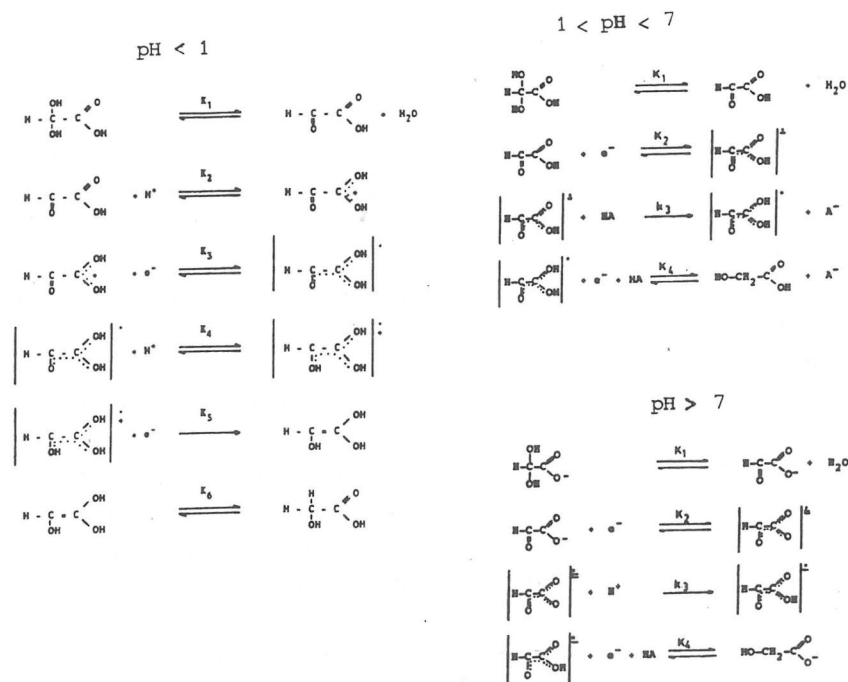


los órdenes de reacción, proponemos los siguientes mecanismos de reducción del ácido glicólico en los diferentes intervalos de pH estudiados:



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ELECTROCHEMICAL BEHAVIOUR OF SOME DINUCLEAR CARBENE COMPLEXES OF Pd OR Pt[†]

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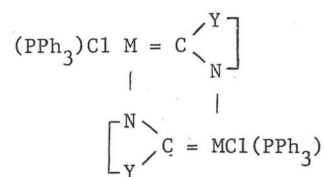
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Introduction

The electrochemical investigation of carbene complexes remains virtually unexplored in spite of the extensive chemistry which has been developed for these species. Therefore, in pursuit of our interest on complexes with multiple metal-carbon bonds [1], we have initiated the electrochemical study of carbene and carbyne complexes of rhenium [2], namely the aminocarbyne species $\text{trans-}[\text{ReCl}(\text{CNHR})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)_2]^+$ (R = H or alkyl) which have been derived upon electrophilic (protic) attack at a ligating isocyanide. Anodic oxidation of these complexes results in proton loss from the aminocarbyne ligand to regenerate the parent isocyanide species, although in an oxidized form.

We now extend this study to Pd and Pt complexes with other types of isocyanide-derived multiple metal-carbon bonded species, the dinuclear carbene complexes formulated as $[(\text{PPh}_3)_2\text{M}(\mu\text{-CYCH}_2\text{CH}_2\text{N-C,N})_2]$ (1; M=Pd or Pt; Y = O, NC₆H₄OMe-4 or NMe), which present the following type of cyclic structure:

[†]Dedicated to the memory of Dr. Joaquim Almeida, a conscientious Pd/Pt-Chemist and a Friend (A.J.L.P.).



Results and discussion

Upon cyclic voltammetry, at a Pt electrode, in NCMe (or CH_2Cl_2)/0.2 M $[\text{Bu}_4\text{N}][\text{BF}_4]$, the aminocarbene complexes (1, $\text{Y} = \text{NC}_6\text{H}_4\text{OMe-4}$ or NMe) undergo a sequence of irreversible anodic waves (3 or 4) with E_p^{ox} in the 0.8-1.9 V (vs. s.c.e.) range (Table). The first two waves overlap partially, are denoted by I and I', and occur at potentials not exceeding ca. 1.1 V (Fig.).

However, for the alkoxy-carbene (1, $\text{Y}=\text{O}$), the first wave is observed at a much higher potential, 1.67 V, at the accessible potential limit imposed by the solvent discharge (CH_2Cl_2 rather than NCMe due to insufficient solubility in the latter solvent).

The high increase of E_p^{ox} when going from the amino- to the alkoxy-carbene ligand ($\text{Y} = \text{NR}$ or O , respectively) parallels the known [3] higher resistance of ethers compared to amines towards oxidation and suggests that the corresponding anodic processes may involve oxidation of the carbene ligands. This is also supported by controlled potential electrolyses (C.P.E.) followed by acid-base titration of the electrolyzed solutions which indicate that proton loss is coupled to the anodic electron transfer.

In fact, by C.P.E., the first anodic waves (I and I') for (1, $\text{Y} = \text{NR}$) involve an overall transfer of ca. 2 electrons with liberation of the same number of protons (measured by acid-base titration), whereas the following wave (II) corresponds to larger and identical numbers of electrons and protons.

Moreover, addition of a base (pyridine) leads to an increase of the C.V. current-functions for those waves, in agreement with the expected promoting effect of proton evolution.

The obtained results can be interpreted on the basis of anodically induced N-H and C-H bond cleavage involving, in the latter case, the methylene moieties of the carbene ligands activated by adjacent amino- or oxy-groups.

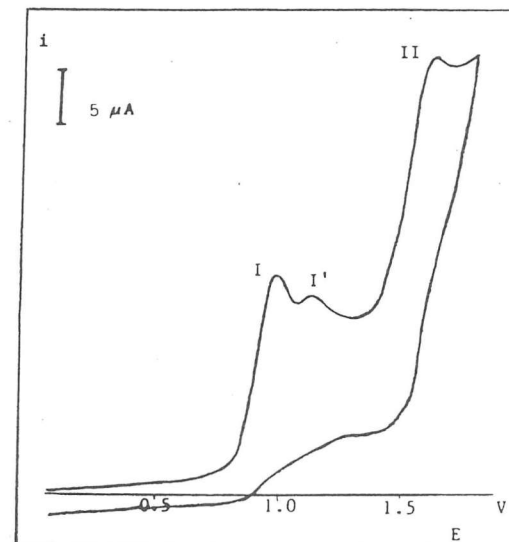


Fig. - Cyclic voltammogram for (1, $\text{M} = \text{Pt}$, $\text{Y} = \text{NC}_6\text{H}_4\text{OMe-4}$) in NCMe/0.2 M $[\text{Bu}_4\text{N}][\text{BF}_4]$, at a Pt electrode ($\nu = 100 \text{ mV s}^{-1}$)

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Table — C.V. and C.P.E. data (a) for the dinuclear carbene complexes $[(PPh_3)_2CIM(\mu-CYCH_2CH_2N-C_2N)]_2$ (1)

M	Y	E_p^{ox} (b)			C.P.E.				
		I	I'	II	I + I'		II		
					$n(e^-)$	$n(H^+)$	$\frac{(c)}{(c)}$	$n(e^-)$	$n(H^+)$
Pt	0	1.67 (d)			0.93 (d')	1.1			
Pt	$NC_6H_4-p-OMe$	0.98	1.13	1.60	1.88	2.0	2.0	4.0	3.4
Pd	$NC_6H_4-p-OMe$	0.96	1.10	1.58		1.8	1.8	4.1	3.4
Pd	NMe	0.80	1.12	1.44	1.80	1.9	1.7		

(a) At a Pt wire (C.V.) or gauze (C.P.E.), in NCMe (unless stated otherwise)/0.2 M $[Bu_4N][BF_4]$.

(b) Values in volt vs. s.c.e., measured by C.V. at 100 mVs⁻¹.

(c) Measured by acid-base titration of the electrolyzed solution.

(d) In CH_2Cl_2 due to insufficient solubility in NCMe

(d') In NCMe/ CH_2Cl_2 (4:1 volume ratio).

VOLUME AND COMPRESSIBILITY CHANGES OF SOLVENTS
IN IONIZING PROCESSES

by

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Volumic properties are of course volume dependent. Concentration is one of these properties and the ratio between the number of molecules and the volume is a very important property which must be taken into account in the study of solvolytic mechanisms.

In this respect two reactions, namely ter-butyl chloride and ethyl iodide/triethylamine in different alcohols are here analysed. The two mechanisms are essentially as follow^{1,2}:

