ture of RuCl$_2$(η-C$_6$Me$_6$)(PPh$_3$) and RuHCl(η-C$_6$Me$_6$)(PPh$_3$). Other reactions of this type with various dienes have been observed and will be reported in a later paper.

Registry No. 1, 90720-51-7; 2, 90720-52-8; {Ru(η-C$_6$Me$_6$)}$_2$HCl$_3$, 90720-53-9; [{Ru(η-C$_6$Me$_6$)}$_2$HCl$_2$]PF$_6$, 90720-55-1; {(η-1,2,4,5-C$_6$H$_2$Me$_4$)}$_2$HCl$_3$, 90741-24-5; [{Ru(η-1,2,4,5-C$_6$H$_2$Me$_4$)}$_2$HCl$_2$]PF$_6$, 90720-57-3; {Ru(η-1,2,4,5-C$_6$H$_2$Me$_4$)}$_2$HBr$_3$, 90720-58-4; {Ru(η-1,3,5-C$_6$H$_3$Me$_3$)}$_2$HCl$_3$, 90720-59-5; {Ru(η-C$_6$H$_4$-1-Me-4-CHMe$_2$)}$_2$HCl$_3$, 90720-60-8; [{Ru(η-C$_6$H$_4$-1-Me-4-CHMe$_2$)}$_2$HCl$_2$]PF$_6$, 90720-62-0; {Ru(η-C$_6$H$_6$)}$_2$HCl$_3$, 90720-63-1; [{Ru(η-C$_6$Me$_6$)}$_2$H(O$_2$CCF$_3$)$_2$]H(O$_2$CCF$_3$)$_2$, 90741-25-6; [{Ru(η-C$_6$Me$_6$)}$_2$H(O$_2$CCF$_3$)$_2$]PF$_6$, 90720-65-3; [{Ru(η-1,2,4,5-C$_6$HzMe$_4$)}$_2$H(O$_2$CMe)$_2$]H(O$_2$CMe)$_2$, 90720-67-5; [{Ru(η-1,2,4,5-C$_6$H$_2$Me$_4$)}$_2$H(O$_2$CMe)$_2$]PF$_6$, 90720-68-6; [{Ru(η-1,3,5-C$_6$H$_3$Me$_3$)}$_2$H(O$_2$CMe)$_2$]PF6, 90720-70-0; [{Ru(η-C$_6$H$_4$-1-Me-4-CHMe$_2$)}$_2$H(O$_2$CMe)$_2$]PF$_6$, 90720-72-2; [{Ru(η-C$_6$H$_6$)}$_2$H-(O$_2$CMe)$_2$]PF$_6$, 90720-74-4; {Ru(η-C$_6$Me$_6$)}$_2$H(O$_2$CMe)Cl$_2$, 90720-75-5; [{Ru(η-C$_6$Me$_6$)}$_2$H(O$_2$CMe)Cl]PF$_6$, 90720-77-7; {Ru(η-C$_6$Me$_6$)}$_2$H(O$_2$CMe)Br,2, 90720-78-8; {Ru(η-C$_6$Me$_6$)}$_i$H(O$_2$CCF$_3$)-Cl$_2$·CF$_3$CO$_2$H, 90720-79-9; {Ru(η-1,2,4,5-C$_6$H$_2$Me$_4$)}$_2$H(O$_2$CMe)Cl$_2$, 90720-80-2; [{Ru(η-1,2,4,5-C$_6$H$_2$Me$_4$)}$_2$H(O$_2$CMe)Cl]PF$_6$, 90720-82-4; {Ru(η-1,2,4,5-C$_6$H$_2$Me$_4$)}$_2$H(O$_2$CMe)Br$_i$, 90720-83-5; {Ru(η-1,3,5-C$_6$H$_3$Me$_3$)}$_2$H(O$_2$CMe)Cl$_2$, 90720-84-6; [{(η-1,3,5-C$_6$H$_3$Me$_3$)}$_2$H(O$_2$CMe)Cl]PF$_6$, 90720-86-8; {Ru(η-1,3,5-C$_6$H$_3$Me$_3$)}$_2$H(O$_2$CMe)Br$_2$, 90720-87-9; {Ru(η-1,3,5-H$_3$Me)},2H-(O$_2$CCF$_3$)Cl$_2$·CF$_3$CO$_2$H, 90720-88-0; {Ru(η-C$_6$H$_4$-1-Me-4-CHMe$_2$)}$_2$H(O$_2$CMe)Cl$_2$, 90720-89-1; [{Ru(η-C$_6$H$_4$-1-Me-4-CHMe$_2$)},2H(O$_2$CMe)Cl]PF$_6$, 90720-91-5; {Ru(η-C$_6$Me$_6$)}$_2$HBr$_3$, 90720-92-6; {Ru(η-1,3,5-C$_6$H$_3$Me$_3$)}$_2$HBr$_3$, 90720-93-7; [{Ru(η-1,2,4,5-C$_6$H$_2$Me$_4$)}$_2$H(O$_2$CMe)$_2$]H(O$_2$CMe)$_2$, 90720-94-8; [{Ru(η-1,3,5-C$_6$H$_3$Me$_3$)}$_2$H(O$_2$CMe)$_2$]H(O$_2$CMe)$_2$, 90720-95-9; [{Ru(η-C$_l$H$_4$-1-Me-4-ChMe$_2$)}$_2$H(O$_2$CMe)$_2$]H(O$_2$CMe)$_2$, 90720-96-0; [{Ru(η-C$_6$Me$_6$)}$_i$H(O[2CCF$_3$)Cl]PF$_6$, 90720-98-2; {Ru(η-C$_6$H$_4$-1-Me-4-CHMe$_2$)}$_2$H(O$_2$CMe)Br$_2$, 90720-99-3; [{Ru(η-1,3,5-C$_6$H$_3$Me$_3$)}$_2$(μ–H)(μ–O$_i$CCF$_0$)$_2$]H(O$_2$CCF$_3$)$_2$, 90721-02-1; RuHCl-(η-C$_6$Me$_6$)(PPh$_3$), 75182-14-8; RuCl$_2$(η-C$_6$Me$_6$)(PPh$_3$), 82498-46-2; [RuCl(η-C$_6$Me$_6$)]$_2$, 67421-02-7; [RuCl$_2$(η-1,3,5-C$_6$H$_3$Me$_3$)]$_2$, 52462-31-4; [RuCl$_2$(η-1,2,4,5-C$_6$H$_2$Me$_4$)]$_2$, 90721-03-2; [RuCl$_2$(η-C$_6$H$_4$-1-Me-4-CHMe$_2$)]$_2$, 52462-29-0; [RuCl$_2$(η-C$_6$H$_6$)]$_2$, 37366-09-9; [RuBr$_2$(η-C$_6$Me$_6$)]$_2$, 90721-04-3; [RuBr$_2$(η-1,2,4,5-C$_6$H$_2$Me$_4$)]$_2$, 88666-26-6; [RuBr$_2$(η-1,3,5-C$_6$H$_3$Me$_3$)]$_2$, 90721-05-4; Ru-(O$_2$CMe)$_2$(η-C$_6$Me$_6$), 81062-49-9; Ru(O$_2$CMe)$_2$(η-1,2,4,5-C$_6$H$_2$Me$_4$), 90721-06-5; Ru(O$_2$CMe)$_2$(η-1,3,5-C$_6$H$_3$Me$_3$), 90721-07-6; Ru-(O$_2$CMe)$_2$(η_6H$_4$-1-Me-4-CHMe$_2$), 90721-08-7; Ru(O$_2$CMe)$_2$(η-C$_6$H$_6$), 90721-09-8; Ru(O$_2$CCF$_3$)$_2$(η-C$_6$Me$_6$), 90721-10-1; Ru(O$_2$CCF$_3$)$_2$(η-1,3,5-C$_6$H$_3$Me$_3$), 90721-11-2; Ru(O$_2$CMe)Cl(η-1,3,5-C$_H$Me$_o$), 90721-12-3; Ru(O$_2$CMe)Cl(η-1,2,4,5-C$_6$H$_2$Me$_4$), 90721-13-4; Ru-(O$_2$CMe)Cl(η-C$_6$Me$_6$), 90721-14-5; Ru(O$_2$CM))Cl(η-C$_6$H$_4$-1-Me-4-CHMe$_2$), 90721-15-6; Ru(O$_2$CMe)Cl(η-C$_6$H$_6$), 90721-16-7.

Electrochemical Investigation of a Series of Organotriruthenium Clusters

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The reduction and oxidation behavior of a series of organotriruthenium clusters, namely, HRu$_3$-(CO)$_9$(μ_3-allenyl), HRu$_3$(CO)$_9$(μ_3-allyl), and HRu$_3$(CO)$_9$ (μ_3-alkynyl) complexes, is investigated by voltammetric techniques at mercury and platinum microelectrodes. The relationships between the resulting electrode potentials and both ^{13}C NMR chemical shifts and ν(CO) frequencies are presented.

Introduction

The reactivity of carbonylmetal clusters with unsaturated hydrocarbons has been widely investigated, and a number of derivatives in which the organic substrate interacts with several metallic centers have been characterized.[1] Their interesting bonding features gave noticeable support to the view that organometal clusters can serve as useful models of chemisorbed molecules on a metallic surface.[2] In particular the triangular cluster Ru$_3$(CO)$_{12}$ reacts with alkynes[3] to afford three main types of organometallic complexes: HRu$_3$(CO)$_9$(RC=C=CR'R'')[4] (I), HRu$_3$(CO)$_9$(RC⇌CR'⇌CR'')[5] (II), and H-

Ru$_3$(CO)$_9$ (C≡C—R)[6] (III) (see Figure 1). Although their chemical reactivity has been investigated,[3] no report has been concerned with their redox behavior. The electrochemistry of carbonylmetal clusters is a matter of increasing interest,[7-13] since the redox properties should

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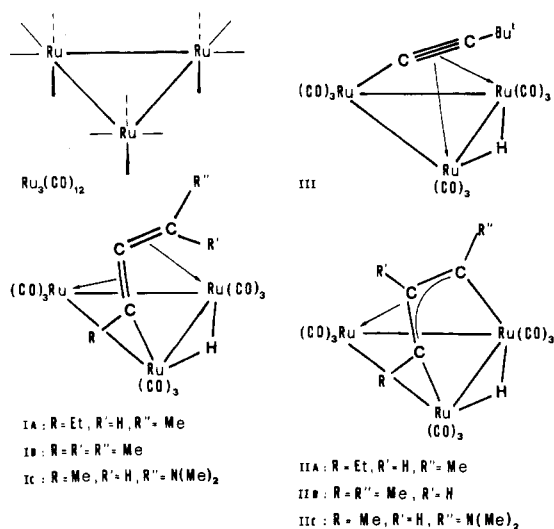(13) Baumann, J. A.; Salmon, D. J.; Wilson, S. T.; Meyer, T. J.; Hatfield, W. E. *Inorg. Chem.* 1978, 17, 3342.

Figure 1. Diagrammatic representation of the structures of $Ru_3(CO)_{12}$ and I–III clusters.

strongly influence the course and the rates of reactions. We report here an electrochemical study of a series of I–II–III type clusters.

Experimental Section

General Data. The I–II–III clusters were synthesized from $Ru_3(CO)_{12}$ and the appropriate alkyne according to the literature procedure.[3,14] After crystallization, their purity was checked by IR, ^{1}H NMR, and MS spectroscopy.

The IR spectra were recorded on a Perkin-Elmer 580 B, the ^{1}H NMR spectra on a JEOL C60-HL, and the MS spectra on a Hitachi Perkin-Elmer RMU-6H instrument.

The solvents used for electrochemical studies [acetonitrile (MeCN), dichloromethane (CH_2Cl_2), and dimethyl sulfoxide (Me_2SO)] were reagent grade products, further purified according to established procedures.[15]

Tetraethylammonium perchlorate (TEAP) supporting electrolyte (Carlo Erba) was dried in a vacuum oven at 50 °C and used without further purification.

Bis(η^5-cyclopentadienyl)iron(II) (ferrocene) (Alfa Products) was used as a standard to evaluate the number of electrons (n) involved in the electrode processes occurring in the voltammetric time scale.

Nitrogen (99.99%) was employed to remove oxygen from the tested solutions.

The electrochemical apparatus has been described elsewhere.[16] Potential values refer to a saturated aqueous calomel electrode (SCE).

All experiments were carried out at 25 ± 0.1 °C.

Electrolysis of HRu₃(CO)₉(EtC≏CH≏CMe) (IIA). IIA (200 mg) was dissolved in 40 mL of a 0.1 M TEAP–acetonitrile solution and exhaustively electrolyzed at –1.60 V vs. SCE at a mercury pool. n was 1.03. As the electrolysis proceeded, the solution changed from yellow to red-brown. The solvent was removed under reduced pressure, and the residue was soluble in MeOH, THF, and MeCN:IR (MeOH) ν(CO) 2041 (vs), 1970 (s, br), 1941 (s, br) cm⁻¹.

No analytical pure salt was isolated from these solvents. The residue was suspended in aqueous H_3PO_4 (1:3) and air passed through the suspension for 30 min.

Extraction with $CHCl_3$ in a separatory funnel gave a bright yellow solution, which was neutralized with solid $Na_2(CO)_3$ and chromatographed on silica column.

Only the yellow $Ru_2(CO)_6C_6H_8$ compound was eluted (yield ~10%): MS [M⁺], m/e 452 followed by loss of six CO's; IR (n-hexane) ν(CO) 2078 (m), 2048 (vs), 2011 (s), 1996 (m), 1979
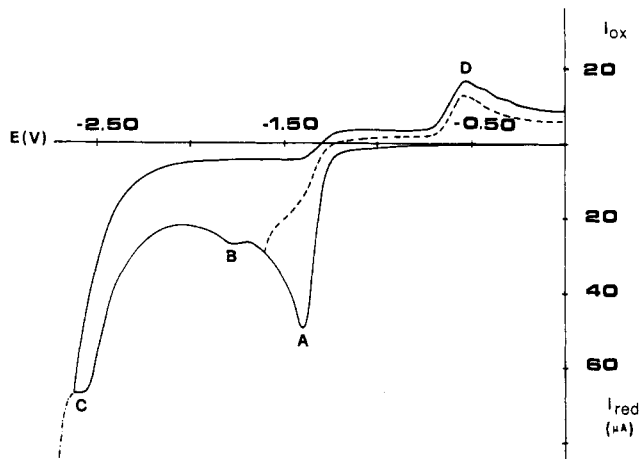

Figure 2. Cyclic voltammetric response of a MeCN solution of IIA (1.02 × 10⁻³ M) and TEAP (0.1 M) (mercury working microelectrode; scan rate = 0.2 V s⁻¹).

(m) cm⁻¹; ^{1}H NMR ($CDCl_3$) δ 6.08 (s, 2), 2.35 (s, 6).

Results

Figure 2 shows the cathodic cyclic voltammetric behavior at a mercury microelectrode of HRu₃(CO)₉(EtC≏CH≏CMe) (IIA) in acetonitrile.

A well-defined reduction peak A is observed, E_p = –1.43 V at v = 0.2 V s⁻¹, followed by a hump, peak B, at about –1.8 V and a further reduction peak, C, E_p = –2.59 V, close to the solvent discharge. The reversal of the scan direction just after the cathodic peak A is transversed leads to an anodic peak, D, E_p = –0.53 V. The analysis of the cyclic voltammetric response[17] at scan rates varying from 0.02 to 100 V s⁻¹ indicates that the process occurring at peak A, to which the reoxidation peak D is related, seems due to a charge transfer with a very low degree of reversibility. The large separation of peak A from peak D resembles that for the reduction of mononuclear and dinuclear metal carbonyls of 5B and 6B groups.[18]

In addition the peak current ratio, $i_{p(D)}/i_{p(A)}$, detectable only at scan rates greater than 0.02 V s⁻¹, increases in the range from 0.05 to 1 V s⁻¹, and then it remains constant.

These data are consistent with a process in which a rapid chemical reaction follows the formation of the primarily electrogenerated species. Peak D is attributed to the oxidation of the resulting electroactive compound (EC mechanism) or, alternatively, to the oxidation of a product resulting from a further chemical reaction (ECC mechanism). A rough evaluation of the lifetime of the species oxidized at peak D indicates a value of about 1 s.

The same cathodic picture is obtained at a platinum microelectrode, except for a shift of the peak potential of A toward more negative values (E_p = –1.50 V at v = 0.2 V s⁻¹), due to either an inner-sphere electrode mechanism[19] or the formation of mercury-stabilized intermediates at the mercury electrode surface.[20]

Both the comparison with the one-electron oxidation of ferrocene and controlled potential coulometric tests show that the reduction process occurring at peak A involves the consumption of one electron/molecule of IIA. In addition cyclic voltammetric tests on the solution of IIA electrolyzed at –1.6 V in a mercury pool do not reveal any presence of the species responsible for peak D, confirming

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Scheme I

$$(IIA) \xrightarrow[\text{peak A}]{+1e^-} (IIA)^- \xrightarrow[\text{peak B}]{+1e^-} (IIA)^{2-} \xrightarrow[\text{peak C}]{+1e^-} \text{products}$$
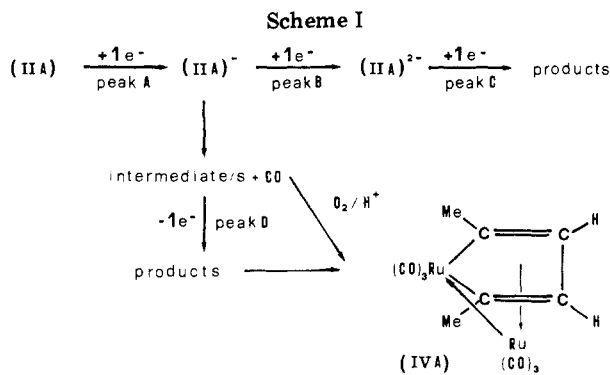
that this species undergoes a chemical reaction; the resulting products give rise to a series of oxidation processes in the range from −0.4 to +0.6 V (namely, at E_p = −0.39 and −0.13 V at mercury electrodes and at E_p = −0.35, 0.00, +0.23, and +0.55 V at platinum electrodes), as well as a reduction process at −1.95 V (at a mercury microelectrode).

A further significant feature of the cyclic voltammetric responses on a mercury microelectrode is that peak B, which appears as a hump at scan rate of 0.2 V s^{-1}, becomes more and more defined as the scan rate increases, and at 100 V s^{-1} its peak height almost equals that of peak A (at 100 V s^{-1}, $E_{p(A)}$ = −1.64 V, $E_{p(B)}$ = −1.90 V, and $i_{p(B)}/i_{p(A)}$ = 0.94). This behavior indicates that the primary one-electron-reduced species undergoes a further one-electron reduction step if chemical complications following the first charge transfer are prevented. Reaching the condition $i_{p(B)}/i_{p(A)} \simeq 1$ allows a rough estimation of the lifetime of the one-electron-reduced species electrogenerated at peak A. The results are in the order of milliseconds, suggesting that the less cathodic process occurs through an ECC electrode mechanism rather than a simple EC mechanism.

The closeness of the solvent discharge prevents any reliable voltammetric analysis of the one-electron cathodic process occurring at peak C.

It is noteworthy that the saturation of the solution of IIA with carbon monoxide leads to the same voltammetric picture as in Figure 1, with the only exception that a further anodic process appears when the potential scan is reversed after the peak A is transversed. This second anodic peak, located at +0.23 V on a platinum electrode, is coincident with one of the oxidation processes of the previously cited electrolysis product. This suggests that the decomposition of the radical anion (IIA)⁻, involving a slow CO dissociation, leads to an intermediate able to react with CO to give a stable product on the electrolysis time scale.

In order to get some insight into the nature of the intermediate, exhaustive electrolysis of IIA was carried out at the potentials of peak A. After removal of the solvent, the residue was soluble only in polar solvents, i.e., MeOH, THF, or MeCN. No attempt to crystallize the ionic intermediates in these solvents was successful. A chemical oxidation was carried out by passage of air (oxygen) through a suspension of the electrolyzed residue in aqueous H₃PO₄. Extraction with CHCl₃ afforded the sole molecular complex Ru₂(CO)₆C₆H₈ (IVA), easily identified by IR, ¹H NMR, and MS spectroscopy. This transformation as result of one-electron reduction completely parallels the thermal decomposition of type II compounds.[21] Thus the overall cathodic process of IA is shown in Scheme I.

· In acetonitrile solution IIA also undergoes an anodic process at a platinum electrode. The process gives re-
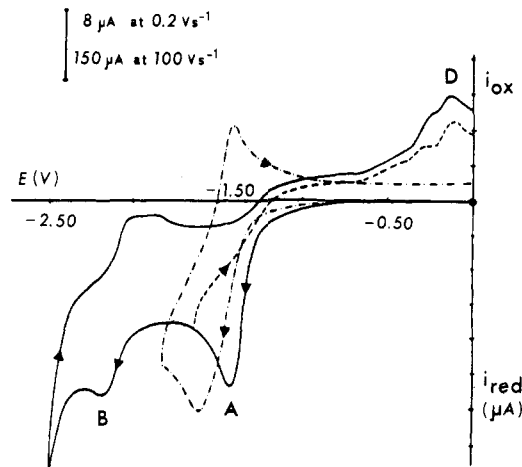

Figure 3. Cyclic voltammetric responses of a MeCN solution of IB (6.0 × 10⁻⁴ M) and TEAP (0.1 M) at 0.2 V s⁻¹ (—) and 100 V s⁻¹ (−·−), respectively (mercury working microelectrode).

producible cyclic voltammetry only if the electrodes are preconditioned each time with an anodic scan from −0.5 to +2.5 V (E_p = +1.21 V at v = 0.2 V s⁻¹).

Cyclic voltammetric tests at increasing scan rates indicate that no cathodic peak directly associated to the anodic one appears even at the highest scan rates. The comparison with the one-electron oxidation of ferrocene and the trend of the current function $i_p/v^{1/2}$ show that in the overall electrode reaction a chemical reaction is interposed between two one-electron charge transfers (ECE mechanism).

The need for a fresh conditioning of the electrode surface, suggesting the occurrence of electrode poisoning phenomena, discouraged us to perform macroelectrolysis experiments.

The only significant observation is that the monocation (IIA)⁺, as the monoanion (IIA)⁻, is totally unstable in these experimental conditions.

The change of solvent from MeCN to CH₂Cl₂ causes no substantial variation in the electrochemical behavior of IIA. On the contrary the use of Me₂SO involves such a change (one cathodic process at −2.0 V and one anodic process at +0.35 V), we think that the high polarity of this solvent causes a marked decomposition of the cluster; similar declusterification processes were noted to occur when trinuclear iron carbonyls were dissolved in polar solvents.[12]

The electrochemistry of the remaining I–II–III compounds is similar to that reported for IIA; however, some interesting differences can be pointed out. For IA, IB, IIB, and III clusters the one-electron-reduced species seems more stable, in that its reoxidation peak is detectable at least at the highest scan rates. Figure 3 reports as a typical example the cyclic voltammetric responses from IB at two extremely different potential scan rates. This behavior gives further information on the nature of the charge transfer involved in the ECC mechanism previously discussed: it results quasi-reversible in character. The lack of a directly associated reoxidation peak to peak A of IIA is likely due to the instability of its radical anion rather than to a very low value of the rate constant for the heterogeneous electron-transfer process k_s. For instance in the case of IB, where at 100 V s⁻¹ the peak-to-peak separation is about 220 mV and the anodic to cathodic peak current ratio reaches unity, a k_s value of 3.5 × 10⁻² cm s⁻¹ has been computed,[22] under the usual assumptions that α = 0.5 and $D_O = D_R = D = 10^{-5}$ cm² s⁻¹.

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Table I. Significant Electrochemical Parameters for Ruthenium Clusters in MeCN Solvent[a]

| | one-electron reduction | | | | further reductn steps | | oxidatn |
	E_p(Hg)	$E_{1/2}{}^r$	$t_{1/2}$	E_p(Pt)	E'_p(Hg)	E''_p(Hg)	E_p (Pt)
Ru$_3$(CO)$_{12}$	−1.05			−1.29	−2.13		+1.09
IA	−1.53	−1.56	16	−1.57	−1.98	−2.20	+1.25
IB	−1.46	−1.54	24	−1.59	−2.18		+1.19
IC	−1.46			−1.75			+0.75
IIA	−1.43		~3	−1.55	−1.80	−2.59	+1.21
IIB	−1.40		~3	−1.56	−1.83		+1.20
IIC	−1.59			−1.78	−1.80	−2.58	+0.95
III	−1.51	−1.60	9	−1.63	−2.26		+1.19

[a] Potential values in V vs. SCE; peak potential values (E_p) refer to 0.2 V s^{-1}; lifetimes $(t_{1/2})$ in ms refer to electro-generated monoanions.

Table II. Spectroscopic Data (^{13}C NMR and IR) of Organoruthenium Clusters

no.	compd	^{13}(CO) (wtd av), ppm	"totally symmetric" ν(CO), cm^{-1}	ref
	Ru$_3$(CO)$_{12}$	198.0		29
IA	HRu$_3$(CO)$_9$(EtC=C=CHMe)	193.8	2094	30
IB	HRu$_3$(CO)$_9$(MeC=C=CMe$_2$)	194.4	2094	31
IC	HRu$_3$(CO)$_9$(MeC=C=CHNMe$_2$)	197.0	2083	32
IIA	HRu$_3$(CO)$_9$(EtC–CH–CMe)	194.5	2097	30
IIB	HRu$_3$(CO)$_9$(MeC–CH–CMe)	194.5	2095	30
IIC	HRu$_3$(CO)$_9$(MeC–CH–CNMe$_2$)	195.5	2089	32
III	HRu$_3$(CO)$_9$(C—C≡Bu)	189.5		29

In those cases where the use of high scan rates allowed us to overcome the chemical complications coupled to the one-electron reduction process, i.e., the obtainment of an anodic to cathodic peak current ratio equal to unity, it was possible to estimate the reversible half-wave potential, $E_{1/2}{}^r$, for the redox couple cluster/anion from the average of cathodic and anodic peak potentials, in the hypothesis that the transfer coefficient α ranges from 0.3 to 0.7. Furthermore an approximate calculation of the half-life of the radical anion comes from the anodic to cathodic peak current ratio, assuming an irreversible first-order reaction to follow the one-electron charge transfer.[23,24] All these findings are summarized in Table I.

Discussion

The formation of I–II–III clusters occurs through an oxidative addition of the alkyne to Ru$_3$(CO)$_{12}$ with cleavage of a C–H bond.[3] The transferred hydrogen bridges two metal atoms while the organic chain substitutes three axial CO and acts as an overall five-electron donor, rearranging as a μ_3-η^3-allenyl in I, a μ_3-η^3-allyl in II, and a μ_3-η^2-alkynyl group in III (see Figure 1). Structural determinations have pointed out very similar geometries for I[4] and II,[5] so explaining the easy isomerization I → II by thermal activation (when R′ = H).[25] In electrochemical terms this substitution of a large organic chain for CO's results in an increase of the redox range: both reduction and oxidation processes become more difficult (i.e., the electrode potentials for reduction become more negative and the electrode potentials for oxidation more positive than those measured for the parent cluster Ru$_3$(CO)$_{12}$ under the same experimental conditions). This finding agrees with the electrochemical behavior of transition-metal complexes with π-electron-delocalized systems.[24]

Interestingly the lifetimes of all the radical anions electrogenerated from I–II–III clusters were qualitatively longer on the electrochemical time scale than that of Ru$_3$(CO)$_{12}$, indicating that the capping organic chains favor

the retention of cluster framework on reduction. A similar effect, with a much higher efficiency, was found for the methylidine capping groups in the Co$_3$(CO)$_9$CX series.[26] A similar capability of the allyl chain for cluster retention has been recently found in the photochemical behavior of the IIA derivative.[27]

The class of clusters IA, IB, IIA, and IIB, in which the organic chain bears aliphatic substituents (R, R′, R″ being H or Me, or Et) shows very similar electrode potentials (+1.19 to +1.25 V for oxidation; −1.55 to −1.63 V for reduction, at a platinum microelectrode). On the contrary, the presence of the dimethylamino group in IC and IIC lowers the range of oxidation potentials (+0.75 to +0.95 V) and increases the range of reduction potentials (−1.75 to −1.78 V). This finding unambiguously indicates a higher electron density in the metallic framework, arising from a π donation from the NMe$_2$ group. This is in agreement with the high barrier to rotation about the C–NMe$_2$ bond previously reported for IC and IIC compounds.[14] Thus a zwitterionic representation of IC and IIC might be more realistic than those given in Figure 1. This point will be more precisely assessed by a X-ray structure determination, which is currently underway.

The energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) correspond approximately to the energy involved in removing to an infinite distance and adding from an infinite distance an electron to the molecule, respectively. In electrochemical terms these HOMO and LUMO energies determine the electrode potential values for oxidation and reduction, provided that the free energies of solvation during the process remain constant and this is probably true for a series of isostructural compounds. Indeed, Fenske found that the $E_{1/2}$ values for oxidation of [Mn(CO)$_{6-n}$(CNMe)$_n$]$^+$ complexes fit very well with the calculated HOMO energies.[28] Unfortunately these theoretical parameters are at present not available for large organometallic molecules.

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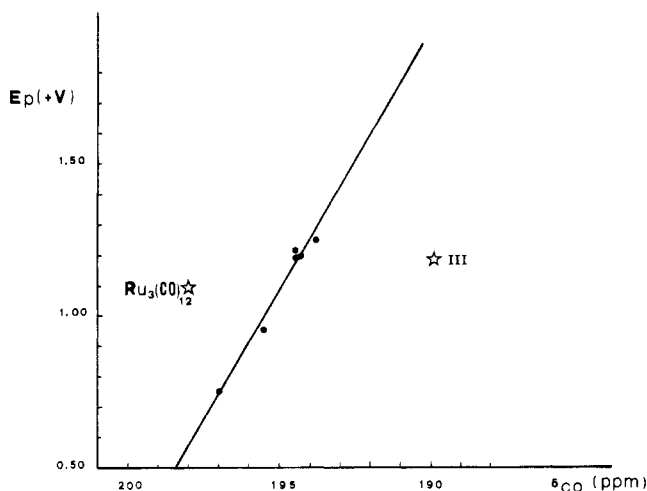(28) Sarapu, A. C.; Fenske, R. F. *Inorg. Chem.* **1975**, *14*, 247.

Figure 4. Plot of E_p (at platinum electrode, V vs. SCE) for oxidation of organoruthenium clusters against $\delta(^{13}C)$ (weighted average) of CO groups. The least-squares slope, drawn only through I–II derivatives (see text), is 0.17 V ppm⁻¹, with an intercept (x axis) of 198.4 ppm. The correlation coefficient is 0.98.

In order to verify if any correlation holds, in terms of the free energy relationship, between these electrochemical and other spectroscopic data, we collected in Table II the weighted average ^{13}C NMR chemical shifts of CO ligands in the compounds studied as well as their highest $\nu(CO)$ ("totally symmetric") bands.

The correlation between NMR and electrochemical data has been elegantly discussed by Bond et al. and applied to a series of mononuclear chromium complexes.[9] Although the origin of the ^{13}C chemical shift in organometallic compounds is not completely understood, within a series of isostructural complexes the variation of chemical shifts should arise from changes in the paramagnetic contribution (σ_p), which in turn is dominated by the average difference in energy (ΔE) between ground and excited states. Thus a linear correlation between electrode potentials and the ^{13}C chemical shift is expected only when both these parameters are governed by electronic effects, which affect the ΔE term, and gross geometrical changes are avoided. In order to treat a significant set of data, peak potential values (E_p) at a platinum electrode have been used instead of formal electrode potentials ($E_{1/2}{}^r$) in the likely hypothesis that all the studied compounds undergo charge transfers with the same degree of reversibility.

In Figure 4 the electrode potentials for oxidation of the title organoruthenium clusters are plotted against $\delta(^{13}C)$ values. The correlation is excellent for the structurally similar I–II clusters, while $Ru_3(CO)_{12}$ and III clearly lie beyond any reasonable relationship. The same trend, although with a minor correlation coefficient, has been found for reduction potentials, as shown in Figure 5. Thus
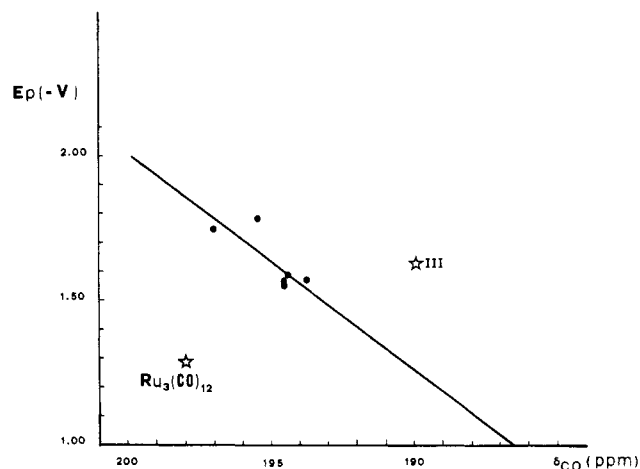
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Figure 5. Plot of Ep (at platinum electrode, V vs. SCE) for reduction of organoruthenium clusters against $\delta(^{13}C)$ of CO groups. The least-squares slope, drawn only through I–II derivatives (see text) is 0.08 V ppm⁻¹, with an intercept (x axis) of 186.5 ppm. The correlation coefficient is 0.83.
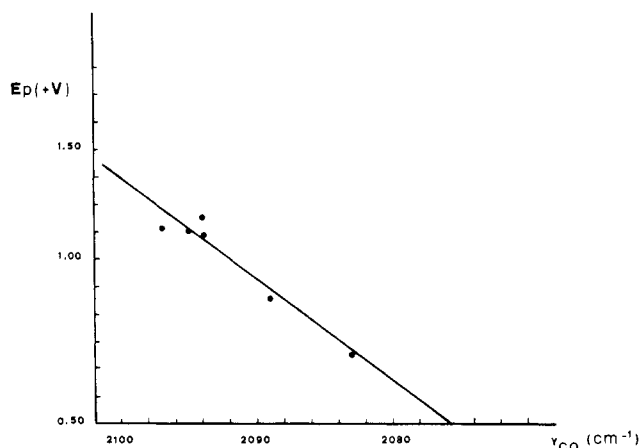

Figure 6. Plot of E_p (at platinum electrode, V vs. SCE) for oxidation of I–II derivatives against "totally symmetric" $\nu(CO)$ frequencies. The least-squares slope is 0.04 V cm, with an intercept (x axis) of 2078 cm⁻¹. The correlation coefficient is 0.97.

the correlation between electrochemical data and $\delta(^{13}C)$, found for the structurally similar allenyl and allyl clusters, seems to confirm that the ^{13}C shielding of CO's is dominated by electronic effects through σ_p also in large organometallic molecules.

Within the class of I–II clusters, the relationship between oxidation potentials and the "totally symmetric" $\nu(CO)$ bands is much more straightforward as the later set is related to the electron density in the metallic framework. In Figure 6 the oxidation potentials are plotted against the highest CO stretching frequencies and the correlation is indeed good.