

Redox Behavior of the Electronically Unsaturated Clusters $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9\text{L}$ and Their Saturated Congeners $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}\text{L}$ (L = CO, PPh_3 , AsPh_3)

Domenico Osella,* Edison Stein, and Carlo Nervi

*Dipartimento di Chimica Inorganica, Chimica Fisica e Chimica dei Materiali,
 Via P. Giuria 7, 10125 Torino, Italy*

Piero Zanello, Franco Laschi, and Arnaldo Cinquantini

*Dipartimento di Chimica dell'Università di Siena,
 Pian dei Mantellini 44, 53100 Siena, Italy*

Edward Rosenberg

Department of Chemistry, California State University, Northridge, California 91330

Jan Fiedler

*J. Heyrovsky Institute of Physical Chemistry and Electrochemistry,
 Czechoslovak Academy of Sciences, 18223 Prague, Czechoslovakia*

Received August 6, 1990

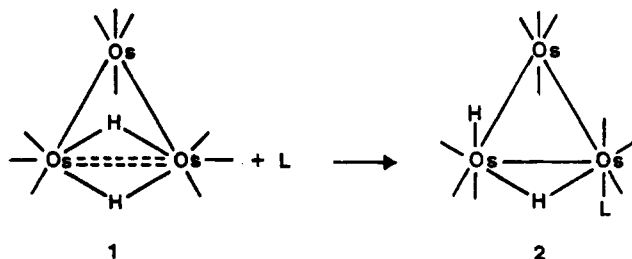
The 46 e cluster $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ exhibits a very complex redox behavior. Its cyclic voltammetric (CV) response consists of two reduction peaks, the latter having an adsorption character. Polarographic, coulometric, and spectroscopic data indicate that the initially electrogenerated monoanion $[\text{Os}_3\text{H}_2(\text{CO})_{10}]^-$ undergoes several chemical side reactions, one being an irreversible cluster breakdown and the others being dimerization reactions. The adducts $\text{Os}_3(\text{H})(\mu\text{-H})(\text{CO})_{10}\text{L}$ with Lewis bases (L = CO, PPh_3 , AsPh_3) exhibit a single 2e, chemically irreversible reduction process at more negative potentials than $\text{Os}_3\text{H}_2(\text{CO})_{10}$. Their electrochemical behavior is similar to that of the saturated cluster $\text{Os}_3(\text{CO})_{12}$. Elimination of one CO on thermolysis produces $\text{Os}_3\text{H}_2(\text{CO})_9\text{L}$ (L = PPh_3 , AsPh_3) where the unsaturated system Os-H₂-Os is restored; accordingly its CV response is very similar to that of the parent compound, $\text{Os}_3\text{H}_2(\text{CO})_{10}$.

Introduction

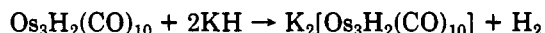
The cluster $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ (1) has been shown to contain a triangular array of three osmium atoms with ten terminally bonded carbonyls and two hydrides bridging the shortest Os-Os edge.¹ The cluster possesses 46 e, two fewer than the 48 e required by the EAN rule and usually found in triangular clusters of the iron triad. Several approaches have been utilized to rationalize the unusual bonding scheme in 1; in particular Churchill et al.^{1a} described the Os-H₂-Os core in terms of a doubly protonated double bond, and Broach and Williams^{1d} described it in terms of a four-center, 4e bond. Finally, Sherwood and Hall^{1e} confirmed that the major part of the bonding in the Os-H₂-Os system is composed of two three-center, 2e bonds, as in diborane with an additional "t_{2g}-t_{2g}" bonding interaction. Indeed, 1 does behave as an electron-deficient compound: its typical reactivity consists of nucleophilic addition of Lewis bases L (phosphines, phosphites, arsines, stibines, CO, nitriles, isonitriles, halides, etc.)² to form the 1:1 adducts $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}\text{L}$ (2) having the 48e closed-shell configuration (Scheme I).

On the basis of spectroscopic studies, all of these adducts have been proposed to contain one bridging and one terminal hydride;^{2,3} X-ray crystallographic determinations

Scheme I



have confirmed this hypothesis by direct location of such ligands in $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(\text{PPh}_3)$ ⁴ and by inference from the ligand geometries in $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{11}$ ⁵ and $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(t\text{-BuNC})$.⁶ Surprisingly, to our knowledge, no electrochemical investigations on 1 have been carried out so far, aimed at verifying this electronic unsaturation. However, Shore et al.,⁷ in a detailed study of the syntheses of anionic derivatives of 1, have reported the preparation of the salt $\text{K}_2[\text{Os}_3\text{H}_2(\text{CO})_{10}]$, obtained by reaction of 1 with excess of KH in THF:



Results and Discussion

Electrochemistry of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ (1). Figure 1 shows the cyclic voltammetric responses at different scan rates of an acetone solution of 1 at a Hg electrode and at

(1) (a) Churchill, M. R.; Hollander, F. J.; Hutchinson, J. P. *Inorg. Chem.* 1977, 16, 2697. (b) Allen, V. F.; Mason, R.; Hitchcock, P. B. *J. Organomet. Chem.* 1977, 140, 297. (c) Orpen, A. G.; Rivera, A. V.; Bryan, E. G.; Pippard, D.; Sheldrick, G. M.; Rouse, K. D. *J. Chem. Soc., Chem. Commun.* 1978, 723. (d) Broach, R. W.; Williams, J. M. *Inorg. Chem.* 1979, 18, 314. (e) Sherwood, D. E.; Hall, M. B. *Inorg. Chem.* 1982, 21, 3458.

(2) (a) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* 1975, 88, C21. (b) Shapley, J. R.; Keister, J. B.; Churchill, M. R.; DeBoer, B. G. *J. Am. Chem. Soc.* 1975, 97, 4145. (c) Deeming, A. J.; Hasso, S. *J. Organomet. Chem.* 1976, 114, 313.

(3) (a) Aime, S.; Osella, D.; Milone, L.; Rosenberg, E. *J. Organomet. Chem.* 1981, 213, 207. (b) Keister, J. B.; Shapley, J. R. *Inorg. Chem.* 1982, 21, 3304.

(4) Churchill, M. R.; DeBoer, B. G. *Inorg. Chem.* 1977, 16, 2397. (5) Churchill, R. M.; DeBoer, B. G. *Inorg. Chem.* 1977, 16, 878. (6) Adams, R. D.; Golembeski, N. M. *Inorg. Chem.* 1979, 18, 1909. (7) Kennedy, S.; Alexander, J. J.; Shore, S. G. *J. Organomet. Chem.* 1981, 219, 385.

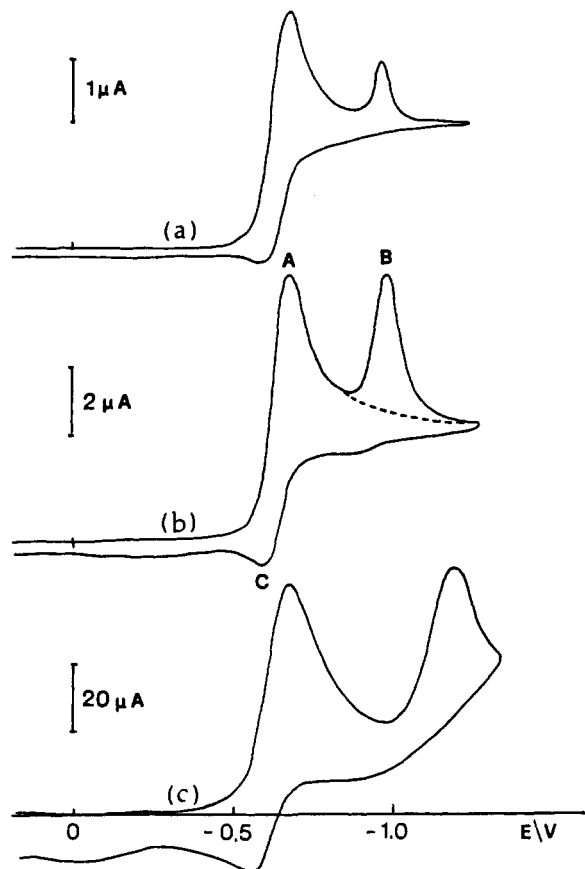


Figure 1. Cyclic voltammograms recorded at different scan rates on an acetone solution containing **1** (1.0×10^{-3} M) and $[\text{NEt}_4][\text{ClO}_4]$ (0.1 M) at a Hg working electrode, temperature 20 °C: (a) 50, (b) 200, (c) 25000 mV s^{-1} .

ambient temperature. Two cathodic peaks are observed, A and B, respectively, only the former exhibiting a directly associated reoxidation process (peak C).

While the first peak A behaves as diffusion-controlled, the character of peak B is dependent on the concentration of **1** and on the scan rate. The $i_p(\text{B})/i_p(\text{A})$ ratio increases as the concentration of **1** decreases as well as the scan rate, ν , increases, since $i_p(\text{A})$ is proportional to $\nu^{1/2}$, as expected.^{8,9} These features and its shape (a sort of spike over the current decay curve; see Figure 1b) indicate that peak B has an adsorption character. Surprisingly, at very high scan rates the adsorption phenomena seem to vanish and the current-potential response assumes the character of an electrochemically irreversible reduction process (Figure 1c).

Controlled-potential coulometry performed at the voltage associated with peak A ($E_w = -0.75$ V) consumes 1 e/molecule. Inspection of Figure 1 indicates that there are chemical complications following the electrogeneration of the monoanion of **1**, $[\text{1}]^-$, at peak A which decrease the height of the associated reoxidation peak C.

For a correct analysis of the peak A/C system, the potential scan has been reverted before peak B to avoid consumption of electroactive species by the irreversible process occurring at peak B and electrode fouling phenomena, which further decrease the height of peak C.

Figure 2 shows that the decomposition of $[\text{1}]^-$ can be somewhat prevented by employing high scan rates or decreasing the temperature.^{8,9} As a matter of fact, on going from 0.05 to 10.24 V s^{-1} at ambient temperature, the $i_p(\text{C})/i_p(\text{A})$ ratio gradually increases from 0.7 to 1; furthermore the ratio reaches unity at -15 °C even at a scan rate as slow as 0.05 V s^{-1} .

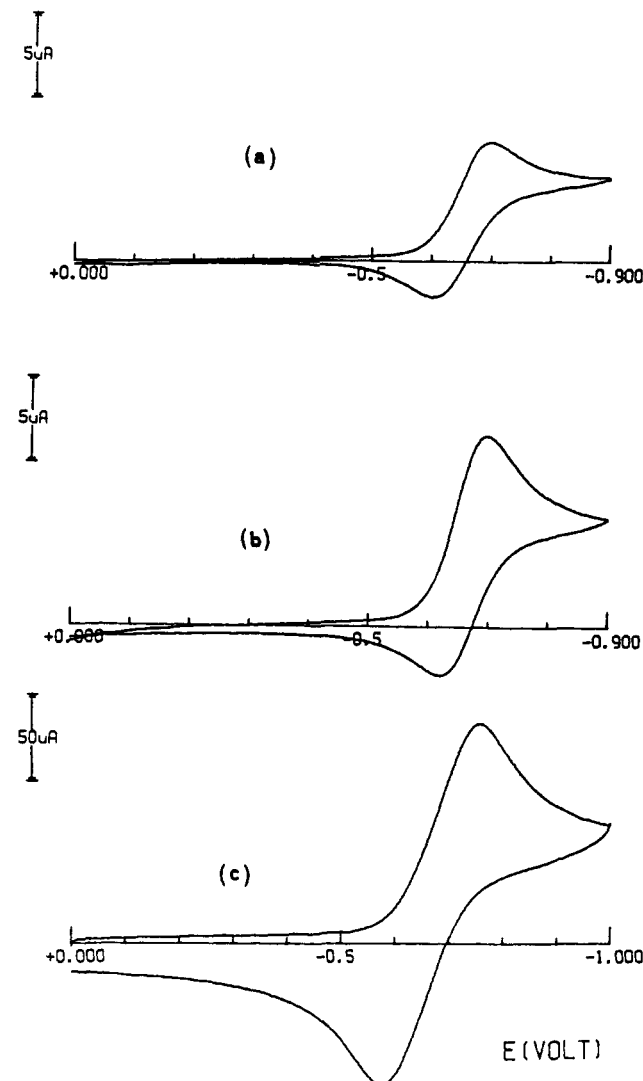


Figure 2. Cyclic voltammograms of an acetone solution of **1** recorded under different experimental conditions: (a) 0.05 V s^{-1} , -15 °C; (b) 0.05 V s^{-1} , 20 °C; (c) 5.12 V s^{-1} , 20 °C.

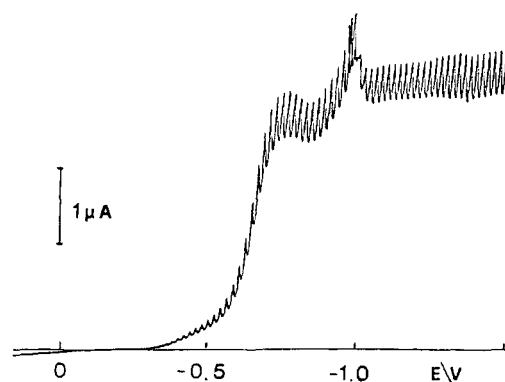


Figure 3. dc polarogram of an acetone solution of **1** (1×10^{-3} M) (drop time 2 s).

Polarography of **1** exhibits a reduction wave distorted with a polarographic maximum on the limiting current (Figure 3).

Investigation of $i-t$ curves on a single mercury drop at the potential of the maximum (-0.8 V) (Figure 4) shows that only at early stages of the mercury drop does the

(8) Heinze, J. *Angew. Chem., Int. Ed. Engl.* 1984, 23, 831.

(9) Geiger, W. E. *Prog. Inorg. Chem.* 1985, 33, 275.

Table I. Electrochemical Parameters for the Reduction Processes Undergone by the Unsaturated Clusters $\text{Os}_3(\mu\text{-H})_2(\text{CO})_{10}$ (1), $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\text{PPh}_3)$ (1b), and $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\text{AsPh}_3)$ (1c) at Room Temperature, in Different Solvents and at Different Electrodes

compd	electrode material	solvent	$E^{\circ}(0/1-)^a$, V	ΔE_p , mV	$i_p(\text{C})/i_p(\text{A})^b$	$E_p(\text{B})^c$, V
1	Pt	Me_2CO	-0.66	76	0.7	-1.13
1	Pt	CH_2Cl_2	-0.88	100	0.3	-1.15
1	Hg	Me_2CO	-0.67	72	0.8	-1.18
1	Hg	CH_2Cl_2	-0.88	97	0.3	-1.13
1	Hg	THF	-0.59	90	0.8	-1.13
1b	Hg	Me_2CO	-0.95	90	0.9	-1.19
1c	Hg	Me_2CO	-0.96	100	0.8	-1.27

^aAll potentials are vs SCE. ^bMeasured at 0.05 V/s. ^cMeasured at 0.2 V/s.

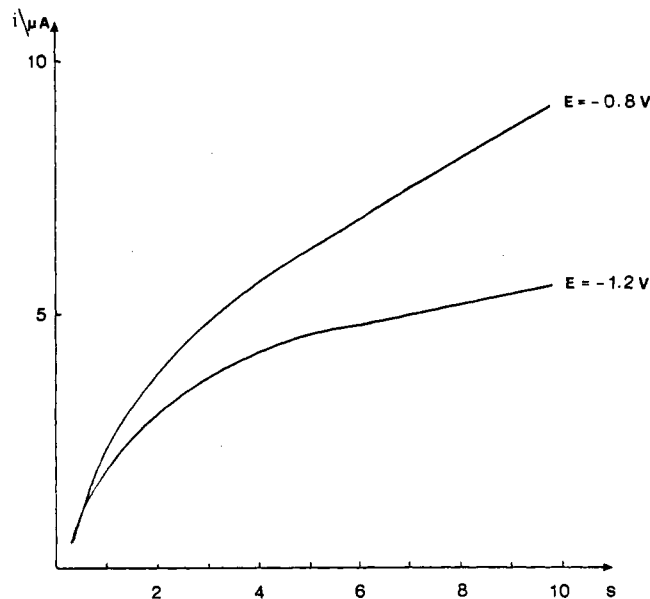


Figure 4. Current-time characteristics of an acetone solution of 1 on a single mercury drop.

current correspond to the diffusion-controlled value, then the current enhances even above the limiting i_d value, which has been recorded at more negative potential (-1.2 V).

When the polarogram is recorded with a shorter drop time, the maximum is suppressed and the polarogram consists of two close-spaced waves (Figure 5) whose $E_{1/2}$ values roughly correspond to the CV potentials. The relative height of the second wave diminishes as the drop time increases and the concentration of 1 increases, so at high concentration the second wave disappears.

In all experimental conditions, the overall height of the polarographic wave(s) does not exceed the height of the 1e oxidation wave of the ferrocene added in equimolar concentration, and hence an overall 1e reduction of two possible forms of the depolarizer 1 should be considered.

Controlled-potential coulometry at a mercury pool confirms the overall consumption of 1 faraday/mol, even if the working potential has been set at the potential corresponding to the second voltammetric peak (-1.20 V).

The change from acetone to THF does not significantly alter such a behavior (Table I); on the other hand, on passing to the less coordinating dichloromethane solvent, there is a shift of the first reduction process at a more negative potential (Table I) and the separation of peaks A and B is lessened. Unfortunately, the use of better coordinating solvents such as acetonitrile is prevented by the rapid transformation of 1 into the corresponding adduct $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(\text{NCMe})$. On the contrary, the change of the electrode material from Hg to Pt does not vary the electrode potentials, but the height of peak B becomes significantly smaller with respect to that of peak

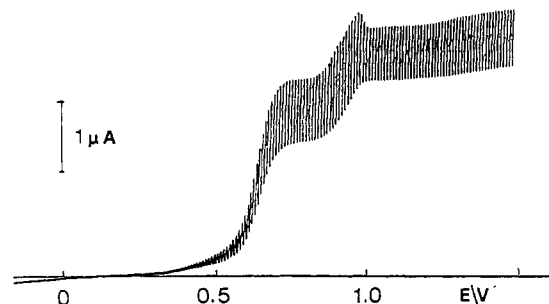


Figure 5. dc polarogram of an acetone solution of 1 (1×10^{-3} M) recorded at a drop time of 0.5 s.

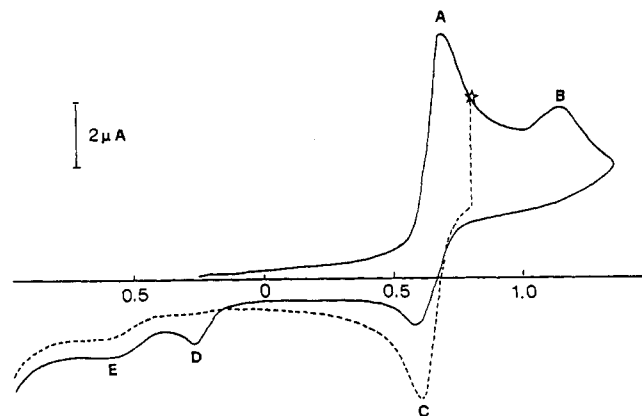


Figure 6. Cyclic voltammogram of an acetone solution of 1 at a Pt electrode, scan rate 200 mV s^{-1} .

A, possibly due to reduced adsorption phenomena. Figure 6 shows the CV response of an acetone solution of 1 at a Pt electrode where two anodic peaks, D and E, are observed in the reverse scan. Peak E corresponds to the reoxidation of the product(s) of the chemical reaction following the electrode process at peak A; peak D is connected with the process occurring at peak B. Indeed, by applying a holding time (5 s) after peak A has been traversed, the height of peak E increases; the same is true for the peak B/D system.

Controlled-potential coulometry at a Pt basket at the voltage corresponding to peak A (-0.75 V) quickly consumes 1 faraday/mol, and in situ polarographic tests indicate the full disappearance of the original reduction waves. However, if the potential of the platinum basket is turned to the voltage corresponding to peak B, a significant current flow is still observed. Since in situ polarography does not indicate any electroreducible product formed after 1e reduction of 1, the coulometric experiments suggest that a slow generation of reducible species occurs on the Pt electrode, possibly associated with $[1]^-$ decomposition (Scheme II).

In view of the reasonable stability of $[1]^-$ in acetone at subambient temperatures, we attempted its characterization by ESR spectroscopy. Figure 7 shows the X-band

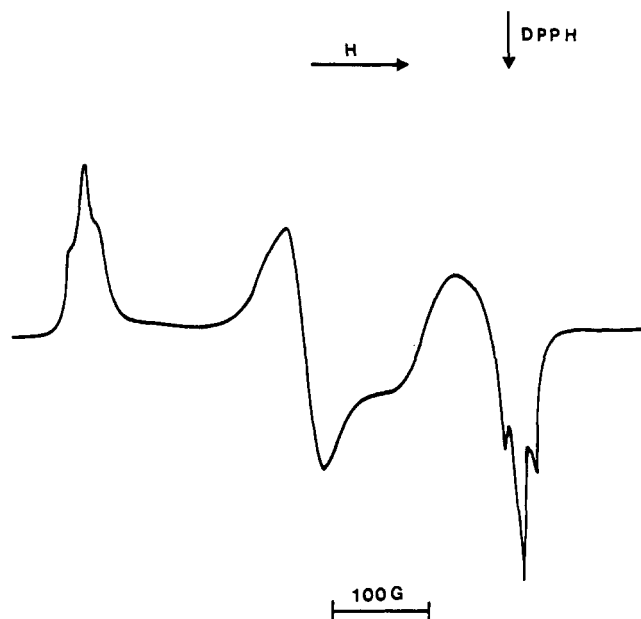
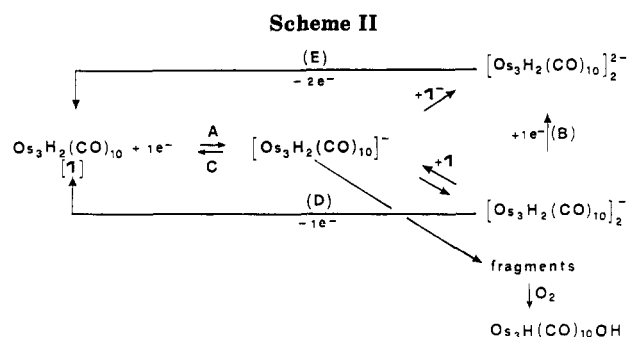


Figure 7. X-Band ESR spectrum of an acetone solution of $[1]^-$ recorded at liquid nitrogen temperature.



ESR spectrum recorded at liquid nitrogen temperature of an acetone solution of **1** after a partial electrolysis at $E_w = -0.75$ V ($0.5 e^-$ /molecule) at -20 °C.

Three absorptions, centered at $g_1 = 2.318$, $g_m = 2.145$, and $g_h = 2.001$ (± 0.005), respectively, are discernible, attributable to a rhombic pattern. The overall peak-to-peak line width, ΔH_{tot} , is 460.0 (± 0.5) G, the signal completely disappears at 180 K in correspondence to the glass-liquid transition. The two absorptions g_1 and g_h clearly indicate a 1:2:1 superhyperfine structure, which is also manifested, although with poorer resolution, for the g_m signal when analyzed in the second-derivative mode. Such an overall line shape indicates that the unpaired electron interacts with two magnetically equivalent nuclei having $I = 1/2$. The superhyperfine coupling constant values, $\langle a_1 \rangle = 14.0$ and $\langle a_h \rangle = 16.5$ G (± 1.0), strongly suggest that the interaction is mainly directed toward two equivalent hydrides. There is no evidence of satellite peaks due to ^{187}Os ($I = 1/2$) or to ^{189}Os ($I = 3/2$) nuclei. These features are consistent with the electronic structure of **1**,^{1d} where the LUMO, which should be occupied by the odd electron, has an Os- μ -H₂-Os antibonding or at least nonbonding character.

As stated above, the $1e^-$ reduction of **1**, even at -20 °C, is followed by relatively slow chemical side reactions involving the electrogenerated anion $[1]^-$. As a matter of fact, after exhaustive $1e^-$ reduction, the solution becomes ESR silent. A CV test in situ indicates the presence of a species oxidizable at the potential of peak E ($E_p \approx +0.6$ V). Interestingly, exhaustive reoxidation of the solution at E_w

$= +0.6$ V regenerates the parent compound **1** in ca. 50% yield, as verified by comparison of CV response recorded in situ on the solution before and after the reduction/oxidation sequence and by IR spectroscopy. This unambiguously indicates that the predominant complication following the first reduction is not framework destroying.

A tentative explanation of these unusual features would be the existence of several separate chemical complications following the $1e^-$ reduction of **1** at peak A (Scheme II).

The first is an irreversible cluster breakdown to fragments, the second a dimerization reaction between the parent compound **1** and its electrogenerated anion $[1]^-$ to give an adsorbed $[1-1]^-$ species, and the third the dimerization reaction of $[1]^-$ to $[1-1]^{2-}$. The two dimeric species $[1-1]^-$ and $[1-1]^{2-}$ are related to one another through the reduction process at peak B. Reoxidation of species $[1-1]^-$ and $[1-1]^{2-}$ at peaks D and E, respectively, restores the parent compound **1**. The progressive formation of the dimer $[1-1]^{2-}$ through an Os-Os bond could account for the ESR results (this species must be diamagnetic). The chemical reversibility of the overall process seems not to be consistent with the high thermal stability of the Os-Os bonds; there are, however, several examples of Os-Os bond breaking and reforming under electrochemical stimuli.¹⁰

Finally, exhaustive electrolysis at the potential of peak A ($E_w = -0.75$ V) produces a cloudy green-brown solution. After oxidation by air (O_2), the acetone is removed at reduced pressure and the residue extracted in hot benzene and chromatographed on a silica column. Apart from the parent compound **1**, several yellow bands are eluted, only one in sufficient quantity to be positively identified by IR and ^1H NMR spectroscopy as $\text{Os}_3(\mu\text{-H})(\text{CO})_{10}(\text{OH})$ (5%). Probably, $\text{Os}_3\text{H}(\text{CO})_{10}(\text{OH})$ arises from the reaction of the formally anhydrous acetone or in the silica chromatographic support. One can find a precedent in the reaction of the lightly activated cluster $\text{Os}_3(\text{CO})_{10}(\text{NCMe})_2$ with water.¹¹

Electrochemistry of $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}\text{L}$ ($\text{L} = \text{CO}$ (2a**), PPh_3 (**2b**), AsPh_3 (**2c**)).** When CO is bubbled into an acetone solution of **1**, there is an immediate change of color from violet to yellow and IR monitoring shows that $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{11}$ (**2a**) is formed quantitatively, as expected.^{2,3} The CV response of this species is totally different. A new peak appears at more negative potential (-1.63 V), completely chemically irreversible, followed in the reverse scan by small peaks due to the reoxidation of the electrogenerated fragments. Coulometry at $E_w = -1.7$ V indicates that the reduction consumes $2 e^-$ /molecule. The $2e^-$ reduction of **2a** is likely a complex ECE¹² process, as elegantly demonstrated for the isoelectronic $\text{Os}_3(\text{CO})_{12}$ cluster by Robinson et al.¹⁴ The same features hold for acetone solutions of authentic samples^{2,3} of $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(\text{PPh}_3)$ (**2b**) and $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(\text{AsPh}_3)$ (**2c**) (Figure 8).

The E_p values of the $2e^-$ reduction process became more negative due to the higher σ -donor/ π -acceptor ratio of phosphine ($E_p = -1.70$ V) and arsine ($E_p = -1.73$ V) with respect to CO (Figure 8). An internal check of the ratio

(10) Drake, S. R. *Polyhedron* 1990, 4, 455.

(11) Gard, D. R.; Brown, T. L. *J. Am. Chem. Soc.* 1982, 104, 6341.

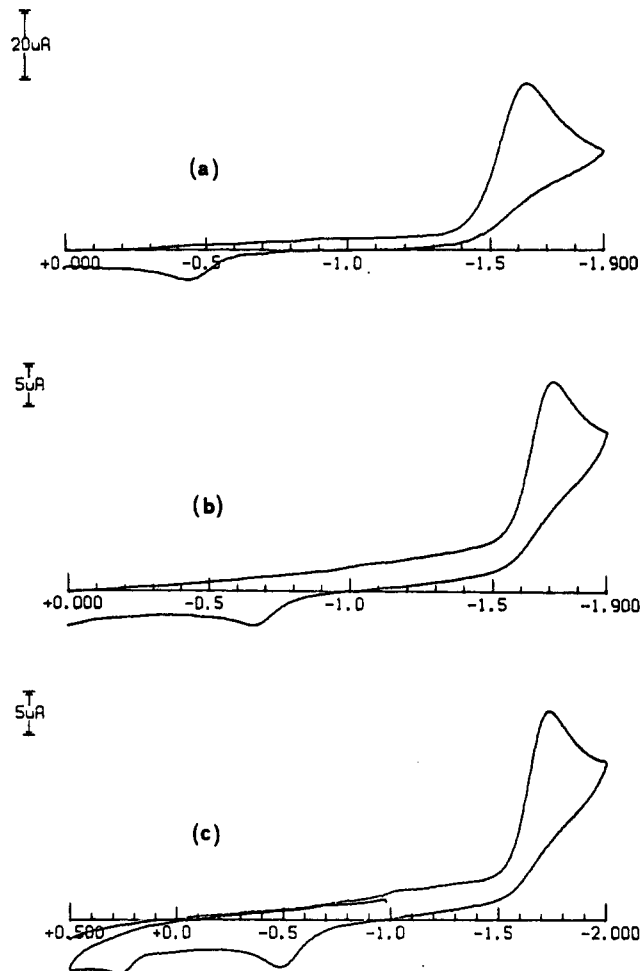
(12) We follow the nomenclature that E represents a heterogeneous electron transfer and C represents a homogeneous chemical reaction. Therefore the symbol ECE represents a stepwise process in which a redox system undergoes a $2e^-$ -transfer step with an intervening chemical reaction coupling the $2e^-$ -transfer step. We allow for the possibility that C may represent an intramolecular rearrangement.¹³

(13) Tulyathan, B.; Geiger, W. E. *J. Am. Chem. Soc.* 1985, 107, 5960.

(14) Downard, A. J.; Robinson, B. H.; Simpson, J.; Bond, A. M. *J. Organomet. Chem.* 1987, 320, 363.

Table II. X-Band ESR Parameters at Liquid Nitrogen Temperature of the Electrogenerated Monoanions $[1]^-$, $[1b]^-$, and $[1c]^-$ in Acetone Containing $[\text{NEt}_4][\text{ClO}_4]$

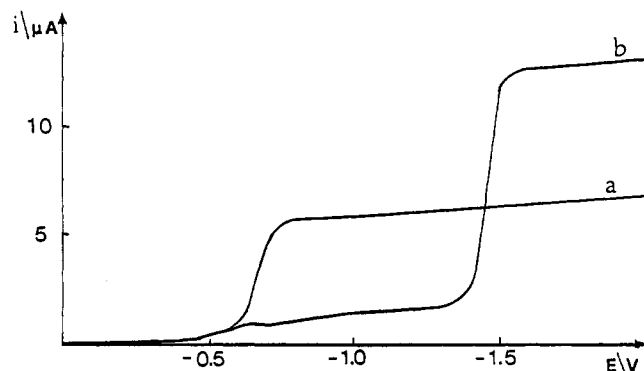
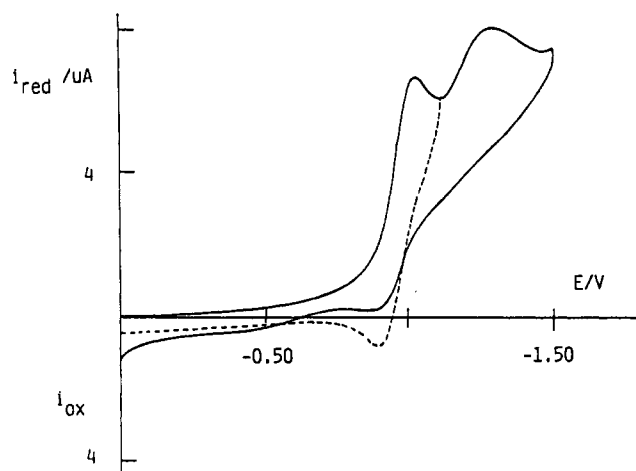
compd	g_1 (± 0.005)	$\langle a_1 \rangle$ (± 1.06)	g_m (± 0.005)	g_h (0.005)	$\langle a_h \rangle$ (± 1.06)	ΔH_{tot} , ± 0.5 G
1	2.318	14.0	2.145	2.001	16.5	460
1b	2.324	11.0	2.087	2.025	12.0	430
1c	2.314	15.0	2.183	2.006	20.0	455

**Figure 8.** Cyclic voltammograms recorded at a Pt working electrode on acetone solutions of $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{11}$ (**2a**) (a), $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(\text{PPh}_3)$ (b), and $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}(\text{AsPh}_3)$ (c), respectively (scan rate 0.2 V s^{-1}).

of the charge consumed by reduction of clusters **1** and **2b** has been obtained by the reaction of **1** with PPh_3 followed in situ by sampled dc polarography (Figure 9). The original 1e polarographic wave of **1** is converted into the 2e wave of the adduct **2b**.

Electrochemistry of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9\text{L}$ ($\text{L} = \text{PPh}_3$ (1b**), AsPh_3 (**1c**)).** Finally, it has been reported^{2a} that on heating, the adduct $\text{Os}_3\text{H}_2(\text{CO})_{10}\text{PPh}_3$ loses CO and forms $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9\text{PPh}_3$ (**1b**), which is the substituted analogue of **1**.

According to this procedure, we have prepared **1b** and the new $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9\text{AsPh}_3$ (**1c**) clusters; their CV responses are similar to that of **1** (in Figure 10 the cyclic voltammogram of **1c** is reported as an example). In acetone solvent two reduction peaks are observed with a shift of the potentials to more negative values and smaller separation in comparison with those found for **1** (Table I). Two very close polarographic waves are also obtained corresponding to the voltammetric peaks. In dichloromethane the separation of the waves is so small that there is an apparent single wave; interestingly, the logarithmic analysis of this wave provides a linear plot with a slope of

**Figure 9.** Reaction of **1** with an equimolar amount of PPh_3 in acetone followed by sampled dc polarography: (a) **1**; (b) **2b**.**Figure 10.** Cyclic voltammograms of an acetone solution of $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9(\text{AsPh}_3)$ (**1c**) (scan rate 0.2 V s^{-1}).

ca. 60 mV , as expected for a 1e reversible process. Both polarographic tests in the presence of equimolar amounts of ferrocene and coulometry experiments confirm that the overall reduction consumes 1 e/molecule. These results show that the redox behaviors of the unsaturated compounds **1**, **1b**, and **1c** are basically the same.

Although the ESR characteristics of the electrogenerated radical monoanions $[1b]^-$ and $[1c]^-$ are similar to those of $[1]^-$, there are some quantitative variations attributable to a slight distortion from rhombic to axial symmetry on passing from $[1]^-$ to its substituted congeners (Table II). This suggests that the substitution of one CO by PPh_3 or AsPh_3 affects the unpaired spin density more structurally than magnetically, i.e. the unpaired electron populates a LUMO slightly modified by the constraint imposed by the bulky ligands. No coupling with the ^{31}P or ^{75}As nuclei has been observed, although (especially for **1b**) the adsorptions are broader than those observed for the parent compound **1**.

The comparison of the electrochemical behavior of the 48e adducts $\text{Os}_3(\mu\text{-H})(\text{H})(\text{CO})_{10}\text{L}$ and of the corresponding 46e products $\text{Os}_3(\mu\text{-H})_2(\text{CO})_9\text{L}$ ($\text{L} = \text{CO}, \text{PPh}_3, \text{AsPh}_3$) confirms unambiguously that the unusual redox behaviors of the clusters **1**, **1b**, and **1c** are associated with the $\text{Os}-\mu\text{-H}_2-\text{Os}$ core.

Experimental Section

The compound $\text{Os}_3\text{H}_2(\text{CO})_{10}$ (**1**),¹⁵ the adducts $\text{Os}_3\text{H}_2(\text{CO})_{10}\text{L}$ ($\text{L} = \text{CO}$ (**2a**), PPh_3 (**2b**), AsPh_3 (**2c**)),^{2,3} and the substituted product $\text{Os}_3\text{H}_2(\text{CO})_9\text{PPh}_3$ (**1b**) were synthesized according to literature procedures and their identities confirmed by IR and ^1H NMR spectroscopy on a Perkin-Elmer 580B and a Jeol GX-270-89 spectrometer, respectively. Elemental analysis of **1c**, namely $\text{Os}_3\text{H}_2(\text{CO})_9(\text{AsPh}_3)$, has been obtained in our laboratories.

Compound **1c** has been obtained in almost quantitative yield by heating a *n*-hexane solution of **2c** at reflux for 2 h under nitrogen. Compound **1c** was crystallized from a hexane/dichloromethane (9:1) mixture.

Anal. Calcd for $\text{C}_{27}\text{H}_{17}\text{O}_9\text{AsOs}_3$: C, 28.66; H, 1.50; Os, 50.47. Found: C, 28.91; H, 1.65; Os, 50.34. IR (ν_{CO} , hexane): 2108 (m), 2070 (s), 2055 (s), 2028 (vs), 2020 (s), 2009 (s), 1999 (s), 1986 (m), 1975 (m) cm^{-1} . ^1H NMR (δ /ppm; CDCl_3): 7.50–7.39 (Ph, 15, m), –10.35 (hydrides, 2, s).

The ESR spectra were obtained from a Bruker 200 D-SCR instrument operating at 9.78 GHz (X-band) equipped with a variable-temperature ER 411 VT unit.

Voltammetric and polarographic measurements were performed with two sets of instrumentation: a PAR 273 electrochemical analyzer connected to an interfaced IBM microcomputer and a BAS 100 electrochemical analyzer.

(15) Knox, S. A. R.; Koepke, J. W.; Andrews, M. A.; Kaesz, H. D. *J. Am. Chem. Soc.* 1975, 97, 3942.

A three-electrode cell was designed to allow the tip of the reference electrode (SCE) to closely approach the working electrode. Compensation for the *iR* drop was applied through a positive-feedback device. All measurements were carried out under nitrogen in anhydrous deoxygenated solvents. Solution concentrations were 1×10^{-3} M for the compounds under study and 1×10^{-1} M for the supporting electrolyte, $[\text{Et}_4\text{N}][\text{ClO}_4]$. The temperature of the solution was kept constant (± 1 °C), by circulation of a thermostated water/ethanol mixture through a jacketed cell. The working electrode was a Pt-disk (area ca. 0.8 mm^2) or mercury dropping (DME) or hanging (HMDE) electrode. Potential data (vs SCE) were checked against the ferrocene (0/1+) couple, under the actual experimental conditions the ferrocene/ferrocenium couple is located at +0.51 in acetone and +0.49 V in dichloromethane.

The number of electrons transferred (*n*) was determined by controlled-potential coulometry at a Pt basket or at a mercury pool. The working potential (E_w) for the reduction process was 0.1 V negative of the corresponding electrode potential (E_p); all coulometric experiments were done in duplicate.

Acknowledgment. We thank the Council of National Research (CNR, Rome) for financial support, Johnson Matthey Ltd. for a generous loan of OsO_4 and P. A. Loveday (University Chemical Laboratory, Cambridge, U.K.) for high-pressure synthesis of $\text{Os}_3(\text{CO})_{12}$. E.S. thanks FAPESP (Brazil) and J.F. thanks MURST (Rome) for a fellowship.

Reactions of Molybdenum- and Tungsten-Propargyl Compounds with Iron and Ruthenium Carbonyls. Synthesis and Reactivity of Heteronuclear Metal- μ -Allenyl Complexes

George H. Young,[†] Marline V. Raphael, and Andrew Wojcicki*

Department of Chemistry, The Ohio State University, Columbus, Ohio 43210

Mario Calligaris,[‡] Giorgio Nardin, and Nevina Bresciani-Pahor

Dipartimento di Scienze Chimiche, Università di Trieste, 34127 Trieste, Italy

Received October 23, 1990

Reactions of transition-metal-propargyl complexes $\text{L}_n\text{MCH}_2\text{C}\equiv\text{CR}$ ($\text{L}_n\text{M} = (\text{CO})_3\text{CpMo}$, $\text{R} = \text{Me}$ (**1a**), Ph (**1b**); $\text{L}_n\text{M} = (\text{CO})_3\text{CpW}$, $\text{R} = \text{Me}$ (**1c**), Ph (**1d**), *p*- MeC_6H_4 (**1e**); $\text{L}_n\text{M} = (\text{CO})_3\text{Cp}'\text{W}$ ($\text{Cp}' = \eta^5\text{-C}_5\text{H}_4\text{Me}$), $\text{R} = \text{Ph}$ (**1f**), *p*- MeC_6H_4 (**1g**); $\text{L}_n\text{M} = (\text{CO})_3\text{IndW}$ ($\text{Ind} = \eta^5\text{-C}_9\text{H}_7$), $\text{R} = \text{Ph}$ (**1h**)) with $\text{Fe}_2(\text{CO})_9$ or $\text{M}'_3(\text{CO})_{12}$ provide the new heteronuclear metal- μ -allenyls $(\text{CO})_3\text{Fe}(\mu\text{-}\eta^2, \eta^3\text{-RC}=\text{C}=\text{CH}_2)\text{MCp}(\text{or Ind})(\text{CO})_2$ (**2**) and $(\text{CO})_6\text{M}'_2(\mu_3\text{-}\eta^1, \eta^2, \eta^2\text{-RC}=\text{C}=\text{CH}_2)\text{MCp}(\text{CO})_2$ ($\text{M}' = \text{Fe}$ (**3**), Ru (**4**)). These new products were characterized by a combination of elemental analysis, mass spectrometry, and IR and ^1H and ^{13}C NMR spectroscopy; the structures of **2e**, **3d**, and **4** were determined by single-crystal X-ray analysis. Crystallographic parameters are as follows: **2e** $P2_1/n$, $a = 17.259$ (5) Å, $b = 8.184$ (3) Å, $c = 26.920$ (7) Å, $\beta = 90.65$ (2)°, $Z = 8$, $R = 0.030$, $R_w = 0.038$ for 6533 independent reflections with $I > 3\sigma(I)$; **3d** $P2_1/c$, $a = 12.185$ (5) Å, $b = 12.754$ (7) Å, $c = 15.418$ (9) Å, $\beta = 111.87$ (4)°, $Z = 4$, $R = 0.029$, $R_w = 0.041$ for 4896 independent reflections with $I > 3\sigma(I)$; **4** $P2_1/n$, $a = 9.936$ (7) Å, $b = 18.98$ (2) Å, $c = 11.752$ (8) Å, $\beta = 93.12$ (6)°, $Z = 4$, $R = 0.053$, $R_w = 0.061$ for 2669 independent reflections with $I > 3\sigma(I)$. Compounds **2** represent rare examples of binuclear metal- μ - η^2, η^3 -allenyls, with **2e** featuring a remarkably sharp angle about the central allenyl carbon (128.9 (6)°). Compounds **3** and **4** are the first reported examples of heterotrinnuclear metal- $\mu_3\text{-}\eta^1, \eta^2, \eta^2$ -allenyl clusters. Reactivity of **2**–**4** toward metal framework expansion, addition of unsaturated compounds, protonation, substitution of CO, and oxidation with I_2 is presented.

Introduction

While heteronuclear metal complexes containing μ -hydrocarbyl ligands represent an important and rapidly growing class of compounds,¹ the synthetic methodology

used to prepare these compounds has not been well developed.² We have therefore investigated the use of

[†] Present address: B. F. Goodrich Research and Development Center, Brecksville, OH 44141.

[‡] To whom inquires concerning the X-ray crystallographic work should be addressed.

(1) General reviews: (a) Roberts, D. A.; Geoffroy, G. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G.; Stone, F. G. A.; Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Chapter 40. (b) Geoffroy, G. L. In *Metal Clusters in Catalysis*; Gates, B. C., Gucci, L., Knozinger, H., Eds.; Elsevier: New York, 1986; Chapter 1. (c) Vargas, M. D.; Nicholls, J. N. *Adv. Inorg. Chem. Radiochem.* 1987, 30, 123. (d) Vahrenkamp, H. *Adv. Organomet. Chem.* 1983, 22, 169.