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Reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with 2,3-bis(2-pyridyl)pyrazine and pyrazyne. Synthesis, characterization and electrochemical behavior of 1:1 and 1:2 ligand:cluster complexes

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Abstract

The diimine-bridged, bis-triosmium carbonyl complexes $[\{Os_3(CO)_{10}(\mu\text{-}H)\}_2(pyz)]$ **1b**, $[\{Os_3(CO)_{10}\}_2(dpp)]$ **2b**, (pyz = pyrazine; dpp = 2,3-bis(2-pyridyl)pyrazine) and their corresponding 1:1 ligand:cluster complexes $[Os_3(CO)_{10}(\mu\text{-}H)(pyz)]$, **1a**, $[Os_3(CO)_{10}(dpp)]$, **2a**, were synthesized by the reaction of $[Os_3(CO)_{10}(MeCN)_2]$ with pyz and dpp ligands. All compounds were characterized by IR, ^{1}H-NMR spectroscopy and elemental analysis. Electrochemistry was used to examine the redox properties of **1**–**2** and of complexes $[Os_3(CO)_{10}(\mu\text{-}H)(py)]$, **3**, for comparison purposes. The electrochemical behavior of the bridged bis-triosmium species **1b**–**2b** provided strong evidence for the electronic interaction between the two metal centers.

Keywords: Syntheses; Electrochemistry; Diimines; Triosmium clusters

1. Introduction

Delocalized π organic ligands can act as electronic bridges between adjacent transition metal clusters [1]. The point of view of the vast research on organometallic polymers having electronic interactions between the adjacent redox centers, is that they could be useful precursors for mixed-valence and conducting materials [2]. In principle, the electrochemical techniques in solution can indicate moderate to strong electronic interactions between the redox centers and then to predict the conducting properties of the corresponding solid materials [3].

The electronic interaction between two identical redox centers of a dimeric compound linked by a polydentate ligand can be detected by electrochemical techniques, using the electrochemical approach extensively developed in previous works [4].

The degree of interaction between metal-containing subunits of a bimetallic complex may be still evaluated by the differences in the first-reduction potentials of the bridging ligand in the mono and binuclear complexes [5].

Since the first report on the now well-known mixed-valence Ru(II)–L–Ru(III) system [6], there have been extensive studies on the electronic interaction between mononuclear components of ligand-bridged dimer complexes [7]. In particular, reports of ligand-bridged species bound between two $M(CO)_5$ moieties, i.e. $(OC)_5M{-}L{-}M'(CO)_5$, and between two $M(CO)_4$ fragments, i.e. $(OC)_4M{-}L{-}M'(CO)_4$ (where M, M′ = Cr, Mo, W) have appeared [8]. These studies have illustrated that the binucleating ligand π^*-electron system has a profound effect on the spectroscopic, photochemical and redox behavior in these complexes.

In this work, we wish to report the syntheses, characterization and electrochemical properties of 1:1 and 1:2 ligand:cluster complexes derived from the reaction of the title complex and dpp and pyz ligands.

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In this connection, the reactions of $[Os_3(CO)_{10}(MeCN)_2]$ with pyrazine (pyz) and 2,3-bis(2-pyridyl)pyrazine (dpp), were found to produce the 1:1 ligand:cluster complexes $[(Os_3(CO)_{10}(\mu\text{-H})(pyz)]$, **1a** and $[Os_3(CO)_{10}(dpp)]$, **2a** and their corresponding 1:2 ligand:cluster complexes $[\{Os_3(CO)_{10}(\mu\text{-H})\}_2(pyz)]$, **1b** and $[\{Os_3(CO)_{10}\}_2(dpp)]$, **2b**.

2. Experimental details

2.1. Materials

Triosmium dodecacarbonyl, pyrazine, 2,3-bis(2-pyridyl)pyrazine, pyridine and acetone-d_6, were purchased from Aldrich Chemical and used as received. Tetrahydrofuran (THF) was distilled from sodium-benzophenone, dichloromethane (DCM) and 1,2-dichloroethane (DCE) were treated with P_2O_5 prior to use. Other solvents were used without further purification.

2.2. Apparatus

Infrared spectra were recorded in solution on a Jasco Model IR-700. ^{1}H-NMR were obtained on a Bruker Model AC300/P spectrometer operating at 300 MHz, using tetramethylsilane as internal standard. Elemental analyses were performed on a Perkin-Elmer Model 2400 CHN apparatus.

Electrochemical measurements were performed on an EG&G Princeton Applied Research (PAR) M273A electrochemical analyzer interfaced to an IBM computer employing PAR M270 Electrochemical Software. A standard three-electrode cell was designed to allow the tip of the reference electrode to closely approach the working electrode. Positive feedback IR compensation was applied routinely. All measurements were carried out under argon in anhydrous deoxygenated solvents; solutions were ca 1×10^{-3} M with respect to the compounds under study and ca 1×10^{-1} M with respect to the supporting electrolyte, $[Bu_4N][BF_4]$. A platinum-disk working electrode, a platinum-wire auxiliary electrode and a saturated calomel reference electrode (SCE) were used in these experiments. The measurements were calibrated with ferrocene, as internal standard in known concentration. Under the experimental conditions used, the ferrocene–ferrocenium couple is $+0.47$ V in CH_2Cl_2 and $+0.56$ V in THF. The low temperature experiments were performed with a reference electrode built with an AgCl-coated silver-wire dipped in a 0.1 M solution of $[Bu_4N][BF_4]$ in CH_2Cl_2, and separated from the cell solution by a Vycor frit. At the end of each experiment, the potential of ferrocene $(0/+1)$ couple was measured versus the pseudo-reference electrode and then versus an aqueous SCE to which the data are referred.

2.3. Syntheses

The complexes $[Os_3(CO)_{11}(MeCN)]$, $[Os_3(CO)_{10}(MeCN)_2]$, $[Os_3(CO)_{10}(\mu\text{-H})(py)]$, **3** were prepared according to literature procedures [9,10].

2.3.1. Synthesis of $[Os_3(CO)_{10}(\mu\text{-H})(pyz)]$ (**1a**) and $[\{Os_3(CO)_{10}(\mu\text{-H})\}_2(pyz)]$ (**1b**)

A mixture of 0.185 g (0.20 mmol) of $[Os_3(CO)_{10}(MeCN)_2]$ and 0.0080 g (0.10 mmol) of pyrazine in 20 cm^3 of cyclohexane/dichloromethane (1:1 v/v), was heated at 45°C for 30 min under argon. At this point, the bright-yellow solution turned orange. The mixture was cooled to r.t. and the solvent was removed under vacuum. The residue was redissolved in a small volume of CH_2Cl_2 and the products were separated by thin layer chromatography, on silica plates, using petroleum ether/CH_2Cl_2 (7:3 v/v) as eluent. The first yellow band eluted was identified as a mixture in the molar ratio 1:2 of *syn*- and *anti*-isomers of **1b**. Yield: 0.230 g (0.13 mmol) 65%. Anal. Calc. for $C_{24}H_4N_2O_{20}Os_6$: C, 16.17; H 0.22; N, 1.57. Found: C, 16.03; H, 0.24; N, 1.61%. IR (CH_2Cl_2; cm^{-1}): $\nu(C\equiv O)$ 2102 (w), 2064 (s), 2050 (s), 2038 (s), 2016 (m), 2002 (s), 1999 (sh), 1980 (m). ^{1}H-NMR (acetone-d_6; ppm): 8.12 (s, 1H); 8.05 (s, 1H); -14.35 (s, 1H); -14.58 (s, 1H). The second orange–yellow band eluted was identified as the 1:1 ligand:cluster **1a**. Yield: 0.037 g (0.040 mmol) 20%. Anal. Calc. for $C_{14}H_4N_2O_{10}Os_3$: C, 18.05; H, 0.43; N, 3.01. Found: C, 17.75; H, 0.40; N, 2.92%. IR (CH_2Cl_2; cm^{-1}): $\nu(C\equiv O)$ 2102 (w), 2064 (s), 2052 (s), 2022 (s), 2008 (s), 1992 (m), 1977 (sh). ^{1}H-NMR (acetone-d_6; ppm): 8.67 (dd, 1H; 1.3 Hz, 3.2 Hz); 8.48 (d, 1H; 1.2 Hz); 8.00 (d, 1H; 3.3 Hz); -14.84 (s, 1H). The mixture of isomers *syn* and *anti* was chromatographed again on silica plates using petroleum ether/CH_2Cl_2 (9:1 v/v), giving as the first band, the mixture in the molar ratio 1:1 of *syn*- and *anti*-isomers of **1b** (yield, 10%) and as a second band, the pure isomer *anti* of **1b** (yield, 90%). IR (CH_2Cl_2; cm^{-1}): $\nu(C\equiv O)$ 2102 (w), 2064 (sh), 2050 (s), 2038 (s), 2016 (m), 2002 (s), 1999 (sh), 1980 (m). ^{1}H-NMR (acetone-d_6; ppm): 8.12 (s, 1H); -14.35 (s, 1H).

2.3.2. Synthesis of $[Os_3(CO)_{10}(dpp)]$ (**2a**) and $[\{Os_3(CO)_{10}\}_2(dpp)]$ (**2b**)

A mixture of 0.125 g (0.134 mmol) of $[Os_3(CO)_{10}(MeCN)_2]$ and 0.0155 g (0.066 mmol) of 2,3-bis(2-pyridyl)pyrazine in 25 cm^3 of CH_2Cl_2, was stirred at r.t. for 45 min under argon, during which time the solution became blue. The solvent was removed under vacuum and the residue chromatographed on a column of SiO_2 (25 × 2 cm). The first green band eluted with CH_2Cl_2 was identified as **2b**. Yield: 0.030 g (0.0155 mmol) 12%. Anal. Calc. for $C_{24}H_{10}N_4O_{20}Os_6$: C, 21.08; H, 0.52; N, 2.89. Found: C, 20.85; H, 0.49; N, 2.77%. IR (CH_2Cl_2; cm^{-1}): $\nu(C{\equiv}O)$ 2082 (m), 2040 (s), 2018 (s), 2000 (s), 1997 (s), 1982 (sh), 1915 (sh). ^{1}H-NMR (acetone-d_6; ppm): 9.75 (d, 2H; 5.3 Hz); 8.79 (s, 2H); 8.63 (d, 2H; 8.3 Hz); 8.10 (td, 2H; 1.1 Hz, 7.3 Hz); 7.66 (td, 2H; 1.5 Hz, 6.0 Hz). The second purple band eluted with methanol was identified as **2a**. Yield: 0.058 g (0.054 mmol) 40%. Anal. Calc. for $C_{24}H_{10}N_4O_{10}Os_3$: C, 26.55; H, 0.92; N, 5.16. Found: C, 26.28; H, 0.87; N, 5.31%. IR (CH_2Cl_2; cm^{-1}): $\nu(C{\equiv}O)$ 2086 (w), 2038 (m), 2008 (s), 1997 (sh), 1977 (sh), 1955 (sh), 1980 (w). ^{1}H-NMR (acetone-d_6; ppm): 9.59 (d, 1H; 5.2 Hz); 9.37 (d, 1H; 3.3 Hz); 8.64 (d, 1H; 3.3 Hz); 8.60 (d, 1H; 4.4 Hz); 8.13 (td, 1H; 1.7 Hz, 6.2 Hz); 8.05 (d, 1H; 7.7 Hz); 7.77 (td, 1H; 1.7 Hz, 6.2 Hz); 7.61 (td, 1H; 1.4 Hz, 6.0 Hz); 7.52 (td, 1H; 1.4 Hz, 6.0 Hz); 7.35 (d, 1H; 8.2 Hz).

3. Results and Discussion

3.1. Synthesis

The synthesis of compounds **1a** and **1b** was achieved by the reaction of title complex and pyrazine in the molar ratio 2:1 in cyclohexane/dichloromethane at 45°C, and gave reasonable yields of both species. The isolation of pure isomer *syn* **1b** was not possible, probably owing to its isomerization to the more stable *anti* **1b** when in contact with the silica in the separation process. Similar behavior was observed for other osmium complexes [11]. However, pure *anti* **1b** was obtained by successive purification of the mixture on silica plate. A higher yield of compound **1a**, ca. 70%, was obtained using excess of the ligand. The same results were obtained when $[Os_3(CO)_{11}(MeCN)]$ is used as starting material.

Compounds **2a** and **2b** were obtained through the reaction of the title complex and the ligand dpp, in the molar ratio 2:1, by simple substitution of two MeCN molecules. Using excess of the ligand, compound **2a** was isolated as the only product in ca. 60% yield. Compound **2b** was obtained in low yield from the reaction with molar ratio 2:1, probably due to the constraints of the ligand in this complex (see later discussion).

All the complexes were air stable in the solid-state and in solution. They were sparingly soluble in non-polar solvents as hexane, cyclohexane, petroleum ether and very soluble in polar solvents such dichloromethane, tetrahydrofuran, acetonitrile and acetone.

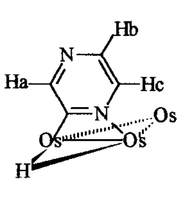
Compounds **3** were synthesized to allow an understanding of the electrochemical behavior of compounds **1a**–**b** and was identified by infrared spectra only.

3.2. Characterization

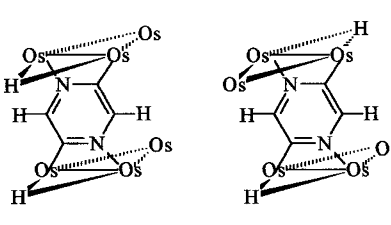
The molecular formulae of the complexes were established by elemental analysis, infrared and ^{1}H-NMR spectroscopy.

The infrared spectra of the complexes **1a**–**b** follow the pattern exhibited by the known complex **3** [9] and complexes **2a**–**b** exhibit the same pattern as the complexes $[Os_3(CO)_{10}$(diphosphine)] ([12]a) and $[Os_3(CO)_{10}(\mu$-H)(benzotriazole)] ([12]b).

Complexes **1a**–**b** gave very simple ^{1}H-NMR spectra, unambiguously assigned. For complex **1a**, the double doublet at $\delta = 8.67$ ($J_{HH} = 1.3$ and 3.2 Hz) was attributed to H_b, the doublet at $\delta = 8.48$ ($J_{HH} = 1.2$ Hz) and the doublet at $\delta = 8.00$ ($J_{HH} = 3.3$ Hz) were ascribed to H_a and H_c, respectively. Compound *syn*-**1b** showed a singlet at $\delta = 8.05$ and the compound *anti*-**1b**, a singlet at $\delta = 8.12$. The transfer of an *ortho*-hydrogen atom of the ligand to the metal was confirmed by the NMR spectra of these compounds that showed signals at $\delta = -14.80$ (**1a**), -14.58 (*syn*-**1b**) and -14.35 (*anti*-**1b**). We believe that the pyrazine ligand in compounds **1a**–**b,** acts as a three-electron donor bridge, forming a four-membered ring shown in Figs. I and II, as previously proposed for complex **3**, triosmium complexes of imidazole and diazaheterocycles ([10]a–d), where the ligand spanning two strictly axial co-ordination sites and the hydride ligand occupying a diequatorial bridging site (see **I** and **II**).



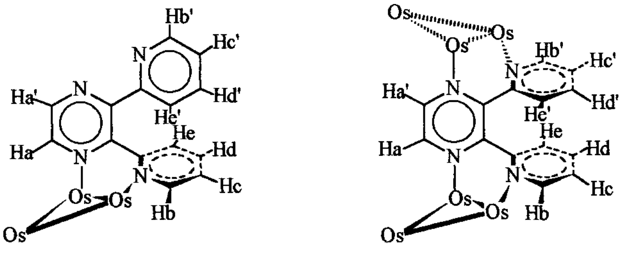
I - 1a



syn *anti*

II - 1b

The 1:1 ligand:cluster complex **2a** showed six doublets attributed to protons H_a, $H_{a'}$, H_b, $H_{b'}$, H_e, $H_{e'}$, and four triple doublets assigned to protons H_c, $H_{c'}$, H_d, $H_{d'}$, corresponding to one proton each, as expected for this type of complexes. Futhermore, dimer **2b** showed one singlet ascribed to the protons $H_{a,a'}$, two doublets attributed to the protons $H_{b,b'}$ $H_{e,e'}$ and two triple doublets assigned to protons $H_{c,c'}$ and $H_{d,d'}$, corresponding to two protons each. Thus, the dpp ligand acts as a four-electron donor bridge, forming a six-membered ring, as shown in Fig. III.



2a **2b**

III

The ligands in the dpp-bridged Ru(II) systems [5,13], [{M(CO)$_4$}$_2$(dpp)], M = Cr, Mo, W) [8] and [{Re(CO)$_3$Cl}$_2$(dpp)] [14], are in a non-planar configuration owing to H$_e$–H$_{e'}$ steric repulsion. In the complex **2b**, the ligand remains in non-planar configuration (twisted). However, the complex could have the Os$_3$ triangles disposed towards opposite faces of the pyrazine ligand (see **III**, above). This would give the molecule a C$_2$ axis that allows protons H$_e$/H$_{e'}$ to be equivalent (Table 1).

3.3. Electrochemistry

The relevant electrochemical data for the complexes **1**–**3** and free ligands are given in Table 1.

*3.3.1. [Os$_3$(CO)$_{10}$(μ-H)(pyz)] (**1a**) and [{Os$_3$(CO)$_{10}$(μ-H)}$_2$(pyz)] (**1b**)*

We have repeated the cyclic voltammetric experiments on [Os$_3$(CO)$_{12}$] in CH$_2$Cl$_2$, at r.t. This compound exhibited a chemically irreversible reduction step at the peak potential, E_p, of −1.46 V versus SCE, followed on the return scan, by a smaller broad oxidation peak at −0.28 V, owing to the reoxidation of an unidentified fragmentation product, whose results are in agreement with previous studies [15] on this complex. Under the same conditions, compound **3** exhibits similar behavior: the cyclic voltammogram response shows a chemically irreversible reduction process at −1.71 V versus SCE, attributed to the triosmium core, followed on the return scan, by a smaller broad oxidation peak at −0.70 V, owing to reoxidation of an unidentified product. These results are in accordance with the observation that the substitution of a basic ligand (py) for CO groups in [Os$_3$(CO)$_{12}$], produce a decrease in the cathodic potential, as observed for others complexes [16].

Table 1
Relevant electrochemical data of compounds [Os$_3$(μ-H)(CO)$_{10}$(pyz)] (**1a**), [{Os$_3$(μ-H)(CO)$_{10}$}$_2$(pyz)] (**1b**), [Os$_3$(CO)$_{10}$(dpp)] (**2b**), [{Os$_3$(CO)$_{10}$]$_2$(dpp)] (**2b**) and [Os$_3$(μ-H)(CO)$_{10}$(py)] (**3**)

Complex	Solvent	E_p ^{a} (V vs. SCE)	$\Delta E^{0'}$ ^{a} (mV)
1a	DCM	−1.55	
trans-**1b**	DCM	−1.35^b; −1.76	90
	DCE	−1.34^b; −1.73	110
2a	THF	−0.950^b	117
2b	THF	−0.555^b; −1.02; −1.64	75
3	DCM	−1.71	
py	DCM	> −2.20	
pyz	DCM	> −2.20	
dpp	THF	−1.83^b	90

[a] From CV responses at scan rate of 200 mV s^{-1}.

[b] Reversible and or quasi-reversible waves.

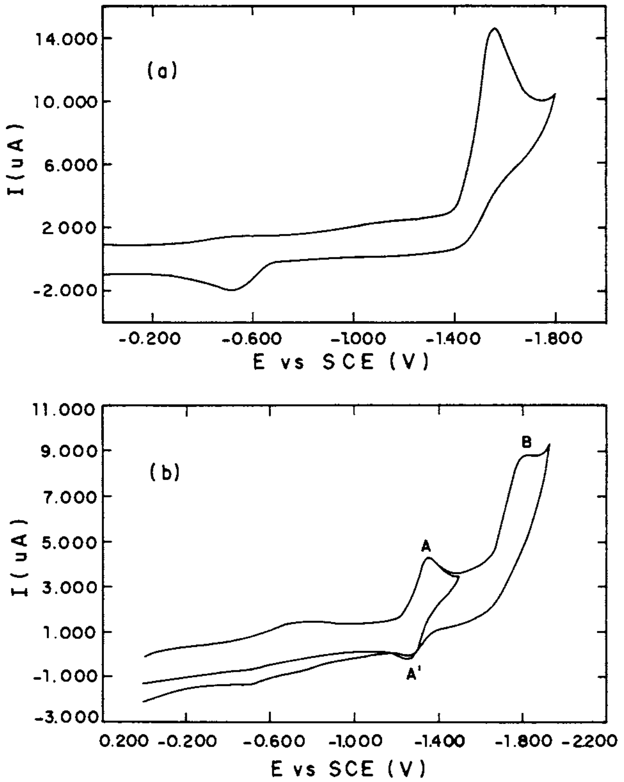


Fig. 1. CV response of a DCM solution of **1a** (up) and **1b** (down), scan rate 200 mV s^{-1} at room temperature. The working electrode is a platinum disk, 0.2 mm diameter.

Fig. 1 shows the cyclic voltammetric response of **1a** and *anti*-**1b** in CH$_2$Cl$_2$ solution, at r.t. The forward cathodic sweep revealed one chemically irreversible reduction process for complex **1a** at −1.55 V versus SCE, ascribed to the triosmium atoms, followed on the return scan, by a smaller broad oxidation peak at −0.53 V, similar to what was observed for [Os$_3$(CO)$_{12}$] and for complex **3** (Table 1). The same behavior is also followed by the complex [Os$_3$(CO)$_{10}$(μ-H)(benzotriazole)] ([12]b). In the potential range investigated (0 to −2.20 V in CH$_2$Cl$_2$), no peak due to the pyrazine was observed. Free pyrazine has a reduction potential > −2.20 V in dichloromethane, and exhibits only a hump near to the solvent discharge in THF, at ca. −2.50 V. From this comparison, we can conclude that the co-ordination of pyrazine causes only a moderate increase in the electron density of the Os$_3$ frame (ΔE = 90 mV) in the complex **1a**. For example, the progressive substitution of the moderately basic P(OPh)$_3$ ligands for CO groups in [Fe$_3$(CO)$_{12}$] produces a decrease in the cathodic potentials of 198 mV for one P(OPh)$_3$, 384 mV for two P(OPh)$_3$ and 712 mV for three P(OPh)$_3$, respectively [16]. This electronic effect seems to play only a minor role in our case.

Two reduction processes were observed in the forward cathodic sweep for the complex *anti*-**1b** (peaks A and B) in CH$_2$Cl$_2$ solution, at r.t. The first reduction peak A shows in the reverse scan the directly associated reoxidation peak A′ ($E_{1/2} = -1.35$ V versus SCE, $i_p^a/i_p^c = 0.60$ at 200 mV s^{-1}, $\Delta E = E_{pa} - E_{pc} = 90$ mV). Under the actual condition the peak-to-peak separation, ΔE of the ferrocene/ferrocenium couple is 75 mV. The reduction potentials for the complex *anti*-**1b** are $E_p(A) = -1.35$ V versus SCE and $E_p(B) = -1.76$ V versus SCE, were ascribed to the Os_3 cores, since as stated above, free pyrazine and complex **1a** have no reduction peak detectable in the actual range of potential, in the solvent studied.

When the temperature is lowered to −65°C and the scan rate is increased, the same behavior is observed in the cyclic voltammogram of compound *anti*-**1b**, nevertheless the i_p^a/i_p^c ratio for the couple A/A′ becomes equal to the unity. Unfortunately, even under this condition, the second reduction peak still exhibits a chemically irreversible reduction step at peak potential, $E_p(B)$ of -1.76 V versus SCE.

Two well-resolved reversible peaks should be observed in dimer complex that has complete charge delocalization over two redox centers [17]. In our case, only the first peak, $E_p(A)$ has reversible character due to reduction of a triosmium core of the complex **1b**. We believe that the second irreversible peak, $E_p(B)$, observed in the voltammogram, is due to the reduction process of the second Os_3 core of **1b**, followed of decomposition of the anion complex generated.

The difference between the reduction potentials of the complex **1b**, $\Delta E = E_p(A) - E_p(B) = 410$ mV, suggests an electronic interaction between the two polymetallic centers in the complex **1b** through the π-electrons of ligand, despite the irreversibility of the second reduction peak $E_p(B)$. The less negative reduction potential and the change from an irreversible to a reversible process, $E_p(A)$, in comparing **1a** and **1b**, is already indicative of a more delocalized system, and so, of a communication between the two metallic centers through of the pyrazine ligand in **1b**.

3.3.2. *[$Os_3(CO)_{10}(dpp)$] (**2a**) and [$\{Os_3(CO)_{10}\}_2(dpp)$] (**2b**)*

Fig. 2 shows the CV response of **2a** and **2b** in a THF solution, at −10°C. The electrochemical reduction of complex **2a** showed a quasi-reversible peak, $E_{1/2} = -0.95$ V versus SCE ($i_p^a/i_p^c = 0.7$, $\Delta E = E_{pa} - E_{pc} = 117$ mV), corresponding to one electron transfer process, ascribed to the reduction of the ligand, since the substitution of a more basic dpp ligand for two CO groups in [$Os_3(CO)_{12}$] complex to produce **2a**, should move the reduction process of the Os_3 core to a more cathodic potential. Free dpp showed in THF solution a quasi-reversible peak, $E_{1/2} = -1.83$ V versus SCE ($\Delta E = E_{pa} - E_{pc} = 90$ mV), corresponding to one electron transfer process.

The cathodic scan for complex **2b** revealed three reduction processes (peaks C–E). Peaks C and D correspond to one electron each, $E_p = -0.555$ V and -1.02 V versus SCE, and were attributed to the reduction of ligand. The broad peak E, $E_p = -1.64$ V versus SCE, has irreversible character and peak current almost four times as high as that of the corresponding peak current of C and could be ascribed to the subsequent reduction of fragments of Os_3 units, originated from the decomposition of complex **2b**, after the second reduction irreversible process of the ligand.

As mentioned above, the first two reduction peaks of the 1:2 ligand:cluster complex **2b** can be assigned specifically to the ligand. The co-ordination of the electron acceptor $Os_3(CO)_{10}$ moiety to the dpp decreases the electronic density on the bridging ligand. Therefore, dpp becomes much easier to reduce in the 1:2 than in the 1:1 ligand:cluster complex, and the ease of reduction potential follows the order **2b** > **2a** > dpp, in accordance with the energy stabilization of the ligand π^*-acceptor. This is clearly shown in the Fig. 2. The first two reduction waves in **2b** were mono-electronic and could be assigned to successive one-electron reductions of dpp. The splitting between these two waves was very high (ca. 0.46 V), as expected for two electrons that enter on the same ligand [5].

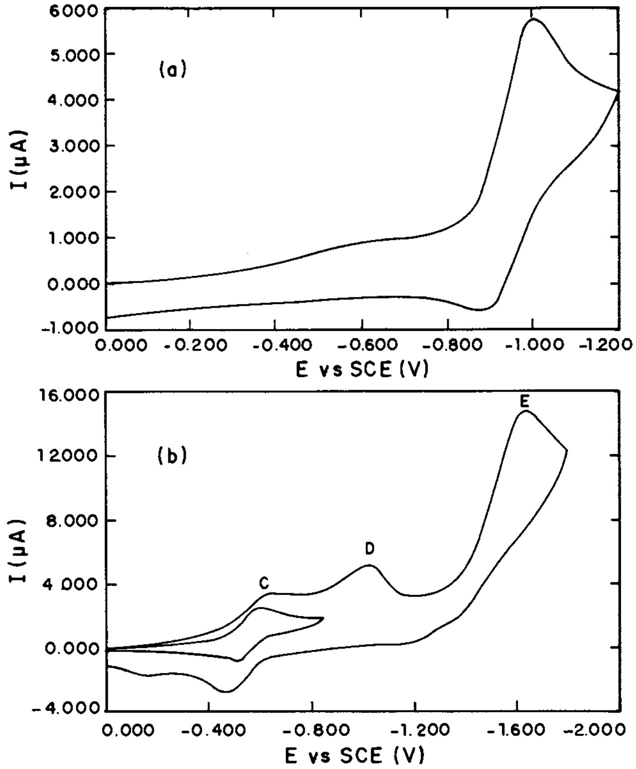


Fig. 2. CV response of a THF solution of (a) complex [$Os_3(CO)_{10}(dpp)$] **2a** and (b) [$\{Os_3(CO)_{10}]_2(dpp)$] **2b**, scan rate 200 mV s^{-1} at −100°C. The working electrode is a platinum disk 0.2 mm diameter.

The difference between the first reduction potential in the complexes **2a** and **2b**, could be due to the electronic interaction between the two metallic centers in the 1:2 ligand:cluster complex through the π-electrons of ligand. The electrochemical properties of previously synthesized bimetallic Ru(II) complexes with dpp indicate little [5,13,18,19] or none $[M(CO)_4]_2$dpp (M = Cr, Mo and W) [8] and $[\{Re(CO)_3Cl\}_2(dpp)]$ [14] interaction between the metal ion and was attributed to a non-planar configuration of the ligand due to $H_e/H_{e'}$ repulsion.

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