Communication

Electronic Interactions in [Ru$_3$(μ_3-R^{2}CCC$_6$H$_4$-4-R^1)(μ-dppm)(μ-CO)(CO)$_7$] (R^1 = NO$_2$ and R^2 = Fc; R^1 = NO$_2$, CN and R^2 = Ph)

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A coordenação de FcCCC$_6$H$_4$-NO$_2$ (**1**) a uma carbonila polinucleada (cluster) de rutênio resultou na formação de [Ru$_3$(μ_3-FcCCC$_6$H$_4$-4-NO$_2$)(μ-dppm)(μ-CO)(CO)$_7$] (**2**). Os voltamogramas cíclicos destes compostos e dos clusters análogos [Ru$_3$(μ_3-η^2-C$_6$H$_5$CCC$_6$H$_4$-4-R)(μ-dppm)(μ-CO)(CO)$_7$] (R= H, **3**; CN, **4**; NO$_2$, **5**) permitiram avaliar as comunicações eletrônicas entre os diferentes sítios de oxi-redução (grupos ferrocenil e -NO$_2$ e o fragmento Ru$_3$) e analisar as capacidades relativas doadora-receptora de cada um dos três centros de oxi-redução que compõem **2**. Além disto, a inércia de **2**, em comparação com os clusters **3-5**, os quais sofrem fácil perda de CO, foi atribuída à interação entre o grupo ferrocenil e a base metálica.

The co-ordination of FcCCC$_6$H$_4$-4-NO$_2$ (**1**) to a ruthenium carbonyl cluster to yield [Ru$_3$(μ_3-FcCCC$_6$H$_4$-4-NO$_2$)(μ-dppm)(μ-CO)(CO)$_7$] (**2**) is reported. The cyclic voltammograms of these compounds and of the analogous clusters [Ru$_3$(μ_3-η^2-C$_6$H$_5$CCC$_6$H$_4$-4-R)(μ-dppm)(μ-CO)(CO)$_7$] (R= H, **3**; CN, **4**; NO$_2$, **5**) allowed an evaluation of the electronic communications between the different redox sites (ferrocenyl and -NO$_2$ groups, and Ru$_3$ moiety) and an analysis of the relative electron donor-acceptor capabilities of each of the three redox centres that compose **2**. Furthermore, the inertness of **2**, compared with clusters **3-5** which loose CO readily was attributed to the interaction between the ferrocenyl group and the metallic frame.

Keywords: ruthenium cluster, ferrocene, alkyne, cyclic voltammetry

Introduction

Studies of electronic interactions in systems containing multiple redox-active centres are of fundamental importance in the development of molecular-based electronic devices.[1] Alkynes can be an elegant option in the search of systems containing multi-redox sites, once they can serve as conjugated bridges between groups of different electronic densities.[2] In addition, they are remarkably versatile in their co-ordinating abilities to different metals (σ or π-fashion), that can result in the generation of novel mono or polynuclear metal complexes with attractive properties.[3] Compounds derived from ferrocene have been extensively investigated for materials science[4] due to their low cost, stability and interesting redox properties, and can be used in molecular ferromagnets, molecular sensors, electrochemical agents, liquid crystals and non-linear optical materials.[5]

The aim of this work was to combine the electronic properties of alkynes, the ferrocenyl fragment and carbonyl clusters to build a new supramolecular compound containing various redox sites. Co-ordination of the ferrocenylalkyne FcCCC$_6$H$_4$-4-NO$_2$ (**1**) to a ruthenium carbonyl cluster to produce [Ru$_3$(μ_3-FcCCC$_6$H$_4$-4-NO$_2$)(μ-dppm)(μ-CO)(CO)$_7$] (**2**) was therefore investigated. In cluster **2**, the ferrocenyl fragment can act as an electron donor in charge-transfer processes,[6] the -NO$_2$ group as an electron acceptor[7] and the ruthenium moiety as a reservoir of electrons, depending on the co-ordinated ligands.[8] The analogous clusters [Ru$_3$(μ_3-η^2-C$_6$H$_5$CCC$_6$H$_4$-4-R)(μ-dppm)(μ-CO)(CO)$_7$] (R= H, **3**; CN, **4**; NO$_2$, **5**) were also synthesized for the sake of comparison of their electronic and chemical properties.

Results and Discussion

Co-ordination of **1**[9] and of the alkynes PhCCC$_6$H$_4$-4-R (R = NO$_2$ and CN)[10] to [Ru$_3$(CO)$_{12}$] to produce [Ru$_3$(μ_3-η^2-FcCCC$_6$H$_4$-4-NO$_2$)(μ-dppm)(μ-CO)(CO)$_7$] (**2**) and the analogous clusters **4** and **5**, respectively, (see Scheme) was carried out as described previously for other RCCR' (R =R' = H, Ph (**3**), Me and R = H, R' =Ph).[11,12] Compounds **2**

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and **4-5** were formulated on the basis of elemental analysis, IR and ^1H and $^{31}P\{^1H\}$ NMR spectroscopy.[13] In the ^{31}P NMR spectra of the unsymmetrical derivatives **2** and **4-5** the dppm phosphorus nuclei appear as two doublets (J_{P-P} ~130Hz) whose chemical shift difference decreases with the decreasing electronic asymmetry of the co-ordinated alkyne (**2**>**5**>**4**). This suggests that these compounds are isostructural with the symmetrical derivative **3**[11] whose dppm phosphorus atoms are equivalent and whose structure is proposed here to contain a CO and a dppm ligands bridging the same edge which is also parallel to the μ_3-η^2-alkyne[14] (see Scheme), although the X-ray molecular structure of the closely related cluster [Ru$_3$(μ_3-η^2-PhC$_2$CCPh)(μ-dppm)(μ-CO)(CO)$_7$] has been reported to be slightly different[15] with the bridging CO bonded to a different metal edge. Contrary to the analogous clusters **3**, **4** and **5** and other clusters of the series containing a dppm instead of two CO ligands,[11,16] it was impossible to decarbonylate **2** to yield the unsaturated cluster [Ru$_3$(μ_3-η^2-FcCCC$_6$H$_4$-4-NO$_2$)(μ-dppm)(CO)$_7$] with the alkyne bonded in the perpendicular mode. Compound **2** was stable when heated in toluene, at 80 °C, for 4 h, but upon increasing the temperature it underwent decomposition. Stabilisation of the alkyne bonded in this mode has been ascribed to the presence of the dppm that induces metal back donation to the alkyne.[17] The electron donating ferrocenyl group seems therefore to counteract the effect of the dppm, possibly by increasing the back donation from the metals to the CO ligands, which then become more strongly bonded to the metal base.
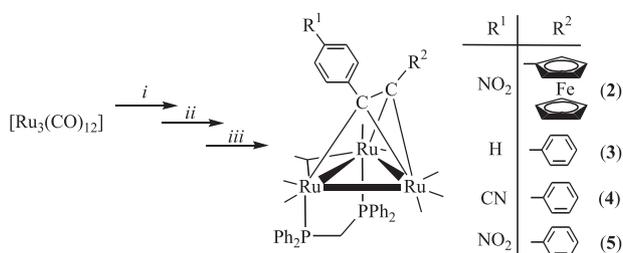
i) bis(triphenylphosphoranylidene)ammonium chloride (PPNCl) in THF/CH$_2$Cl$_2$ under argon; *ii*) alkyne; *iii*) dppm/CO in MeOH/CH$_2$Cl$_2$

Scheme

The relevant electrochemical data for compounds **1-5**, HCCC$_6$H$_4$-4-NO$_2$, PhCCC$_6$H$_4$-4-NO$_2$, and ferrocene are given in Table 1. Full cyclic voltammograms of **1** and **2** are shown in Figure 1, and (reduction) cyclic voltammograms of clusters **2-5**, in Figure 2.

The redox behaviour of **1** indicates that the ferrocenyl and -NO$_2$ groups are strongly coupled, since the oxidation
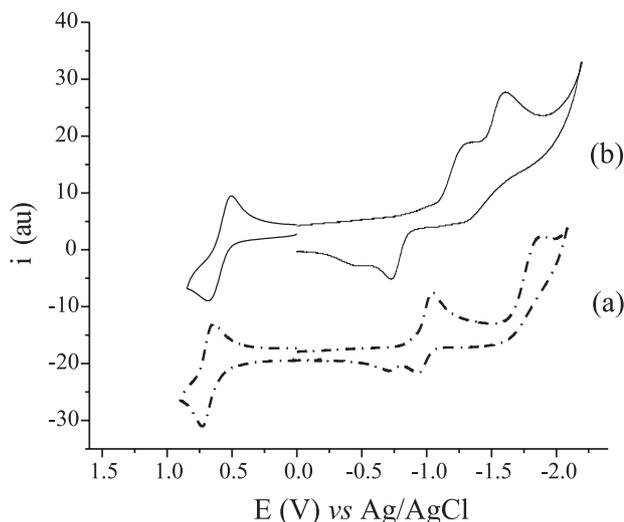
Figure 1. Cyclic voltammograms (CH$_2$Cl$_2$, 1x10^{-3} mol L^{-1}, 200 mV s^{-1}, RT): (a) alkyne **1**; (b) cluster **2**. The number of electrons involved in the redox processes was evaluated through normal pulse voltammetric experiments (*npv*) using ferrocene as standard, and comparing the intensity of the reduction potentials.
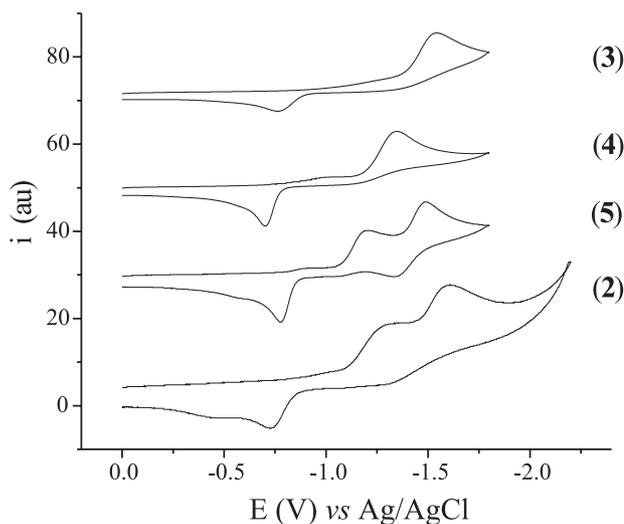
Figure 2. Cyclic voltammogram (reduction) of clusters **2-5** (CH$_2$Cl$_2$, 1x10^{-3} mol L^{-1}, 200 mV s^{-1}, RT).

and reduction potentials differ from those of the starting materials (ferrocene and HCCC$_6$H$_4$-4-NO$_2$). The cyclic voltammogram of **1** (Figure 1a) reveals in the anodic scan one chemically reversible one electron process at 0.73 V *vs* Ag/AgCl ($\Delta E_p = 78$ mV) ascribed to the ferrocenyl group. The E_{pa} of the ferrocenyl group in **1** (+0.73 V) is more anodic compared to that of ferrocene (+0.56 V) because of the ability of the -NO$_2$ to accept electronic density thus hindering oxidation of the ferrocenyl group. In the cathodic scan two one electron peaks were observed, both attributed to the -NO$_2$ group, the first of which is *quasi*-reversible, at

Table 1. Electrochemical data

Compound	E$_{pa}$/V (ΔE$_p$/mV)	E$_{pc}$/V (ΔE$_p$/mV)
HCCC$_6$H$_4$-4-NO$_2$	—	-1.25 (43)
C$_6$H$_5$CCC$_6$H$_4$-4-NO$_2$	—	-1.06 (45)
ferrocene	+0.56 (77)	—
1	+0.73 (78)	-1.05 (125) and -1.89 (irreversible)
2	+0.66 (160) and +1.12 (irreversible)	-1.31 (irreversible) and -1.62 (irreversible)
3	+0.84; +1.60 and +1.91 (all irreversible)	-1.54 (irreversible)
4	+1.18; +1.59 and +2.01 (all irreversible)	-1.35 (irreversible)
5	+1.02; +1.62 and +1.92 (all irreversible)	-1.21 (irreversible) and -1.50 (irreversible)

E$_{pa}$ = anodic potential; E$_{pc}$ = cathodic potential; ΔE$_p$ = (E$_{pa}$-E$_{pc}$)/n, where n = number of electron involved. Scan rate: 200 mVs^{-1} at room temperature. Solutions in CH$_2$Cl$_2$ were *ca* 1x10^{-3} mol L^{-1} with respect to the compounds and *ca* 1x10^{-1} mol L^{-1} with respect to the supporting electrolyte, [Bu$_4$N][ClO$_4$]. A Platinum-disk working electrode, a platinum-wire auxiliary electrode and a Ag/AgCl reference electrode were used in the experiments. Obs.: the alkynes PhCCPh and PhCCC$_6$H$_4$-4-CN did not show any reduction potential in these conditions.

−1.05 V vs Ag/AgCl (ΔE$_p$= 125 mV), and the second, irreversible, at −1.89 V vs Ag/AgCl.

The cyclic voltammogram of cluster **2** (Figure 1b) revealed in the anodic scan a one electron *quasi*-reversible process at +0.66 V vs Ag/AgCl (ΔE =165 mV) ascribed to the ferrocenyl group and an irreversible process at +1.12 V corresponding to the oxidation of the Ru$_3$ moiety. In the cathodic scan, two irreversible reduction processes most probably involving the transfer of two electrons as observed for other analogous Ru$_3$ systems[17] were identified: the one at -1.62 V vs Ag/AgCl, was ascribed to the reduction of the -NO$_2$ group and the other at −1.31 V vs Ag/AgCl was assigned to the reduction of the '[Ru$_3$dppm(CO)$_8$]' fragment. This assignment was confirmed by the observation of the corresponding process in the voltamograms of clusters **3-5**, which contain R^1 = H, -CN and -NO$_2$ respectively on the co-ordinated PhCCC$_6$H$_4$-4-R^1 (see Scheme). Compound **3** exhibited only one reduction wave at -1.54 V in the cathodic scan, attributed to the reduction of the Ru$_3$ moiety. Replacement of R^1 = H for the electron withdrawing groups -CN (compound **4**) and -NO$_2$ (compound **5**) led to the expected anodic shifts in the reduction of the Ru$_3$ moiety (E$_{pc}$ **4**= -1.35 V and E$_{pc}$ **5**= -1.21 V). The ΔE$_p$ of the irreversible reduction process decreased slightly from 335 mV (**3**) to 310 mV (**4**), however the presence of the -NO$_2$ group in compound **5** turned the process *quasi*-reversible (ΔE$_p$= 200 mV). Furthermore, as expected the NO$_2$ reduction potential (E$_{pc}$ **5** = -1.50 V) was more cathodic than that of free PhCCC$_6$H$_4$-4-NO$_2$ (E$_{pc}$= -1.06 V). The fact that the reduction process of the Ru$_3$ fragment in cluster **2** (E$_{pc}$ **2**= -1.31 V) occurs at an intermediate potential between those observed for **4** (-1.35 V) and **5** (-1.21 V), and that the reduction potential of the −NO$_2$ group in **2** (-1.62 V) is even more cathodic than in **5** (-1.50 V) indicate that the ferrocenyl interacts both with

the metallic frame and the -NO$_2$ group. Peaks around -0.7 V were observed in the voltammograms of clusters **2-5** and were ascribed to the oxidation of unidentified fragmentation products formed after the "irreversible" reductions.

In conclusion, in compound **2**, μ_3-η^2-// co-ordination of the C≡C bond of alkyne **1** to the '[Ru$_3$dppm(CO)$_8$]' fragment has led to a decrease in the interaction between the ferrocenyl and –NO$_2$ groups, most probably as the result of loss of linearity of the alkyne and lengthening of the C-C bond: from the molecular structure of the related species [Ru$_3$(μ_3-η^2-PhC$_2$CCPh)(μ-dppm)(μ-CO)(CO)$_7$],[15] average C-C-C angles (123°) and C=C bond [1.383(8)Å] are typical of sp^2 hybridization. However, the electrochemical data suggest that the three redox sites are not kept isolated in **2** and therefore that this cluster is a push-pull type molecule. Further evidence for the communication between the ferrocenyl group and the metallic frame comes from the peculiar inertness of cluster **2**, compared to clusters **3-5**, which readily undergo CO dissociation.

Acknowledgements

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13. Cluster **2** (yield: 30%): Anal. Calcd. for $C_{51}H_{33}NO_{10}P_2Ru_3Fe$: C 49.24, H 2.68, N 1.13. Found: C 49.42, H 2.65, N 1.27 %. IR (CH_2Cl_2, ν_{CO}/cm^{-1}): 2055s, 2000vs, 1973m, 1826vw. ^1H NMR ($CDCl_3$): δ 7.10-8.40(m, 4H, C_6H_4), 4.30(s, 5H, Cp), 4.20(m, 4H, C_5H_4), 3.70(m, 1H, CH_2), 3.10(m, 1H, CH_2). $^{31}P\{H\}$ NMR ($CDCl_3$): δ 35.7 (d, J_{P-P} 136Hz), 33.6 (d). $[Ru_3(\mu_3-\eta^2-C_6H_4CCC_6H_4-4-R)(\mu-dppm)(\mu-CO)(CO)_7]$ (R= H,[12] **3**; CN, **4**; NO_2, **5**): IR spectra in the ν_{CO} region similar to that of **2**. Compound **4** (yield: 56%), Anal. Calcd. for $C_{48}H_{21}NO_8P_2Ru_3$: C 51.71, H 2.80, N 1.26; Found: C 51.12, H 2.74, N 1.22. **5** (yield: 65%), Anal. Calcd. for $C_{47}H_{21}NO_{10}P_2Ru_3$: C 49.74, H 2.75, N 1.23; Found: C 50.53, H 2.87, N 1.17%. $^{31}P\{H\}$ NMR ($CDCl_3$): **3**: δ 35.5 (s);[12] **4**: δ 36.2 (d, J_{P-P} 132Hz), 34.9; **5** δ 36.5 (d, J_{P-P} 135Hz), 35.1 (d).

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