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Electronic interactions in multicluster arrays. An electrochemical approach. Part III*

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Abstract

The electrochemical reduction of *triangulo*-dodecacarbonyl triruthenium, $Ru_3(CO)_{12}$, is re-investigated in strictly controlled experimental conditions and corresponds to an EC mechanism. $Ru_3(CO)_{12}$ undergoes a primary one-electron reduction process followed by a set of surface chemical reactions all producing electroactive species, giving rise to apparent stoichiometry of the overall reduction process (n_{app}) between 1 and 2, depending on the concentration of depolarizer. Competition between solvent-assisted dissociation, disproportionation and redox condensation is assumed. The μ-bridged derivative $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$, (dppa = bis(diphenylphosphino)acetylene, $Ph_2PC{\equiv}CPPh_2$) is reduced in one two-electron step followed by chemical decomposition reaction generating the 'dangling' complexes $Ru_3(CO)_{11}(\eta^1\text{-dppa})$ and $[Ru_3(CO)_{11}]^{2-}$. The electrochemical behaviour of $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$ indicates no electrochemically detectable interaction between the two $Ru_3(CO)_{11}$ redox units in the dimer, but a deeper evaluation of the electronic communication through the dppa bridge is hindered by the following fast chemical complications.

Introduction

There is uprising interest in mixed-valence compounds [2] because of the opportunity for new conducting, magnetic and optical properties to be developed [3]. Polydentate organic ligands having delocalized π systems can efficiently act as electronic bridges between adjacent transition metal centres [4]. Organometallic compounds are suitable for producing mixed-valence materials because of their propensity to: (i) adopt a wide range of valence states, (ii) have redox potentials tuneable by the electronic properties of ancillary ligands, (iii) often undergo electrochemically and chemically reversible electron transfer reactions, (iv) be easily linked by polydentate ligands to form polymers [5]. Robinson and co-workers have studied in great detail a number of such ligand-linked clusters [6]. In principle, the electrochemical techniques in solution are able to reveal moderate to strong electronic interactions between the redox centres and then to forecast the possibility to generate mixed-valence compounds in solution and the conducting properties of the corresponding solid materials [7].

We have previously chosen for such investigations on the electronic interactions dyines as the bridging ligands between two tri-metallic clusters [1]. Indeed, the σ/π coordination of the polymetallic moieties to the acetylenic 'arms' of the bridging ligand is generally able to guarantee some degree of electronic interaction between the two polymetallic redox centres.

In this paper we report the electrochemical investigation of $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$ (dppa = bis(diphenylphosphino)acetylene, $Ph_2PC{\equiv}CPPh_2$) (Fig. 1). Several reports have dealt with diphosphines as the bridging ligands between clusters [8]. Moreover, the electrochemical behaviour of the dimer $[RCCo_3(CO)_8]_2(dppe)$ (R = Me,Ph; dppe = bis(diphenylphosphino)ethane, $Ph_2PCH_2CH_2PPh_2$), has been studied in detail by Robinson and co-workers [9]: although the *i–E* responses are complicated by subsequent fast chemical reactions, the authors concluded that there is no interaction in the electrochemical sense between the two redox clusters. This result is not unexpected since the two $RCCo_3$

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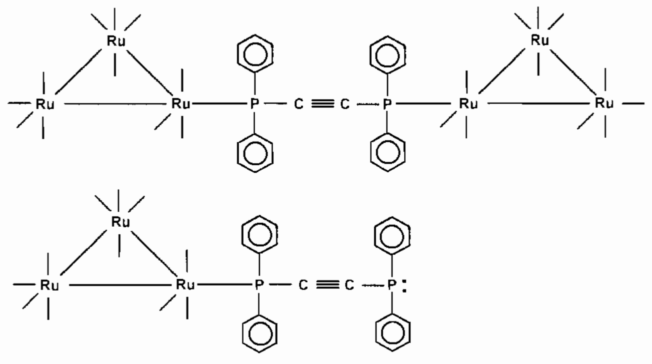

Fig. 1. Sketch of the structure of dimeric and dangling compounds. CO ligands are represented by lines.

centres are linked by a saturated $-CH_2CH_2-$ chain. In the actual case, the presence of unsaturation in the carbon chair of dppa could permit some degree of electronic interaction between the Ru_3 cores, provided that the two σ Ru–P bonds are able to transmit the electronic communication (possibly through the participation of the virtual d orbitals of P atoms). We have then re-investigated the electrochemical behaviour of the parent cluster $Ru_3(CO)_{12}$ in the same experimental conditions employed for the dimer in order to assess the actual electron stoichiometry of the reduction process. Indeed, the published data on the electrochemistry of $Ru_3(CO)_{12}$ are rather contradictory. At the beginning, an irreversible 1*e* reduction step was proposed [10]. Recently, detailed works by Rieger and co-workers [11] and Robinson and co-workers [12] have indicated a complex electrode mechanism, where the apparent electron stoichiometry obtained from controlled-potential coulometry depends on the experimental conditions.

Experimental

Reagents

1,2-Dichloroethane, DCE, was purchased from Fluka GmbH, dried over activated molecular sieves (3 Å), and then distilled from phosphorus pentoxide.

Tetrabutylammonium tetrafluoroborate, $[NBu_4][BF_4]$, used as supporting electrolyte, was prepared according to published methods [13] and dried in vacuum at 333 K before use. Ferrocene and $Fe_3(CO)_{12}$ used as internal standard were purchased from Aldrich, twice recrystallized from ethanol, and dried over phosphorus pentoxide. $Ru_3(CO)_{12}$ was prepared as described in the literature [14]. Dppa was purchased from Strem Chemicals and used as received. Argon and carbon monoxide were supplied by Technoplyn, CSFR. Other chemicals were reagent grade from Lachema, Prague, CSFR.

Synthesis of $[Ru_3(CO)_{11}]_2(\mu$-dppa)

The title compound was synthesized by a benzophenone kethyl (BPK) radical ion initiated reaction between $Ru_3(CO)_{12}$ and dppa with the procedure previously reported by Bruce *et al.* [15]. Separation work-up afforded $[Ru_3(CO)_{11}]_2(\mu$-dppa) [15] and $Ru_3(CO)_{11}(\eta^1$-dppa) in 70 and 10% yield, respectively.

$[Ru_3(CO)_{11}](\eta^1$-dppa): IR (cyclohexane) ν(CO): 2099m, 2050vs, 2032s, 2018vs, 2000m, 1993m, 1983w, 1987w. ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.5 (m, Ph). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 161.9 MHz): δ 6.5 (d, 1), -31.1 (d, 1) (^3J(P–P) $\approx$ 6 Hz). FAB MS: 1008 *m/z* M^+ (based on ^{102}Ru).

All solutions for electrochemical studies were freshly prepared and immediately analysed. Only using such a procedure could an appropriate level of reproducibility be achieved.

Apparatus

The electrochemical measurements were performed on both a PAR Instrument model 273 and a laboratory-built multipurpose electrochemical system featuring ohmic drop compensation and circuit stabilization. Slow scan voltammograms were recorded on an EMG 79182 x-y recorder (Hungary), fast sweep voltammograms on a Tektronix 5301 oscilloscope with 5D10 digitizer. Polarograms were taken by means of a polarographic analyser PA4 (Laboratorni pristroje, Prague, CSFR).

A three-electrode electrochemical cell was used with an Ag/AgCl reference electrode in saturated aqueous potassium chloride separated from the test solution by a salt bridge with a ceramic frit. An immiscible interface between the aqueous saturated potassium chloride and supporting electrolyte solution, 0.1 mol dm^{-3} $[NBu_4][BF_4]$ in DCE, was established by a salt bridge which prevents water from entering the solution under study. Under the actual experimental conditions, the (ferrocene)$^{0/1+}$ couple is located at +0.627 V. All the potentials are reported with respect to this reference electrode, RE. The working electrodes were a static mercury drop electrode, SMDE, (Laboratorni pristroje, Prague, CSFR) and a hanging mercury drop electrode, HMDE (Metrohm model 6.0335). Two dropping mercury electrodes with flow rates, *m*, of 0.244 and 1.22 mg s^{-1} at a reservoir height of 0.5 m were employed. Drop time in the range of 0.5–5 s was controlled by an electromechanical hammer. The auxiliary electrode was a platinum wire sealed in glass. Oxygen was removed by bubbling argon or carbon monoxide directly into the solution. All manipulation with samples and solutions was made using a Schlenk-type glassware technique under a controlled atmosphere of argon purified by passing over a column of BTS copper catalyst (BASF, Ludwigshafen, Germany) and dried in columns filled with sodium hydroxide and phosphorus pentoxide.

UV–Vis and IR spectra were recorded on Hewlett Packard 9153C and Perkin-Elmer 5800 spectrophotometers, respectively. Optically transparent thin-layer electrochemistry (OTTLE) was performed using the previously described cell [16].

The mass spectrum of $Ru_3(CO)_{11}(\eta^1\text{-dppa})$ was recorded on an AEI FAB MS 902 instrument; NMR spectra were recorded on a Jeol EX400.

Results and discussion

Reduction mechanism of $Ru_3(CO)_{12}$

We focused our re-investigation on the reduction of $Ru_3(CO)_{12}$ at a mercury electrode and in 1,2-dichloroethane, DCE. Polarograms of $Ru_3(CO)_{12}$ exhibit, at concentrations higher than 2 mM, a main reduction wave (B) in the accessible potential window (Fig. 2) which corresponds to the main peak B in the cyclic voltammograms (see Fig. 4) accompanied by a small pre-wave A. Log analysis of the polarographic wave B shows that the plot of E versus $\log[(i_d-i)/i]$ is linear and slopes 75 mV with $E_{1/2}=-0.89$ V versus RE. Drop time shortening causes a cathodic shift of the half-wave potential, approaching 50 mV per decade. A plot of the limiting currents of the polarographic waves versus the square root of the height of the mercury column is linear through the origin of axes in a wide range of concentrations of depolarizer indicating a diffusion-controlled process as predicted from the Ilkovich equation [17]. The plot of limiting diffusion currents versus the concentration of $Ru_3(CO)_{12}$ in the range 0.01–5 mM (the upper concentration limit is due to the moderate solubility of $Ru_3(CO)_{12}$ in DCE) is more complicated. We have found a high sensitivity of the limiting current to temperature, the temperature coefficient being higher than that expected for a simple diffusion-controlled process. Furthermore, the age of the solutions plays an important role in the electrochemical responses. We have employed a freshly prepared solution of the depolarizer in strictly controlled experimental conditions (especially temperature). The limiting current is then compared to those of two standards, namely ferrocene and $Fe_3(CO)_{12}$. The oxidation of ferrocene at a mercury electrode is well known in several organic solvents [18]. In our experimental conditions, one reversible 1*e* oxidation step is expected. For $Fe_3(CO)_{12}$ two subsequent 1*e* reduction steps have been observed [19]. The limiting diffusion current depends on the number of electrons exchanged (n_{app}) as well as on the square root of the diffusion coefficient (D) of the species [20]. Assuming all molecules have a spherical geometry, applying the Stokes-Einstein law [20], and comparing the crystallographic data of $Ru_3(CO)_{12}$ [21], ferrocene [22] and $Fe_3(CO)_{12}$ [23], we can take into account the different diffusion coefficients of the two standards with respect to $Ru_3(CO)_{12}$ and then normalize their limiting diffusion currents, in the hypothesis that the solvation process is very similar for these three compounds. In Fig. 3 straight lines passing through the origin of axes are observed for ferrocene (full line) and $Fe_3(CO)_{12}$ (dotted line) which represent the diffusion-controlled 1*e* and 2*e* transfer processes, respectively. The dashed curve (corresponding to $Ru_3(CO)_{12}$) approaches the 2*e* behaviour at low concentration and tends to the 1*e* behaviour at high concentration. This non-linearity points to a complicated mechanism for the electrode process. Since the limiting current is diffusion-controlled over the whole concen-

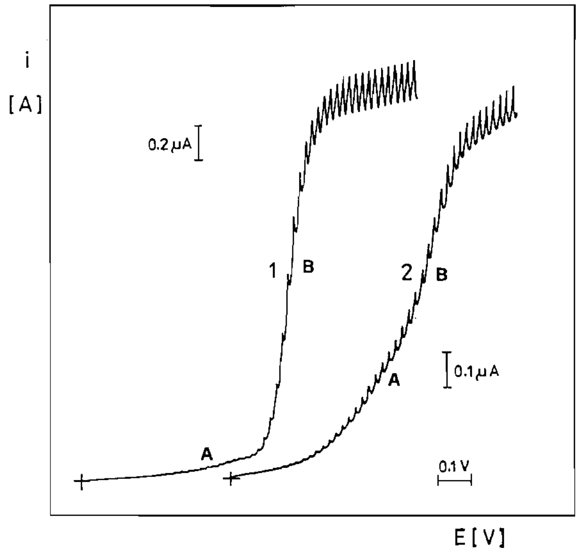

Fig. 2. D.c. polarogram of $Ru_3(CO)_{12}$ in DCE; curve 1: $m=0.244$ mg s^{-1}, $h=0.5$ m, $t_1=4$ s, $T=273$ K, $c=1$ mM; curve 2: $m=1.22$ mg s^{-1}, $h=0.5$ m, $t_1=4$ s, $T=298$ K, $c=0.2$ mM. Starting potential $=-0.3$ V. (m = flow rate; h = height of the mercury column; t_1 = drop time; c = concentration of depolarizer.)

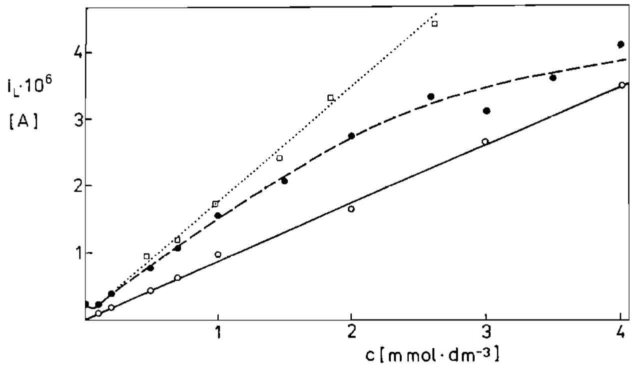

Fig. 3. Plot of limiting current of redox processes of ferrocene (full line), $Ru_3(CO)_{12}$ (dashed line), and $Fe_3(CO)_{12}$ (dotted line) in DCE vs. the concentration of depolarizer. $m=0.244$ mg s^{-1}, $h=0.5$ m, $t^1=0.5$ s, $T=273$ K.

tration range, the chemical complications are faster than diffusion.

The plot of the current of the reduction peak B obtained from cyclic voltammetry versus the concentration of $Ru_3(CO)_{12}$ is entirely analogous. Moreover, in the polarographic response reported in Fig. 2 one can observe a small pre-wave (A). Decreasing the concentration of the depolarizer leads to an increase of wave A with respect to wave B. This behaviour is strongly affected by temperature and drop time. In cyclic voltammetry a broad pre-peak A is also observed at about the same potential (Fig. 4, curve 1).

Using carbon monoxide instead of argon as the controlled atmosphere, wave A disappears and, when the concentration of depolarizer is as low as 0.2 mM, the total limiting current decreases by about 20%. In these experimental conditions, the residue wave B shows a 60 mV slope from the logarithmic analysis, corresponding to the uncomplicated reduction of $Ru_3(CO)_{12}$. In the cyclic voltammogram peak A disappears too under a CO atmosphere.

These experimental data suggest a fast pre-equilibrium between depolarizer and $[Ru_3(CO)_{11}]$, probably in a solvated form, and then the electrochemical reduction of both species (CE mechanism).

$$[Ru_3(CO)_{12}] \longrightarrow [Ru_3(CO)_{11}] + CO$$

This solvent dissociation of $Ru_3(CO)_{12}$ agrees with previous investigations in other solvents [11, 12] and is obviously suppressed by the presence of CO.

This equilibrium is associated to the proper electron transfer processes:

$$[Ru_3(CO)_{12}] + e \longrightarrow [Ru_3(CO)_{12}]^- \qquad \text{(wave B)}$$

$$[Ru_3(CO)_{11}] + 2e \longrightarrow [Ru_3(CO)_{11}]^{2-} \qquad \text{(wave A)}$$

In Fig. 3 one can observe that for all the solutions at concentration $c > 1$ mM the total limiting current is between the 1e (full line) and the 2e (dotted line) stoichiometry. It is well known that every EE mechanism can be treated as disproportionation (EC_{disp} mechanism) [24]. An enhancement of the limiting current of the wave over the value corresponding to the diffusion-controlled one-electron process can be assigned to a disproportionation reaction with a sufficiently large rate constant, according to the following equation:

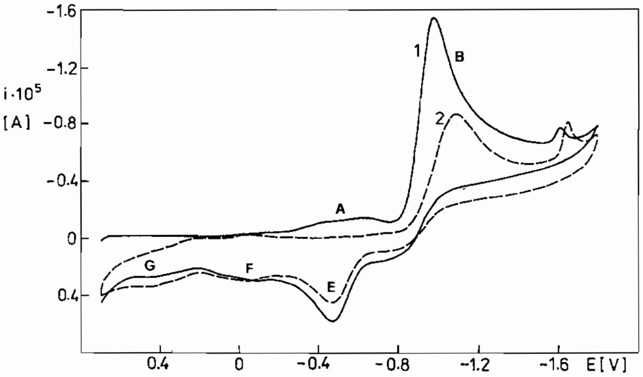

Fig. 4. Cyclic voltammogram of $Ru_3(CO)_{12}$ in DCE at a SMDE. $T = 298$ K; scan rate $v = 1$ V s^{-1}; curve 1 and 2: first and second sweep, respectively.

$$2[Ru_3(CO)_{12}]^- \longleftrightarrow [Ru_3(CO)_{12}] + [Ru_3(CO)_{12}]^{2-}$$

Theoretical treatment of the EC_{disp} mechanism shows that the influence of the disproportionation and self-exchange reactions depend on the relative concentration of the species [24]. We should then observe a two-electron polarographic wave under certain concentration conditions. However, Fig. 3 shows that the limiting current at a higher concentration of depolarizer tends to the 1e process. It could be explained by means of a coproportionation reaction, likely the redox condensation reaction [25]:

$$[Ru_3(CO)_{12}] + [Ru_3(CO)_{12}]^{2-} \longrightarrow [Ru_6(CO)_{18}]^{2-} + 6CO$$

The $[Ru_6(CO)_{18}]^{2-}$ cluster has indeed been identified as the predominant product of the controlled potential exhaustive reduction of $Ru_3(CO)_{12}$ [11, 12].

The cyclic voltammetric response reported in Fig. 4 lends support to this hypothesis. In the second cycle (curve 2) there is a dramatic decrease of peak B indicating that a chemical reaction between reduction products and depolarizer occurs.

In conclusion, the mechanism of the reduction of $Ru_3(CO)_{12}$ can be tentatively described as a set of surface redox reactions initiated by the primary diffusion-controlled 1e transfer step. The overall electrochemical response of this complex mechanism strongly depends on experimental conditions (i.e. concentration of depolarizer, temperature, time scale of experiment) and this precludes quantitative studies.

Reduction of $[Ru_3(CO)_{11}]_2(\mu\text{-dppa})$

The structure of the title compound has been originally proposed by Bruce *et al.* [15] on the basis of spectroscopic data and its sketch is reported in Fig. 1. The two ruthenium triangles are symmetrically linked by the diphosphino acetylene via the two phosphorus atoms which occupy two equivalent equatorial sites on each Ru_3 moiety. This hypothesis has been corroborated by a subsequent X-ray structural determination of the isoelectronic $[Os_3(CO)_{11}]_2(\mu\text{-dppa})$ dimer [26]. The d.c. polarogram of $[Ru_3(CO)_{11}]_2(dppa)$ in DCE is reported in Fig. 5. The major reduction wave (C) with $E_{1/2} = -1.040$ V versus RE is followed by a small wave (D) with $E_{1/2} = -1.250$ V versus RE. The ratio of limiting currents $i(C)/i(D)$ is about 10. Plots of total limiting current versus the square root of the height

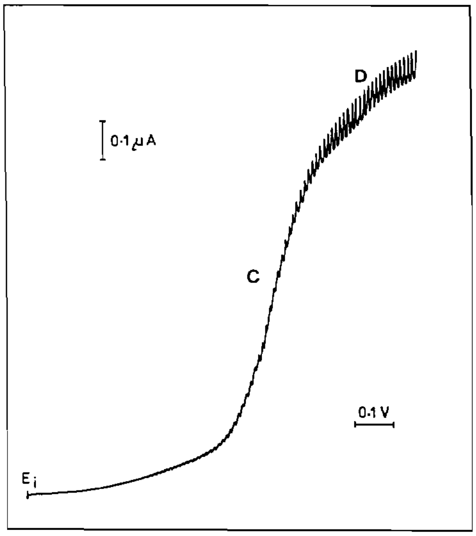

Fig. 5. D.c. polarogram of $[Ru_3(CO)_{11}]_2(dppa)$ in DCE; $m=1.2$ mg s^{-1}; $h=0.5$ m; $t_1=2$ s; initial potential $= -0.4$ V.

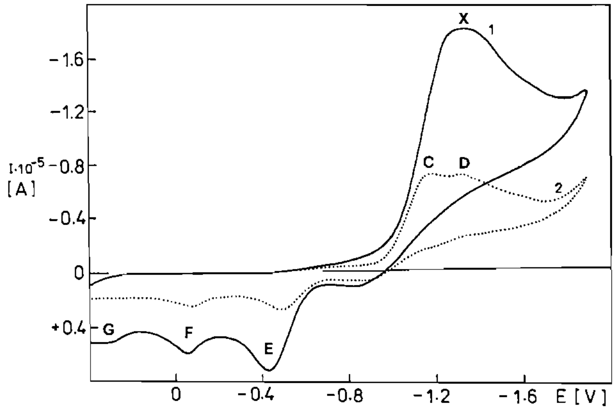

Fig. 6. Cyclic voltammogram of $[Ru_3(CO)_{11}]_2(dppa)$ in DCE at a HMDE; curve 1, $v=0.5$ V s^{-1}; curve 2, $v=0.1$ V s^{-1}.

of the mercury reservoir and versus the concentration of depolarizer in the range 0.05–2 mM are both linear through the origin of axes indicating a diffusion-controlled process.

The minor polarographic wave D is sensitive to experimental conditions. The ratio of limiting currents $i(C)/i(D)$ increases as the drop time is shortened or the temperature is lowered. This behaviour is typical for an EC mechanism [20]. In the experimental conditions for which only wave C is observed, the apparent number of electrons has been determined by using ferrocene as an internal standard. The ratio of diffusion current constants of $[Ru_3(CO)_{11}]_2(dppa)$ (wave C) and ferrocene is about 2.

A cyclic voltammogram of $[Ru_3(CO)_{11}]_2(dppa)$ at a mercury electrode is shown in Fig. 6. At scan rates higher than 0.5 V s^{-1} only one reduction peak X is observed (curve 1). Plots of peak current versus both the square root of scan rate and the concentration of depolarizer are linear through the origin confirming the diffusion-controlled behaviour previously established by polarography. Decreasing the scan rate causes the splitting of peak X into two peaks, namely C and D (curve 2, Fig. 6). A cathodic shift of $E_p(C)$ as the scan rate is increased and the absence of a directly associated re-oxidation peak even at low temperature indicates that this reduction step is chemically irreversible. On the reverse scan one can observe three oxidation peaks (Fig. 6, curve 1) with peak potentials $E_p(E) = -0.480$ V, $E_p(F) = -0.080$ V and $E_p(G) = 0.303$ V versus RE. These peaks can be assigned to the oxidation of products of the primary reduction step. These peaks are identical to those observed for the re-oxidation of $Ru_3(CO)_{12}$ in the same experimental conditions. In particular, peak E is assigned to the oxidation of $[Ru_3(CO)_{11}]^{2-}$. In the actual case peak E is diffusion-controlled, and, for sweep rate $\geqslant 0.5$ V s^{-1}, its current corresponds approximately to half of that of peak X. Taking into account these data we can propose a possible mechanism for the reduction of $[Ru_3(CO)_{11}]_2(dppa)$ as follows:

$$[Ru_3(CO)_{11}]_2(\mu\text{-dppa}) + 2e \longrightarrow [\{Ru_3(CO)_{11}\}_2(\mu\text{-dppa})]^{2-} \qquad \text{(wave C)}$$

$$[Ru_3(CO)_{11}]_2(\mu\text{-dppa})]^{2-} \longrightarrow [Ru_3(CO)_{11}(\eta^1\text{-dppa})] + [Ru_3(CO)_{11}]^{2-}$$

$$Ru_3(CO)_{11}(\eta^1\text{-dppa}) + 2e \longrightarrow [Ru_3(CO)_{11}(\eta^1\text{-dppa})]^{2-} \qquad \text{(wave D)}$$

The first step represents the $2e$ reduction of $[Ru_3(CO)_{11}]_2(dppa)$, followed by dissociation of the dianion into $[Ru_3(CO)_{11}]^{2-}$ and the 'dangling' complex $Ru_3(CO)_{11}(\eta^1\text{-dppa})$ (Fig. 1) which is reduced at more negative potentials (peak D) in the $2e$ step. The CV response of an authentic sample of $[Ru_3(CO)_{11}dppa]$ confirms this view. The 'dangling' complex has been isolated as a by-product from the reaction of $Ru_3(CO)_{12}$ with dppa (see 'Experimental'). The $^{31}P\{^1H\}$ NMR spectrum is very diagnostic since it exhibits two doublets ($^3J(P–P) \approx 6$ Hz) in a relative integration ratio of 1:1 in the region of coordinated and free dppa, respectively [27].

The course of the electrochemically induced reaction between $[Ru_3(CO)_{12}]$ and dppa in DCE followed by polarography is shown in Fig. 7. Addition of dppa to the solution of $[Ru_3(CO)_{12}]$ (curve 1) results in a dramatic change of the original polarographic response. The new waves C (curve 2) and D (curve 3) are easily assigned to the reduction of substitution products, namely $[Ru_3(CO)_{11}]_2(dppa)$ and $[Ru_3(CO)_{11}dppa]$. At low concentration of dppa the only detectable reaction product is the dimer (wave C); when excess of dppa

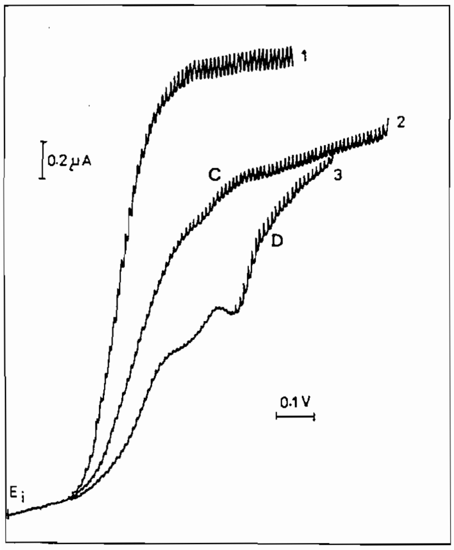

Fig. 7. Influence of stepwise addition of dppa on the d.c. polarogram of $Ru_3(CO)_{12}$ in DCE; curve 1, polarogram of a 1 mM solution of $Ru_3(CO)_{12}$; curve 2, after the addition of 1 mM of dppa; curve 3, after the addition of 10 mM of dppa. The polarographic parameters are those of Fig. 2.

is employed the dangling derivative (wave D) is also easily observed, although the response is distorted by adsorption phenomena.

The overall mechanism of reduction of $[Ru_3(CO)_{11}]_2$(dppa) is similar to that discussed by Robinson and co-workers for the dimer $[RCCo_3(CO)_8]_2$-(μ-dppe) where the electrochemical induced formation of the 'chelate' monomer $RCCo_3(CO)_7$(dppe) is also proposed [9]. In the actual case, the rigidity of the linear –C≡C– chain and the long P–P distance in the dppa skeleton prevents chelation to a single metal atom or across a metal–metal bond [28].

The cathodic behaviour of $[Ru_3(CO)_{11}]_2$(dppa) at a Pt electrode is very similar to that found at the mercury electrode. This allows us to follow the electrolysis by using the optical transparent thin layer electrode (OTTLE) cell [16], which employs a Pt grid as working electrode.

Figure 8 shows the UV–Vis spectrum of $Ru_3(CO)_{11}]_2$(dppa) in DCE (curve 1, $\lambda_{max} = 418$ and 94 nm). During the potential-controlled ($E_w = -1.1$ V versus RE) reduction, the sequential spectra pass hrough isosbestic points (curves 2 and 3). The main and at 418 nm decreases and a new band with $\lambda_{max} = 490$ m appears. The broad absorbance at shorter wavength increases as well. These experimental data agree ith the proposed mechanism. The absorption band at 90 nm is due to the dangling $[Ru_3(CO)_{11}$dppa] complex verified on an authentic sample. The other species sponsible for the spectrum change at shorter wavength is certainly a product of the reduction of $u_3(CO)_{12}$, probably $[Ru_3(CO)_{11}]^{2-}$. This is evinced by comparison with the spectra of $Ru_3(CO)_{12}$ in DCE before (curve 4) and after (curve 5) its reduction, shown in Fig. 8.

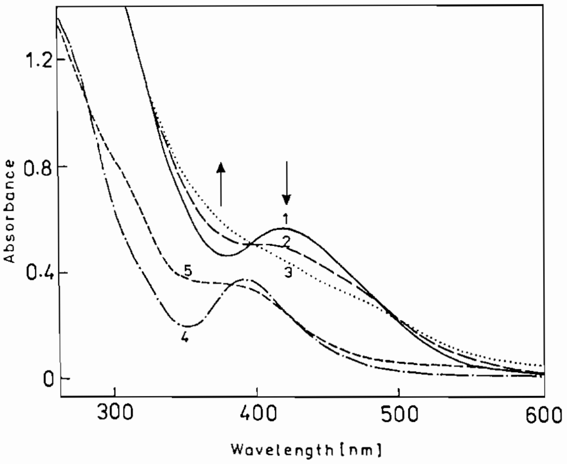

Fig. 8. UV–Vis OTTLE spectra of $[Ru_3(CO)_{11}]_2$(dppa) in DCE; curve 1 before electrolysis; curve 2 and 3, after partial (1 Faraday) and total (2 Faradays) electrolysis at $E_w = -1.1$ V vs. RE; curve 4 and 5: $Ru_3(CO)_{12}$ in DCE before and after exhaustive electrolysis.

Conclusions

The 2*e* reduction of the dimer $[Ru_3(CO)_{11}]_2$(dppa) indicates that the two $Ru_3(CO)_{11}$ units are independent in the electrochemical sense, in other words there is no electrochemically detectable electronic communication between them. However, weak electronic interactions through the dppa bridge cannot be completely ruled out, since the fast chemical complications following the reduction of $[Ru_3(CO)_{11}]_2$(dppa) prevent more subtle electrochemical analyses (i.e. semintegral or semiderivative analyses [29]).

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