ELECTROCHEMICAL BEHAVIOUR OF PLATINUM(II) COMPLEXES WITH LIGATING UNSATURATED CARBON SPECIES

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Abstract

The electrochemical behaviour of some Pt(II) complexes of the type *trans*-$[Pt(PPh_3)_2LL']^n$ [n = 0, L = CH_3 , L' = $C{\equiv}CC_6H_4Me$-4 **(1)**; n = 1, L = CH_3, L' = $C(OCH_2CH_2Cl)CH_2C_6H_4Me$-4 **(2a)**, $C(OCH_2CH_2Br)CH_2C_6H_4Me$-4 **(2b)** or $COCH_2CH_2CHC_6H_4Me$-4 **(3)**; n = 1, L = CO, L' = $C{\equiv}CC_6H_4Me$-4 **(4a)** or $CH{=}C(OCH_2CH_2Cl)C_6H_4Me$-4 **(4b)**] and $[PtH(CH_2CF_3)(PPh_3)(C{\equiv}NC_6H_4OMe\text{-}4)]$ **(5)** have been studied by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) in aprotic media and at platinum electrodes. While the cationic compounds exhibit irreversible cathodic reductions and most of the above complexes undergo anodic processes, also irreversible, whose peak potentials can be related to the electronic properties of the unsaturated carbon ligands and of their binding metal centres, the oxidation of the neutral isocyanide compound could only be achieved by means of an electron-transfer mediator, $N(C_6H_4Br\text{-}4)_3$. The mechanism of the electrocatalytic process thus observed was studied by digital simulation of the cyclic voltammograms.

Key Words: platinum, cyclic voltammetry, controlled potential electrolysis, electrocatalysis, digital simulation.

Introduction

Within our interest on the investigation of the electrochemical behaviour of organometallic complexes of platinum and palladium, we have already reported the electrochemistry of some Pt(0)-olefin complexes [1] , as well as of a variety of dithio- [2], dioxy-, diamino- and aminooxy-carbene [3] complexes of Pd(II) and Pt(II) stabilized by hydride or halide co-ligands. We now extend this study to other Pt(II) complexes with ligating oxycarbenes and related alkynyl, vinyl and isocyanide groups (Fig. 1) which have been prepared according to published [4] procedures.

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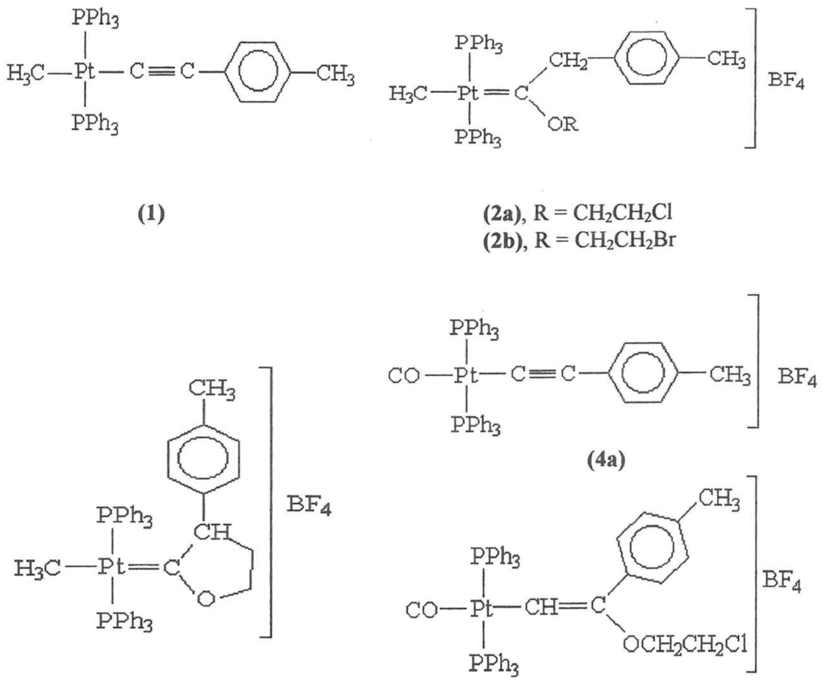
Results and Discussion

I. Electrochemical behaviour of some Pt(II) complexes

The neutral platinum (II) complex *trans*-[Pt(CH_3)(C≡CC_6H_4Me-4)(PPh_3)$_2$] **(1)** (Fig. 1), in acetonitrile , presents by CV one irreversible anodic wave at the peak potential of *ca.* 1.2 V *vs.* S.C.E. (Table). No cathodic process was observed within the potential range studied. This anodic wave involves *ca.* one electron, as indicated by CPE, and conceivably involves Pt(II) → Pt(III) oxidation. The neutrality of the complex can explain the relatively low anodic peak potential as well as the absence of a cathodic process.



(1)

(2a), R = CH_2CH_2Cl
(2b), R = CH_2CH_2Br

(4a)

(3)

(4b)

Fig. 1- Platinum(II) complexes with ligating unsaturated carbon species : *trans*-[Pt(PPh_3)$_2$LL']^n [n = 0, L = CH_3 , L' = C≡CC_6H_4Me-4 **(1)**; n = 1, L = CH_3, L' = C(OCH_2CH_2Cl)$CH_2C_6H_4$Me-4 **(2a)**, C(OCH_2CH_2Br)$CH_2C_6H_4$Me-4 **(2b)** or $\overline{\mathrm{COCH_2CH_2C}}\mathrm{HC_6H_4Me\text{-}4}$ **(3)**; n = 1, L = CO, L' = C≡CC_6H_4Me-4 **(4a)** or CH=C(OCH_2CH_2Cl)C_6H_4Me-4 **(4b)**].

The cationic complexes **(2a)**, **(2b)**, **(3)**, **(4a)** and **(4b)** (Fig. 1) exhibit one irreversible cathodic wave and usually one irreversible anodic wave [a partially reversible one is observed for compound **(4b)**], with exception of *trans*-[Pt(CH_3)($\overline{\mathrm{COCH_2CH_2}}\mathrm{CHC_6H_4Me\text{-}4}$)($PPh_3$)$_2$][$BF_4$] **(3)** for which no anodic process was detected (Table). This observation suggests a larger overpotential for the reduction of the cyclic carbene complex **(3)** in comparison with the analogous acyclic oxycarbene complexes **(2)**, conceivably resulting from a more drastic redox-induced structural rearrangement (*e.g.*, rupture of the ring) in the former compound.

The cyclic voltammograms for the complexes **(2a)** and **(2b)** are very similar. Both present one anodic wave at a peak potential of *ca.* 2.2 V *vs.* S.C.E. and one cathodic wave at a peak potential of *ca.* -1.5 V *vs.* S.C.E.. This similarity is expected in view of the identical structure of these complexes that only differ in the halogen atom of the oxycarbene ligand. However, the numbers of electrons involved in the anodic processes of these two complexes are different, as obtained by CPE. The higher number of electrons measured for complex **(2a)** can tentatively be explained by the higher electronegativity of Cl compared with Br with resulting increase of the acidity character of the adjacent protons which, upon oxidation of the complex, can be released by reductive elimination (with a lowering of the metal oxidation state which can be oxidazed again by further electron-transfer to the electrode). Potentiometric titration will be attempted to testify the H^+ loss in the anodic process.

The complex *trans*-[Pt(CO)(C≡CC_6H_4Me-4)(PPh_3)$_2$][BF_4] **(4a)** is unstable in solution and decomposition was observed during the cyclic voltammetric study. This complex presents one irreversible anodic wave at E_p^{ox} *ca.* 1.8 V *vs.* S.C.E. and one irreversible cathodic wave at E_p^{red} *ca.* -1.1 V *vs.* S.C.E., and during the cyclic voltammetric study these waves disappear and are replaced by others at *ca.* 1.6 V and *ca.* -1.6 V *vs.* S.C.E., respectively. The lowering of the redox potentials in the decomposition product, relative to the starting complex, can possibly be due to the replacement of the carbonyl group by a solvent molecule (CH_3CN) which has a stronger electron release capacity.

Table

Electrochemical data[a] for platinum(II) complexes.

Complexes	Cathodic behaviour		Anodic behaviour	
	E_p^{red} [a]	n [b]	E_p^{ox} [a]	n [b]
(1)[c]	-[d]	-[d]	1.22	0.9
(2a)	-1.50	-[e]	2.25	3.0
(2b)	-1.49	3.1	2.24	1.2
(3)	-1.64	3.7	-[d]	-[d]
(4a)	-1.13	0.9	1.79[f]	1.6
(4b)	-1.27	0.8	1.42	1.8

[a] Values in Volt *vs.* S.C.E., measured by CV at a Pt-disc electrode (∅=0.5 mm), in a 0.2M [NBu_4][BF_4]/CH_3CN solution (unless stated otherwise), scan rate of 200 mVs^{-1}.

[b] Number of electrons as obtained by CPE.

[c] In a 0.2M [NBu_4][BF_4]/THF.

[d] Not observed.

[e] Not possible to estimate due to passivation of the electrode.

[f] Partially reversible wave (i_p^{red}/i_p^{ox} = 0.2) at 200 mVs^{-1}.

The lower redox potentials of *trans*-[Pt(CO)(CH=C(OCH$_2$CH$_2$Cl)C$_6$H$_4$Me-4)(PPh$_3$)][BF$_4$] **(4b)** in comparison with **(4a)** suggests that the vinyl ligand in the former is a stronger electron-donor than the alkynyl ligand in the latter complex. The anodic waves of these complexes involve, by CPE, more than one electron; this number approaches two in the case of **(4b)**, suggesting that Pt(II) is oxidised to Pt (IV). The cathodic waves of both compounds **(4a)** and **(4b)** involve *ca.* one electron, detected by CPE, possibly corresponding to the Pt(II) $\rightarrow$ Pt(I) reduction.

The lower values of the oxidation potential of the complexes **(4)** relative to those of compounds **(2),** in spite of the weaker net electron-donor character of CO compared to the other ligands, are indicative of a stronger net electron-donor ability of the alkynyl and vinyl ligands in the former complexes than that of the methyl ligand in the latter compounds.

II. Electrocatalytic oxidation of [PtH(CH$_2$CF$_3$)(PPh$_3$)(C≡NC$_6$H$_4$OMe-4)]

When solutions of the neutral isocyanide complex [PtH(CH$_2$CF$_3$)(PPh$_3$)(C≡NC$_6$H$_4$OMe-4)] **(5)** are investigated by CV in NCMe , no anodic process is observed. However, oxidation of the complex can be achieved homogeneously by means of the electron-transfer catalyst tris(4-bromophenyl)amine.

The cyclic voltammogram of the organic mediator presents a reversible anodic wave whose monoelectronic process is well established [5]. When this amine is oxidized in the presence of the platinum complex under study, the anodic peak current increases and further current enhancements are observed upon increasing the amount of substrate (complex) in solution (Fig. 2).

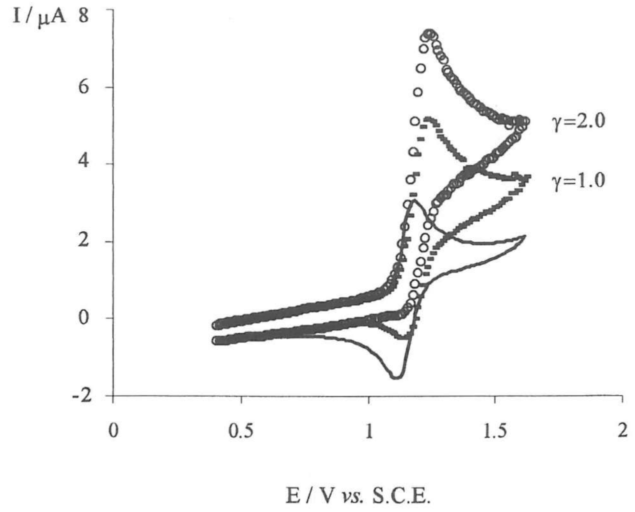


Fig. 2- Cyclic Voltamograms for N(C$_6$H$_4$Br-4)$_3$ alone (solid line) and in the presence of increasing amounts of [PtH(CH$_2$CF$_3$)(PPh$_3$)(C≡NC$_6$H$_4$OMe-4)] (symbols), in 0.2M [NBu$_4$][BF$_4$]/ NCMe, at a platinum disc electrode (∅ = 0.5 mm) and at a scan rate (v) of 0.2 Vs^{-1}. The γ (excess factor) values indicate the ratio between the Pt complex and the mediator concentrations, [Pt]/[M].

The involvement of a complicated catalytic process in the homogeneous oxidation of the substrate is indicated by varying the scan rate and the substrate concentration. Indeed, the catalytic effect tends to be suppressed at low scan rates (Fig. 3, symbols). The low solubility of the platinum complex, and therefore the limited range of substrate concentrations under study, precluded the study of an eventual saturation effect with this parameter.

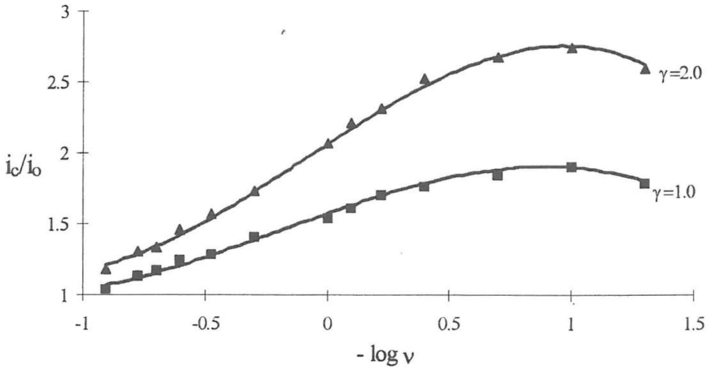


Fig. 3 - Plot of experimental (symbols) and simulated (lines) i$_c$/i$_o$ [ratio between the current intensities of the anodic wave of the mediator in the presence (i$_c$) and in the absence (i$_o$) of the complex] *vs.* log v for different values of the excess factor (γ); v in Vs^{-1}.

The experimental results so far obtained suggest (as indicated in Scheme 1) the progressive quenching of the mediator by reaction with the oxidized substrate. This general mechanism has been investigated by digital simulation of the cyclic voltammograms (program CVSIM [6]) and a good fit was obtained (Fig. 3, lines) for k$_1$= 14.5 and k$_2$=0.24. Hence, the homogeneous electron-transfer reaction between the mediator and the substrate (k$_1$) is faster than the quenching reaction of the mediator (k$_2$).

$$\mathrm{M} - e \rightleftharpoons \mathrm{M}^{+}$$

$$\mathrm{M}^{+} + \mathrm{Pt} \xrightarrow{k_1} \mathrm{M} + \mathrm{Pt}^{ox}$$

$$\mathrm{M} + \mathrm{Pt}^{ox} \xrightarrow{k_2} \{\mathrm{M\text{-}Pt}\} \qquad k_2 < k_1$$

Scheme 1

Acknowledgements

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COMPARATIVE ELECTROCHEMICAL BEHAVIOUR OF PROTONATED DERIVATIVES OF *trans*-$[Mo(NCN)_2(Ph_2PCH_2CH_2PPh_2)_2]$ AND *trans*-$[Mo(NCNEt)(NCN)(Ph_2PCH_2CH_2PPh_2)_2]^+$

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Abstract

The bis(cyanoimido) complex *trans*-$[Mo(NCN)_2(dppe)_2]$ (**1**, dppe = $Ph_2PCH_2CH_2PPh_2$) is susceptible to electrophilic attack to form protonated compounds *trans*-$[Mo(NCNH)(NCN)(dppe)_2]^+$ (**2**) and *trans*-$[Mo(NCNH)_2(dppe)_2]^{2+}$ (**3**), as well as the alkylated derivative *trans*-$[Mo(NCNEt)(NCN)(dppe)_2]^+$ (**4**) which in turn can be protonated to give *trans*-$[Mo(NCNEt)(NCNH)(dppe)_2]^{2+}$ (**5**). A preliminary description of the electrochemical behaviour of these complexes is presented and the observed redox induced interconversion of some of them is discussed in terms of their activation upon electron transfer.

Key Words: Molybdenum complexes; bis(cyanoimido) complex; alkylcyanoimido complex; protonation; alkylation; electrochemistry; electron transfer activation.

1. Introduction

Cyanamide, N≡C–NH_2, is a small, unsaturated molecule with biological and industrial relevance. In particular, it has recently been recognized as an alternative substrate of both Mo- and V-nitrogenases [1], the N_2-reducing enzymes.

The versatility of cyanamide [2] is being explored in the field of coordination chemistry at transition metal centres, in particular with Mo. Its activation at an electron-rich and readily oxidisable Mo(0) centre such as *trans*-$[Mo(N_2)_2(dppe)_2]$ results in the metal induced reductive dehydrogenation of the substrate and the concomitant formation of the bis(cyanoimido) complex **1** [3], which can be of potential significance towards the development of a chemical mimetic system for the activity of Mo-nitrogenase.

Compound **1** undergoes electrophilic attack (by H^+ or Et^+) at the terminal nitrogen of the NCN ligand to form the addition products **2**, **3**, **4** and **5**. We now describe the electrochemical behaviour of these complexes as studied by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) in 0.2 M $[NBu_4][BF_4]$ / CH_2Cl_2, and at glassy carbon or platinum disc working electrodes.