Electronic Interactions in \([\text{Ru}_3(\mu_3-R^2\text{CCC}_6\text{H}_4-4-R^1)(\mu-\text{dppm})(\mu-\text{CO})(\text{CO})_7]\) 
\((R^1 = \text{NO}_2\) and \(R^2 = \text{Fc}; R^1 = \text{NO}_2, \text{CN}\) and \(R^2 = \text{Ph})\)

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A coordenação de \(\text{FcCCC}_6\text{H}_4-4-\text{NO}_2\) (1) a uma carbonila polinucleada (cluster) de rutênio resultou na formação de \([\text{Ru}_3(\mu_3-\text{FcCCC}_6\text{H}_4-4-\text{NO}_2)(\mu-\text{dppm})(\mu-\text{CO})(\text{CO})_7]\) (2). Os voltamogramas cíclicos destes compostos e dos clusters análogos \([\text{Ru}_3(\mu_3-\eta^2-\text{C}_6\text{H}_5\text{CCC}_6\text{H}_4-4-R)(\mu-\text{dppm})(\mu-\text{CO})(\text{CO})_7]\) (R= H, 3; CN, 4; NO2, 5) permitiram avaliar as comunicações elétricas entre os diferentes sítios de oxido-redução (grupos ferrocenil e -NO2 e o fragmento Ru3) e analisar as capacidades relativas doadora-receptoras de cada um dos três centros de oxido-redução que compõem 2. Além disto, a inércia de 2, em comparação com os clusters 3-5, os quais sofreem fácil perda de CO, foi atribuída à interação entre o grupo ferrocenil e a base metálica.

**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, since 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 science4 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 \(\text{FcCCC}_6\text{H}_4-4-\text{NO}_2\) (1) to a ruthenium carbonyl cluster to produce \([\text{Ru}_3(\mu_3-\text{FcCCC}_6\text{H}_4-4-\text{NO}_2)(\mu-\text{dppm})(\mu-\text{CO})(\text{CO})_7]\) (2) was therefore investigated. In cluster 2, the ferrocenyl fragment can act as an electron donor in charge-transfer processes,6 the -NO2 group as an electron acceptor7 and the ruthenium moiety as a reservoir of electrons, depending on the co-ordinated ligands.8 The analogous clusters \([\text{Ru}_3(\mu_3-\eta^2-\text{C}_6\text{H}_5\text{CCC}_6\text{H}_4-4-R)(\mu-\text{dppm})(\mu-\text{CO})(\text{CO})_7]\) (R= H, 3; CN, 4; NO2, 5) were also synthesized for the sake of comparison of their electronic and chemical properties.

**Results and Discussion**

Co-ordination of 1° and of the alkynes \(\text{PhCCC}_6\text{H}_4-4-R\) (R = NO2 and CN)10 to \([\text{Ru}_3(\text{CO})_7]\) to produce \([\text{Ru}_3(\mu_3-\eta^2-\text{FcCCC}_6\text{H}_4-4-\text{NO}_2)(\mu-\text{dppm})(\mu-\text{CO})(\text{CO})_7]\) (2) and the analogous clusters 4 and 5, respectively, (see Scheme) was carried out as described previously for other \(\text{RCCR}’\) (R =R’ = H, Ph (3), Me and R = H, R’ =Ph).11,12 Compounds 2
and 4-5 were formulated on the basis of elemental analysis, IR and $^1$H and $^{31}$P{$^1$H} NMR spectroscopy. 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 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 $\mu$-$\eta^2$-alkyne (see Scheme), although the X-ray molecular structure of the closely related cluster [Ru$_3$(µ$_3$-$\eta^2$-PhC$_2$CCPh)(µ-dppm)(µ-CO)(CO)$_7$] has been reported to be slightly different 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, it was impossible to decarboxylate 2 to yield the unsaturated cluster [Ru$_3$(µ$_3$-$\eta^2$-FcCCC$_6$H$_4$-4-NO$_2$)(µ-dppm)(µ-CO)(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. 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.

![Scheme](image)

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 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

![Figure 1](image)

![Figure 2](image)
–1.05 V vs Ag/AgCl (ΔE = 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 Ru3 moiety. In the cathodic scan, two irreversible reduction processes most probably involving the transfer of two electrons as observed for other analogous Ru3 systems27 were identified: the one at –1.62 V vs Ag/AgCl, was ascribed to the reduction of the -NO2 group and the other at –1.31 V vs Ag/AgCl was assigned to the reduction of the [Ru3(dpmm)(CO)7]µ+ fragment. This assignment was confirmed by the observation of the corresponding process in the voltammograms of clusters 3-5, which contain R1 = H, -CN and -NO2 respectively on the co-ordinated PhCCC6H4-4-R1 (see Scheme). Compound 3 exhibited only one reduction wave at –1.54 V in the cathodic scan, attributed to the reduction of the Ru3 moiety. Replacement of R1 = H for the electron withdrawing groups -CN (compound 4) and -NO2 (compound 5) led to the expected anodic shifts in the reduction of the Ru3 moiety (Epa = –1.35 V and Epa = –1.21 V). The ΔEp of the irreversible reduction process decreased slightly from 335 mV (3) to 310 mV (4), however the presence of the -NO2 group in compound 5 turned the process quasi-reversible (ΔEp = 200 mV). Furthermore, as expected the NO2 reduction potential (Epa = –1.50 V) was more cathodic than that of free PhCCC6H4-4-NO2 (Epa = –1.06 V). The fact that the reduction process of the Ru3 fragment in cluster 2 (Epa = –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 –NO2 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 -NO2 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-η2-µ-η2-µ-η2-µ-η2/µ-η2-co-ordination of the C≡C bond of alkyne 1 to the [Ru3(dpmm)(CO)7]µ+ fragment has led to a decrease in the interaction between the ferrocenyl and –NO2 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 [Ru3(µ-η2-PtPh3)(µ-dpmm)(µ-CO)(CO)3]15 average C-C-C angles (123°) and C≡C bond [1.383(8)Å] are typical of sp2 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.

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References

13. Cluster 2 (yield: 30%); Anal. Calcd. for C_{n}H_{m}NO_{p}P_{q}Ru:F: C 49.20, H 2.68, N 1.13. Found: C 49.42, H 2.65, N 1.27 %. IR (CH_{2}Cl_{2}, ν_{CO}/cm^{-1}): 2055s, 2000vs, 1973m, 1826vw. NMR (CDCl_{3}; δ 7.10-8.40(m, 4H, C_{6}H_{4}), 4.30(s, 5H, Cp), 4.20(m, 4H, C_{5}H_{4}), 3.70(m, 1H, CH_{2}), 3.10(m, 1H, CH_{2}). 31P{H} NMR (CDCl_{3}; δ 35.7 (d, J_{P-P} 136Hz), 33.6 (d). [Ru(μ-η^{2}-C_{6}H_{4}CCC_{6}H_{4}-4-R)(μ-dppm)(μ-CO)(CO)]) (R= H, 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_{6}H_{8}NO_{2}P_{2}Ru: 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_{6}H_{8}NO_{2}P_{2}Ru: C 49.74, H 2.75, N 1.23; Found: C 50.53, H 2.87, N 1.17%. 31P{H} NMR (CDCl_{3}; δ 35.5 (s); 12 3: δ 36.2 (d, J_{P-P} 132Hz), 34.9; 5 δ 36.5 (d, J_{P-P} 135Hz), 35.1 (d). 14. Rosseto, R.; Stein, E.; Vargas, M. D.; manuscript in preparation.

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