

STUDY OF THE ELECTROCHEMICAL BEHAVIOUR OF THE CYANAMIDE COMPLEXES OF RHENIUM(I), $\text{trans}-[\text{Re}(\text{CNR})(\text{NCR}_1)(\text{dppe})_2]^+$ ($\text{R}_1=\text{NH}_2$ or $\text{NHC}(\text{NH})\text{NH}_2$).

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INTRODUCTION

In order to have a better insight into the electronic features of cyanamide and cyanoguanidine as ligands we have prepared some new complexes of general formula $\text{trans}-[\text{Re}(\text{CNR})(\text{NCR}_1)(\text{dppe})_2]\text{BF}_4^-$ [$\text{R}=\text{Me}$ or Bu^t ; $\text{R}_1=\text{NH}_2$ or $\text{NHC}(\text{NH})\text{NH}_2$] and studied their electrochemical behaviour by cyclic voltammetry and, in one case, by controlled potential electrolysis.

Since the electronic properties of a ligand can be evaluated through their influence on the redox properties of the binding centre, as indicated by the electrochemical $\bar{\rho}_L$ ligand parameter [1] (a measure of the net π -acceptor minus σ -donor ability), we have also estimated the values of this parameter for the cyanamide and cyanoguanidine ligands which thus have been correlated with related species binding the same metal centre.

RESULTS AND DISCUSSION

Substitution of chloride by another ligand (L) at complexes $\text{trans}-[\text{ReCl}(\text{CNR})(\text{dppe})_2]$, using TlBF_4 as a chloride abstractor, is a general procedure to obtain the cationic species $\text{trans}-[\text{Re}(\text{CNR})(L)(\text{dppe})_2]^+$ [2,3]. Using this method we have obtained compounds where L is either cyanamide or cyanoguanidine (and CNR is the methyl or the t-butyl isocyanide).

The study by cyclic voltammetry of the anodic behaviour of these complexes, in an aprotic solvent (either tetrahydrofuran or dichloromethane) using tetrabutylammonium tetrafluoroborate as electrolyte and a platinium working electrode, shows, for each

of them, a first quasi-reversible single electron oxidation process at an half-wave oxidation potential, 0.38-0.42V versus s.c.e. (table 1), attributed to the Re(I)->Re(II) oxidation. These systems also display a second irreversible oxidation wave at a higher potential (1.3-1.5V), apart from a third wave, only seen in CH_2Cl_2 .

Table 1 Electrochemical data^a for complexes $\text{trans-}[\text{Re}(\text{CNR})(\text{NCNR}_1)(\text{dppe})_2]\text{BF}_4$ [R=Me, $\text{R}_1=\text{NH}_2$ (Ia), $\text{R}_1=\text{NHC}(\text{NH})\text{NH}_2$ (IIa); R=Bu^t, $\text{R}_1=\text{NH}_2$ (Ib)] and $\text{trans-}[\text{Re}(\text{NCNH})(\text{CNR})(\text{dppe})_2]$ (R=Me (IIIa) or Bu^t (IIIb))

COMPLEX	$E_{\frac{1}{2}}^{\text{ox}}$	$E_{\frac{1}{2}}^{\text{ox}}$	$E_{\frac{1}{2}}^{\text{ox}}$	$E_{\frac{1}{2}}^{\text{ox}}$	E_{red}
	I	II	III	C	B _p
Ia	0.38	(1.05)	1.34	-0.76	
Ib	0.42	(1.21)	1.40	-0.85	
IIa	0.41	(1.24)	1.45	-1.25	
IIIa	-0.06	0.52		-1.11	
IIIb	-0.09	0.48		-1.26	

a) Values in Volt/20 mV versus s.c.e., measured by cyclic voltammetry (at 100 mVs⁻¹), at a Pt electrode, in thf (unless stated otherwise) /0.2 M [Bu₄N][BF₄], by using as internal standard [$\text{Fe}(\eta^5\text{C}_5\text{H}_5)_2$]^{0/+} ($E_{\frac{1}{2}}=0.545\text{V}$) or $\text{trans-}[\text{ReCl}(\text{CNMe})(\text{dppe})_2]$ ($E_{\frac{1}{2}}=0.08\text{V}$). b) Values in parentheses for irreversible waves. c) In CH_2Cl_2 .

Both complexes $[\text{Re}(\text{CNR})(\text{NCNR}_1)(\text{dppe})_2]^+$ [I; $\text{R}_1=\text{NH}_2$; R=Me(a) or Bu^t(b). II; $\text{R}_1=\text{NHC}(\text{NH})\text{NH}_2$; R=Me(a)] display, upon cathodic sweep, an irreversible one-electron cathodic wave, as measured by controlled potential electrolysis of complex (Ia). The reduction of complexes $\text{trans-}[\text{Re}(\text{CNR})(\text{NCNH}_2)(\text{dppe})_2]\text{BF}_4$ followed by cyclic voltammetry generates a new species (figure) which undergoes two reversible oxidation processes. The wave at a higher potential partially superimposes that of the Re(I)->Re(II) process for the parent complex. The intensity of the generated waves depends on the scan rate (at higher scan rates the conversion into the product is more clearly observed, but this behaviour has not yet been fully investigated).

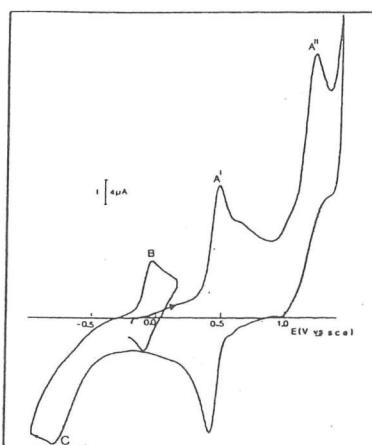


Figure-Cyclic voltammogram of $\text{trans-}[\text{Re}(\text{CNMe})(\text{NCNH}_2)(\text{dppe})_2]\text{BF}_4$ at a Pt electrode. I, II first and second anodic waves, respectively. C-cathodic wave. B-first anodic wave of the cathodically generated (at C) complex.

The cathodically generated waves are attributed to new complexes formed upon the redox induced dehydrogenation of cyanamide. These species are also obtained by chemical reaction of $\text{trans-}[\text{Re}(\text{CNR})(\text{NCNH}_2)(\text{dppe})_2]\text{BF}_4$ with a base, such as Et₃N or Bu^tOK, and characterized as $\text{trans-}[\text{Re}(\text{NCNH})(\text{CNR})(\text{dppe})_2]$, and the study of their electrochemical behaviour confirms the abovementioned interpretation of the cathodic behaviour of the cyanamide complexes. These neutral complexes, $\text{trans-}[\text{Re}(\text{NCNH})(\text{CNR})(\text{dppe})_2]$ (III), obtained by chemical deprotonation of bound cyanamide, display by cyclic voltammetry two reversible single-electron oxidation waves. The first one, corresponding to the Re(I)->Re(II) oxidation, occurs at a potential considerably lower than that of their parent complexes (table 1) in agreement with the expected better electron σ-donor and/or worse π-acceptor ability of the anionic hydrogen-cyanamide ligand (NCNH) compared with cyanamide.

In contrast with cyanamide complexes, the cyanoguanidine compound (IIa) does not "lead to the NCNH complex upon electrochemical reduction. However, addition of base to a solution of (IIa), in the electrochemical cell, results in a new

anodic wave at a lower potential than that corresponding to the Re(I)→Re(II) oxidation of the original species. The characterization of the derived product is under progress.

Since the net electron donor/acceptor character of a ligand (as measured by P_L) can be correlated with the redox potential of its complexes by equation $E_{\frac{1}{2}}^{OX} = E_S + \beta P_L$ [1], where the E_S (electron-richness) and β (polarizability) parameters are known [3] for the $\text{trans}-\{\text{Re}(\text{CNMe})(\text{dppe})_2\}^+$ metal site, we have estimated P_L for the N-containing ligands of this study and compared their electron donor/acceptor properties.

The calculated P_L values for cyanamide and cyanoguanidine are similar (-0.85 and -0.81V, respectively) thus indicating similar electronic properties, although cyanoguanidine behaves as a slightly weaker net electron donor.

The considerably lower values of the P_L parameter for cyanamide and cyanoguanidine when compared with, for instance, acetonitrile ($P_L=-0.57$) or methyl isocyanide ($P_L=-0.17$) when coordinated at the same binding centre, indicate a higher net electron donor ability for the former ligands. Moreover, hydrogen-cyanamide (NCNH^-) presents a rather low P_L value (-1.34V, which is even lower than that known for Cl^-), thus reflecting an even better electron donor character, in view of its anionic charge.

REFERENCES

- [1]- J.Chatt, C.T.Kan, G.J.Leigh, C.J.Pickett, D.R.Stanley, J. Chem.Soc., Dalton Trans. (1980) 2032
- [2]- A.J.L.Pombeiro, C.J.Pickett, R.L.Richards, J.Organometal. Chem., 224 (1982) 285
- [3]-M.F.N.N.Carvalho, A.J.L.Pombeiro, J.Chem.Soc., Dalton Trans., (1989) 1209

COMPORTAMIENTO ELECTROQUÍMICO DEL POLIPIRROL EN MEDIO POLIESTIRENSULFONATOSODICO.

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Resumen:

Se han preparado películas de PPy en medio poliestirensulfonato sódico (NaPSS), potencióstática y potenciodinámicamente.

Se ha hecho el estudio electroquímico a diferentes velocidades de barrido. Se ha medido la conductividad de las películas crecidas sobre platino y se han hecho micrográficas de barrido electrónico (SEM) a fin de poder esclarecer su textura, utilizando contraiones de carácter hidrofílico polar polímericos.

Introducción.

El análisis de los trabajos publicados en los últimos doce años sobre la generación de portadores de carga en los sistemas poliméricos conjugados y su transporte a lo largo y a través de las cadenas, pone de manifiesto las dificultades de investigación e interpretación del mecanismo de la conductividad eléctrica en estos sistemas. El PPy es un buen ejemplo de esta situación, por lo que no podemos decir que su estructura, entrecruzamiento y morfología estén bien definidos (1).

El uso del poliestirensulfonatosodico (NaPSS) como contraión hace que la distribución de este contraión polímero no sea homogénea en la matriz del PPy y no tenga facilidad para su salida de esta en el proceso de reducción (2), hecho que debe ponerse de manifiesto en el trazado de los voltamogramas en este medio (3-4). Hemos estudiado potenciodinámicamente este efecto. Por la obtención de micrografías de barrido electrónico (SEM) a películas de diferentes espesores, hemos aportado datos sobre la textura sólida obtenida, de excelente flexibilidad y características semejantes a las descritas por Kanazawa y col (4).

La medida de conductividad eléctrica potencia su mayor aplicación como electrodos