

the higher partial molar volume of the film (compared with the one of the metal) would prevail, thus causing the rupture.

Returning again to the analysis of Figure 2, region II points out that, in the correspondent OH⁻ concentrations, dissolution, rupture and/or more growth of the film with posterior rupture processes could exist.

REFERENCES

1. D.D. MacDonald, *Transient Techniques in Electrochemistry*, New York, Plenum, 1977, p.290.
2. S. Srinivasan and E. Gileadi, *Electrochim. Acta*, 11, 321 (1966).
3. A.J. Calandra, N.R. de Tacconi, R.Pereiro and A.J.Arvia, *Electrochim. Acta*, 19, 901 (1974).
4. H. Kozłowska and B.E. Conway, *J. Electroanal. Chem.*, 95, 1 (1979).
5. C.V. D'Alkaine and J.M. Cordeiro, In: *Advances in Lead-Acid Batteries* (K.R. Bullock and D. Pavlov, Eds.). Pennington, The Electrochemical Society, 1984.v.84-14 p. 190-200.
6. S.R. Biaggio, *Ph.D.Thesis*, São Paulo University, IFQSC, São Carlos (1986).
7. N. Bocchi, *Ph.D.Thesis*, *ibid*, (1986).
8. N. Sato, *Electrochim. Acta.*, 16, 1683 (1971).

ELECTROCHEMICAL STUDY OF ISOCYANIDE DERIVATIVES OF FERROCENE AND OF THEIR COMPLEXES WITH THE {Cr(CO)₅} CENTRE

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INTRODUCTION

Within our broad interest on the study of the redox and electronic properties of coordination compounds by electrochemical methods,⁽¹⁾ we embarked upon the investigation of the redox behaviour of series of ferrocene derivatives, FcX [where Fc stands for Fe(η^5 -C₅H₅)(η^5 -C₅H₄)], with different types of substituents (X);⁽²⁾ the latter may ligate an aromatic ring through, for instance, a sp³ or an unsaturated sp² hybridized C atom, and some homo- and hetero-annular disubstituted ferrocenes have also been investigated. However, in this preliminary communication, we wish to report the results we have obtained with a type of substituents we are particularly interested⁽³⁻⁵⁾ from a coordination point of view: that with the isocyano functional group.

In the ferrocene derivatives under study, CNR [1; R=Fc (a), CH₂Fc (b) or CH(Men)Fc (c) where Men=(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl], the isocyano group is prone to coordination to a metal centre and the derived ferrocenyl-isocyanide complexes [Cr(CO)₅(CNR)] (2) can be prepared by reaction of the former with [Cr(CO)₅(thf)].

The electrochemical study, by CV and CPE, of these species was performed at a Pt electrode, in NCMe - 0.2 M [NBu₄][BF₄].

FERROCENYLISOCYANIDE COMPOUNDS (1)

Each of the ferrocenylisocyanides (1) shows a quasi-reversible one-electron oxidation, and relevant CV data are quoted in Table 1.

The E_{1/2}^{ox} values fall in the usual range observed^(2,6) for other substituted ferrocene compounds and, as reported for the latter, the anodic wave is assigned to the oxidation of the ferrocenyl redox centre.

Although compounds (1b) and (1c) present E_{1/2}^{ox} values which are only slightly more anodic than that known⁽²⁾ for the oxidation of ferrocene (0.545 V vs. SCE), complex (1a), with the electron-acceptor isocyano group directly bound to an aromatic ring, displays a much higher E_{1/2}^{ox} (0.85 V, a value which is ca. +0.30 V more anodic than that of ferrocene). This observation indicates a much stronger effect of the isocyano substituent on the ferrocenyl redox centre, possibly as a result of the interaction of a π* orbital of the former with the π-system of the latter. A somehow related type of π-interaction, although involving the p_z orbital of a sp² hybridised carbene carbon atom, has been suggested for ferrocenylcarbene species.^(2,7)

FERROCENYLISOCYANIDE COMPLEXES WITH
PENTACARBONYLCHROMIUM (2)

Cyclic voltammograms of complexes (2) (Table 1) exhibit two successive one-electron quasi-reversible anodic waves which are assigned to the stepwise oxidation of the two metal sites, the ferrocenyl redox centre being easier to oxidize than the {Cr(O)₅} moiety (equation 1).

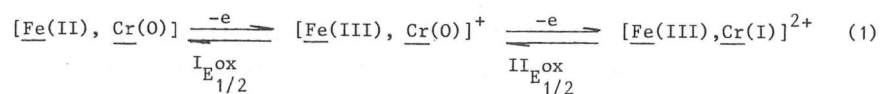


Table 1 - Relevant CV data^(a) for ferrocenylisocyanides CNR (1) and their complexes [Cr(CO)₅(CNR)] (2); P_L ligand parameter for the oxidized isocyanide CNR⁺ ligands

Compound	I _{E1/2} ^{ox}	II _{E1/2} ^{ox}	P _L (CNR ⁺)
<u>CNR</u>			
CNFc (1a)	0.85		
CNCH ₂ Fc (1b)	0.60		
CNCH(Men)Fc (1c)	0.62		
<u>[Cr(CO)₅(CNR)]</u>			
[Cr(CO) ₅ (CNFc)] (2a)	0.85	1.31	
[Cr(CO) ₅ (CNCH ₂ Fc)] (2b)	0.67	1.25	
[Cr(CO) ₅ (CH(Men)Fc)] (2c)	0.65	1.25	
<u>CNR⁺</u>			
CNFc ⁺			-0.22
CNCH ₂ Fc ⁺			-0.28
CNCH(Men)Fc ⁺			-0.28

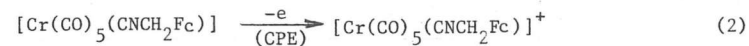
(a) Values in Volt relative to SCE, measured in 0.2 M [NBu₄][BF₄]/NCMe at a Pt wire electrode

The evidence is as follows:

- i - The first anodic wave presents $E_{1/2}^{ox}$ at values which fall in the usual range of the ferrocenyl compounds,⁽²⁾ whereas the second anodic wave occurs at $E_{1/2}^{ox}$ values which are in the range known for the oxidation of related $[\text{Cr}(\text{CO})_5\text{L}]$ complexes [e.g., $\text{L}=\text{CO}$ ⁽⁸⁾ or CNMe ,⁽⁹⁾ with corresponding $E_{1/2}^{ox}$ at 1.53 or 1.10 V vs SCE].

Moreover, since the ferrocenyl and the methyl substituents appear to have similar electron donor abilities (as measured by the Hammett's σ_p constant, with values of ca. -0.18 and -0.17; respectively),⁽¹⁰⁾ the hypothetical oxidation of $\text{Cr}(\text{O})$ at complex (2a) should occur at a value of $E_{1/2}^{ox}$ close to that known (1.10 V)⁽⁹⁾ for $[\text{Cr}(\text{CO})_5(\text{CNMe})]$; the observed value of 0.85 V for the first anodic wave of (2a) is well below this estimated value.

- ii - CPE at the first anodic wave of (2b) affords $[\text{Cr}(\text{CO})_5(\text{CNCH}_2\text{Fc})]^+$ (equation 2), isolated as the BF_4^- salt, which displays the expected CV behaviour, and shows, in the i.r. spectrum, $\nu(\text{CN})$ at 2105 cm^{-1} (a value which is lower than that observed, 2165 cm^{-1} , in the neutral parent complex), whereas $\nu(\text{CO})$ is only slightly shifted from 1905 (in the parent compound) to 1915 cm^{-1} . These observations are only rationalized by considering the oxidation at the $\text{Fe}(\text{II})$ rather than at the $\text{Cr}(\text{O})$ site.



Other related complexes with a ferrocenyl-containing ligand are known to present a similar electrochemical behaviour, with discrete oxidation steps for the distinct redox active metal centres.

Hence, e.g., $[\text{M}(\text{CO})_5\text{L}]$ ($\text{M}=\text{Mo}$ or W , $\text{L}=\text{PPh}_{3-n}\text{Fc}_n$, $n=1-3$), with a ferrocenylphosphine ligand (L), undergo a sequence of anodic processes at the ferrocenyl and the coordinated M centres.^(11,12) For example, cyclic voltammograms of $[\text{W}(\text{CO})_5(\text{PPh}_2\text{Fc})]$, in $\text{CH}_2\text{Cl}_2/0.2\text{M} [\text{Bu}_4\text{N}][\text{ClO}_4]$, at a Pt electrode, show the ferrocenyl reversible redox wave at $E_{1/2}^{ox} = 0.76 \text{ V}$ and an irreversible tungsten

anodic wave at 1.54 V vs. SCE, whereas $[\text{W}(\text{CO})_5(\text{P}^{\text{Fc}}_3)]$ exhibits three reversible redox waves at 0.64, 0.82 and 0.90 V (due to the stepwise oxidation of the three ferrocenyl centres) followed by a fourth, irreversible, anodic wave at $E_p^{ox} = 1.92 \text{ V}$ vs. SCE associated with the W centre.⁽¹¹⁾

P_L LIGAND PARAMETER FOR THE OXIDIZED FERROCENYLISOCYANIDES, CNR^+

The detection of the oxidation of the $\{\text{Cr}(\text{CO})_5\}$ centre at the cationic $[\text{Cr}(\text{CO})_5(\text{CNR}^+)]$ complexes allows one to estimate the values of the P_L ligand parameter for the cationic ferrocenylisocyanide ligand, CNR^+ [$\text{R}=\text{Fc}$, CH_2Fc or $\text{CH}(\text{Men})\text{Fc}$].

This parameter is defined⁽¹³⁾ by equation (3) which, in these systems, assumes form (4); it is a measure of the net electron donor/acceptor character of the ligand: the stronger in this character, the lower (i.e., the more negative) is P_L .

$$P_L = E_{1/2}^{ox} [\text{Cr}(\text{CO})_5\text{L}] - E_{1/2}^{ox} [\text{Cr}(\text{CO})_6] \quad (\text{volt}) \quad (3)$$

$$P_L = E_{1/2}^{ox} [\text{Cr}(\text{CO})_5(\text{CNR})] - 1.53 \quad (4)$$

The P_L values estimated for those ferricinium-isocyanide ligands (Table 1) fall in a narrow range (-0.22 to -0.28 V) which indicates that they do not differ considerably in their electron donor ability, the CNFc^+ ligand being, as expected, a slightly poorer donor than the others. These ligands behave as better net electron donors than, e.g., $\text{P}(\text{O}^{\text{Ph}})_3$, or CO (with $P_L = -0.18$ or 0.00 V , respectively)⁽¹³⁾ but are weaker than PPh_3 ($P_L = -0.35 \text{ V}$).⁽¹³⁾

The P_L values of CNR^+ are much higher than those known for related neutral isocyanide ligands,^(4,13) in agreement with the increase of the electron withdrawing ability of the isocyanides as a result of the oxidation of the substituent. Since P_L of the neutral CNFc ligand is not expected to differ significantly from that of CNMe (see above), with a value of -0.43 V, this suggests that the positive charge at the isocyanide substituent has a positive effect of ca. +0.2 V on the P_L value.

FINAL REMARKS

Up to this study we applied electrochemical methods to the investigation of the electronic properties of isocyanide ligands binding different transition-metal phosphinic sites of Mo,⁽³⁾ W,⁽³⁾ Re⁽⁴⁾ or Fe,⁽⁵⁾ but we were limited to the common case where the isocyanide substituent was a redox inactive group at the potential range under study. We have now extended our research to a situation where the isocyanide R moiety is redox active, presenting the ferrocenyl group, and the ligating metal site is pentacarbonyl-chromium.

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REFERENCES

- (1) See, e.g., A.J.L. Pombeiro, Portugaliae Electrochimica Acta, 1983, 1, 19 and references cited therein.
- (2) R. Herrmann, A.J.L. Pombeiro, M.E.N.P. Rodrigues, I. Ugi, Portugaliae Electrochimica Acta, 1984, 2, 57
- (3) J. Chatt, C.M. Elson, A.J.L. Pombeiro, R.L. Richards, G.H.D. Royston, J.C.S. Dalton, 1978, 165.
- (4) A.J.L. Pombeiro, Inorg. Chim. Acta, 1985, 103, 95; A. J.L. Pombeiro, Rev. Port. Quím., 1981, 23, 179; A.J.L. Pombeiro, C.J. Pickett, R.L. Richards, J. Organometal. Chem., 1982, 224, 285
- (5) M.A.N.D.A. Lemos, A.J.L. Pombeiro, J. Organometal. Chem., 1987, 332, C17.
- (6) J.C. Kotz, Ch.3 in "Topics in Organic Electrochemistry", A.J. Fry and W.E. Britton, Eds., Plenum Publ. Corp., 1986.
- (7) E.O. Fischer, F.J. Gammel, J.O. Besenhard, A. Frank, D. Neugebauer, J. Organometal. Chem., 1980, 191, 261.
- (8) C.J. Pickett, D. Fletcher, J.C.S. Dalton, 1975, 879
- (9) M.K. Lloyd, J.A. McCleverty, D.G. Orchard, J.A. Connor, M.B. Hall, I.H. Hillier, E.M. Jones, G.K. McEwen, J.C.S. Dalton, 1973, 1743.
- (10) A.N. Nesmeyanov, E.G. Perevalova, S.P. Gubin, K.I. Grandberg, A.G. Kozlovsky, Tetrahedron Letters, No. 22, 1966, 2381.
- (11) J.C. Kotz, C.L. Nivert, J.M. Lieber, R.C. Reed, J. Organometal. Chem., 1975, 91, 87
- (12) J.C. Kotz, C.L. Nivert, J. Organometal. Chem., 1973, 52, 387
- (13) J. Chatt, C.T. Kan, G.J. Leigh, C.J. Pickett, D.R. Stanley, J.C.S. Dalton, 1980, 2032.