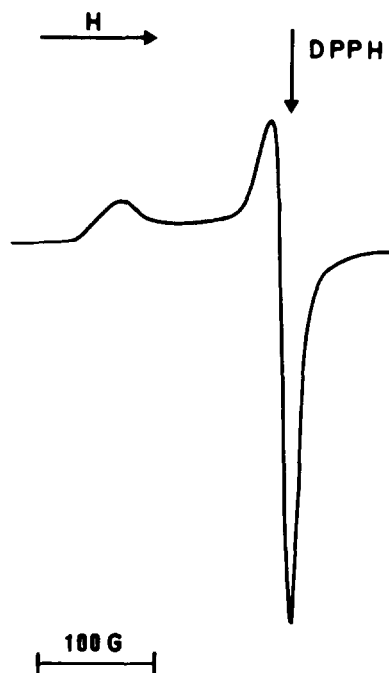


Fig. 2. X-band EPR spectrum of a one-electron reduced acetonitrile solution of **1** recorded at liquid nitrogen temperature. DPPH (2,2'-diphenylpicrylhydrazyl) was used as reference.

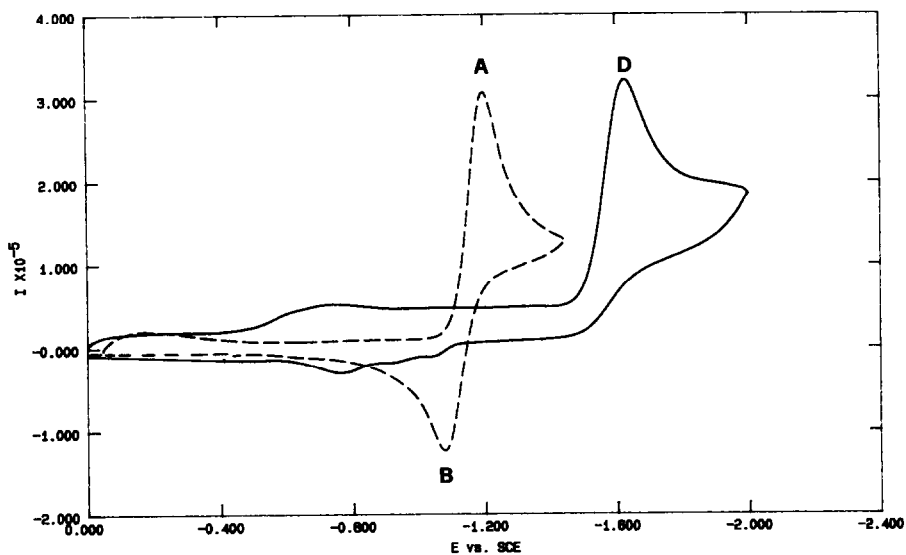


Fig. 3. Cyclic voltammograms of an acetonitrile solution of **1** at 400 mV s^{-1} recorded before (dotted line) and after (bold line) bubbling of CO for 2 h.

When the temperature is raised to the glass-liquid transition, the signal becomes sharp and isotropic with $g_{\text{iso}} = 2.04 (\pm 0.02)$ and $\Delta H_{\text{pp}} = 11 (\pm 1) \text{ G}$. There are no hyperfine couplings with H, P and magnetically active Os isotopes; this could indicate that the added electron in $[\mathbf{1}^*]^-$ is highly delocalized. Interestingly, in the case of $[\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}]^-$, the EPR spectrum [3] exhibits a hyperfine structure, indicating that the unpaired electron interacts with the two hydrides and then occupies a LUMO having “Os–H₂–Os” character [3].

When CO was bubbled at room temperature through an acetonitrile solution of **1** in the electrochemical cell there was a change in colour from green to yellow, and IR monitoring indicated that after 2 h $[\text{Os}_3(\text{H})(\text{CO})_9(\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4)]$ (**2**) had been quantitatively formed [4]. Also the CV responses changed during the $\mathbf{1} + \text{CO} \rightarrow \mathbf{2}$ transformation; a new peak, D, grew at a more negative potential, $E_p(\text{D}) = -1.60 \text{ V}$ at 200 mV s^{-1} , followed in the reverse scan by small peaks probably due to the reoxidation processes of electrogenerated fragments. Comparison of the heights of peaks A and D indicates that **2** undergoes a chemically irreversible one-electron reduction (Fig. 3). This is even clearer from a comparison of the dc polarograms recorded on a solution of **1** before and after addition of CO.

Finally, stirring of an acetonitrile solution of **2** under CO atmosphere for a week at room temperature gradually but completely [4], converted the yellow cluster **2** into the orange $\text{Os}_3(\text{CO})_{10}(\text{dppm})$ cluster (**3**). The CV response showed a new peak E ($E_p(\text{E}) = -1.71 \text{ V}$ at 200 mV s^{-1}) followed in the reverse scan by small reoxidation peaks of the fragmentation products. Comparison of the peak heights recorded on the same solution before and after the $\mathbf{1} + 2\text{CO} \rightarrow \mathbf{3}$ transformation (peaks A and E respectively) indicates that peak E corresponds to a chemically irreversible two-electron reduction process [8*] (Fig. 4), probably a complex ECE process, as elegantly demonstrated by Robinson et al. [9] for $\text{Os}_3(\text{CO})_{12}$. The negative shift of potential on passing from $\text{Os}_3(\text{CO})_{12}$ [9] to $\text{Os}_3(\text{CO})_{10}(\text{dppm})$ is

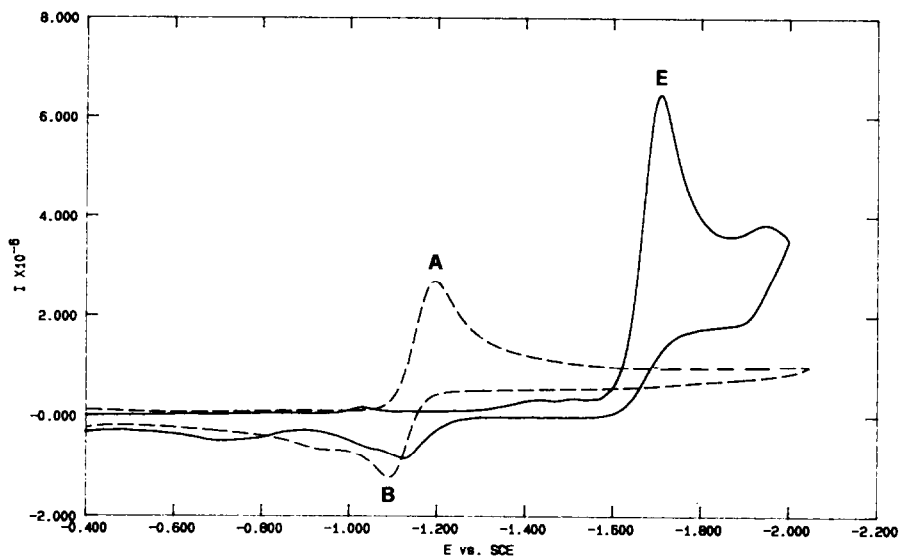


Fig. 4. Cyclic voltammograms of an acetonitrile solution of **1** at 200 mV s^{-1} recorded before (dotted line) and after (bold line) stirring under a CO atmosphere for 1 week.

consistent with the higher σ donor/ π acceptor ratio of diphosphines relative to that to of the CO ligand [10]. It is noteworthy that the cluster $\text{Os}_3(\text{CO})_{10}(\text{PPh}_3)_2$ could not be reduced within the CH_2Cl_2 solvent range [9].

The work has shown that the CV technique can be used to monitor the stepwise sequence $1 \rightarrow 2 \rightarrow 3$.

Experimental section

The compound $[\text{Os}_3(\text{H})(\text{CO})_8(\text{Ph}_2\text{PCH}_2\text{P}(\text{Ph})\text{C}_6\text{H}_4)]$ **1** was synthesized as previously described [4], and its purity and that of its CO adducts **2** and **3** was confirmed by IR and ^1H - and ^{31}P -NMR spectroscopy on a Perkin Elmer 580 B and a Jeol GX-270 spectrometer, respectively.

The EPR spectra were recorded on a Bruker 200 D-SCR instrument operating at 9.78 GHz (X-band) and equipped with a variable-temperature ER 411 VT unit.

The electrochemical apparatus for voltammetric and polarographic measurements has been previously described [3]. The solvents, supporting electrolytes, and gases (Ar or CO) were purified by established procedures [3]. All potentials are referred to the saturated calomel electrode (SCE). Ferrocene was used as an internal standard; under the experimental conditions used the $\text{FcCp}^{0/1+}$ couple is located at +0.38 in CH_3CN , +0.51 in CH_3COCH_3 , and +0.49 V vs. SCE in CH_2Cl_2 respectively.

Before running CV and dc polarographic experiments in the coordinating CH_3CN solvent we confirmed that **1** is inert in such a medium. Stirring of **1** in CH_3CN at room temperature for 1 week caused no change in the IR and ^{31}P -NMR spectra, indicating that no adduct of **1** with CH_3CN is formed.

The CO was saturated with CH_3CN before being bubbled into the electrochemical cell; this prevents removal of the solvent and subsequent change in the concentration in the solution under study.

Acknowledgments

We thank the Consiglio nazionale delle Ricerche (CNR, Rome), the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (MURST, Rome), and the SERC for financial support. We also thank Johnson Matthey Ltd. for a generous loan of OsO₄, P.A. Loveday (University Chemical Laboratory, Cambridge, U.K.) for a high-pressure synthesis of Os₃(CO)₁₂, and Dr. F. Laschi (University of Siena) for recording the EPR spectra. M.R. thanks the Associazione Sviluppo Piemonte (ASP, Turin) for a fellowship.

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- 6 We use the convention that E represents a heterogeneous electron transfer and C a homogeneous chemical reaction. We note that C may be an intramolecular rearrangement.
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