ELECTROCHEMICAL BEHAVIOR OF Pt-CINNAMONITRILE CYCLOPHOSPHAZENE COMPLEXES

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ABSTRACT

The redox properties of some Pt(0)- and Pt(II)-cinnamonitrile cyclophosphazene complexes, as well as of free cinnamonitrile and the related free substituted cyclophosphazene, have been investigated by cyclic voltammetry (CV) and controlled potential electrolysis (CPE) in aprotic media (THF, CH_2Cl_2 or NCMe/0.2 M $[NBu_4][BF_4]$), at Pt electrodes. Cathodic processes have been detected only when the unsaturated C=C bond of the cinnamonitrile group is uncoordinated, while irreversible anodic processes are displayed only by the complexes with at least one Pt(0) site, and they are interpreted in terms of the expected redox MOs.

INTRODUCTION

The electrochemical behavior of phosphazenes has not yet been fully explored, in spite of their structural versatility, rich reactivity and technological applications.

Although the basic phosphazene structure does not appear to be redox active, substituted phosphazenes with suitable reducible substituents can be electrochemically reduced, namely in a single-electron process [1-3] to form the corresponding radical anions.

Aiming to prepare new materials with particular electronic and chemical properties, the synthesis of polyphosphazenes containing groups able to selectively coordinate metals in different oxidation states has been initiated. In this study we

have investigated the electrochemical behavior of the cyclic phosphazene $N_3P_3(OC_6H_4CH{=}CHC{\equiv}N)_6$ with cinnamonitrile substituents (which are potential redox active centers) and of its Pt(0) and Pt(II) complexes, as well as, for comparative purposes, of a related cinnamonitrile, PhHC=CHC≡N, and also of its Pt(0) and Pt(II) compounds.

RESULTS AND DISCUSSION

trans-CINNAMONITRILE COMPLEXES

Cathodic behavior

Free *trans*-cinnamonitrile in THF exhibits, by CV at 200 mV s^{-1}, a partially reversible cathodic wave at $E_{1/2}^{red}$ = -1.87 V (E_p^{red} = -1.99 V) *vs.* SCE (Table), involving *ca.* 1 electron as measured by CPE, which appears to be due to the reduction of the unsaturated C=C double bond (addition of the electron to the empty π^* orbital) probably forming a radical anion which reacts further, as is known to occur in alkenes [4-7].

Table - Voltammetric data [a] for cinnamonitrile and its Pt(0) and Pt(II) complexes, and for cyclophosphazene and its Pt(0) and Pt(II) complexes.

Compound	E_p^{red}	E_p^{ox}
PhCH=CHC≡N	-1.99[b]	-
$[Pt(CF_3)(N{\equiv}CCH{=}CHPh)(PPh_3)_2][BF_4]$	-1.86[b]	-
$[Pt(\eta^2\text{-}PhCH{=}CHC{\equiv}N)(PPh_3)_2]$	-	0.79[c]
$[(PPh_3)_2Pt(\eta^3,\mu\text{-}PhCH{=}CHC{\equiv}N)Pt(CF_3)(PPh_3)_2][BF_4]$	-	0.72[c]
$N_3P_3(OC_6H_4CH{=}CHC{\equiv}N)_6$	-1.74[d]	-
$N_3P_3\{[(OC_6H_4CH{=}CHC{\equiv}N)Pt(CF_3)(PPh_3)_2][BF_4]\}_6$	-1.31[b, e]	
$N_3P_3\{[(PPh_3)_2Pt(\eta^2\text{-}OC_6H_4CH{=}CHC{\equiv}N)]\}_6$		0.91[d]

[a] In electrolyte solutions of $[NBu_4][BF_4]$ (0.2M) and at 200 mV s^{-1}. Potentials in Volts *vs.* SCE. [b] In THF solution. [c] In NCMe solution. [d] In CH_2Cl_2 solution. [e] In NCMe solutions, E_p^{red} = -1.50 V *vs.* SCE.

For the cinnamonitrile-platinum species, two distinct situations have to be considered concerning the mode of binding of cinnamonitrile to the metal. Indeed, in

the Pt(II) species $[Pt(CF_3)(N{\equiv}CCH{=}CHPh)(PPh_3)_2][BF_4]$ the metal center binds the cinnamonitrile *via* the nitrile group; an irreversible single-electron cathodic wave is observed at slightly less cathodic value (E_p^{red} = -1.86 V *vs.* SCE) which agrees with the expected electron donation of the ligand to the metal thus resulting in a stabilisation of the π^* orbital. In contrast, no cathodic process was detected for the Pt(0) species $[Pt(\eta^2\text{-}PhCH{=}CHC{\equiv}N)(PPh_3)_2]$ or $[(PPh_3)_2Pt(\eta^3,\mu\text{-}PhCH{=}CHC{\equiv}N)Pt(CF_3)(PPh_3)_2]$ $[BF_4]$, in which η^2-bonding of the cinnamonitrile through the C=C bond occurs, probably due to the electron release from a filled Pt(0) orbital to the π^* orbital of the ligand resulting in its substantial destabilisation and cathodic shift of the reduction potential.

Anodic behavior

The complexes with a Pt(0) site, $[Pt(\eta^2\text{-}PhCH{=}CHC{\equiv}N)(PPh_3)_2]$ and $[(PPh_3)_2Pt(\eta^3,\mu\text{-}PhCH{=}CHC{\equiv}N)Pt(CF_3)(PPh_3)_2][BF_4]$ present, in NCMe, an irreversible anodic wave at an oxidation potential (E_p^{ox} = 0.79 or 0.72 V *vs.* SCE, respectively) which is close to that known for the related ethylene complex $[Pt(CH_2{=}CH_2)(PPh_3)_2]$ (0.82 V, in NCMe [8]), thus indicating that the anodic processes are centered at the Pt(0) site.

Moreover, by controlled potential electrolyses at these anodic waves, the overall number of electrons transferred is *ca.* 1.5 per molecule, which agrees with previously reported values for related olefin complexes [8]. Therefore, the anodic processes may involve the overall oxidation (although possibly incomplete) of Pt(0) to Pt(II) with associated chemical reactions.

CINNAMONITRILE-SUBSTITUTED CYCLOPHOSPHAZENE COMPLEXES

Cathodic behavior

The free cyclophosphazene $N_3P_3(OC_6H_4CH{=}CHC{\equiv}N)_6$ exhibits, by CV, an irreversible cathodic wave at E_p^{red} = -1.74 V *vs.* SCE (Fig. 1-a) which is believed to be due to the reduction of the cinnamonitrile moieties in view of the cathodic potential value (see above), the number of electrons involved (6 Faraday/mol) and the fact that no redox processes were detected for other related cyclophosphazenes [1-3].

A six-electron cathodic process is also observed when six Pt(II) centres bind the six nitrile groups to form the cationic complex $N_3P_3\{[(OC_6H_4CH{=}CHC{\equiv}$

N)Pt(CF_3)(PPh_3)$_2$][BF_4]}$_6$. The potential shift is now very pronounced and solvent dependent (Fig. 1-c) (Table).

Therefore, an important feature when going from the cinnamonitrile to the cyclophosphazene and to the cyclophosphazene/Pt(II) species is that the cathodic potential is shifting anodically. This can be interpreted by considering the known strong electron-withdrawing ability of the phospazene group and the combined effects of the electron release from the cinnamonitrile group to the Pt(II) centre and of the positive charge of the compound.

Anodic behavior

When the CC double bond is involved in the coordination to six Pt(0) metal centres in complex N_3P_3\{(η^2-$OC_6H_4CH{=}CHC{\equiv}N$)Pt(PPh_3)$_2$\}$_6$, an anodic process is observed at a potential of 0.91 V (Fig. 1-b) (substantially higher than the 0.79 V previously shown for the correspondent Pt(0)-cinnamonitrile complex). However, the exact determination of the number of electrons involved was precluded due to passivation of the Pt working electrode.

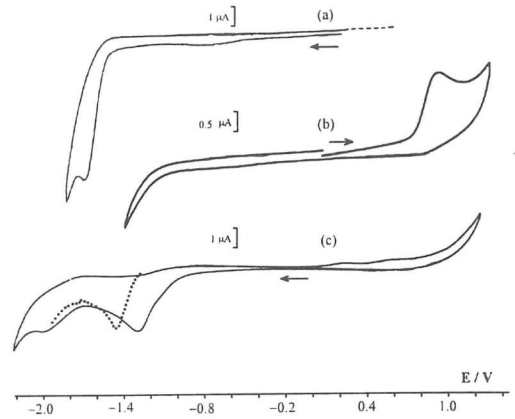

Fig.1- Cyclic voltammograms for $N_3P_3(OC_6H_4CH{=}CHCN)_6$ (0.53 mM in CH_2Cl_2) (a); N_3P_3\{(η^2-$OC_6H_4CH{=}CHCN$)Pt(PPh_3)$_2$\}$_6$ (0.17 mM in CH_2Cl_2) (b); N_3P_3\{[($OC_6H_4CH{=}CHCN$)Pt(CF_3)(PPh_3)$_2$][BF_4]}$_6$ [0.17 mM in THF (—) or 0.33 mM in NCMe (---)] (c); with [NBu_4][BF_4] as electrolyte (0.2 M), at a Pt disc electrode (ϕ = 1 mm) and at a scan rate of 200 mV s^{-1}. Potentials in Volts *vs.* SCE..

The cyclophosphazene derivative with six Pt(0) and six Pt(II) metal centres, N_3P_3[(η^3,μ-$OC_6H_4CH{=}CHC{\equiv}N$){Pt(PPh_3)$_2$}{Pt(CF_3) (PPh_3)$_2$}(BF_4)]$_6$, behaves differently according to the solvent.

In THF, an anodic wave is detected at about 1.16 V but the determination of the number of electrons involved was precluded due to its low solubility.

In NCMe an anodic adsorption wave is detected at 0.67 V, as well as a cathodic process similar to the one in the Pt(II)-cyclophosphazene compound discussed previously. The situation can be interpreted by considering loss of its six Pt(PPh_3)$_2$ fragments probably stabilised by solvation or adsorption on the electrode surface, or both, as described bellow.

$$N_3P_3[(\eta^3,\mu\text{-}OC_6H_4CH{=}CHC{\equiv}N)\{Pt(PPh_3)_2\}\{Pt(CF_3)(PPh_3)_2\}(BF_4)]_6 \longrightarrow$$
$$\longrightarrow N_3P_3\{[(OC_6H_4CH{=}CHC{\equiv}N)Pt(CF_3)(PPh_3)_2][BF_4]\}_6 + 6[Pt(PPh_3)_2]_{solvated/adsorved}$$

CONCLUSIONS

The cathodic behavior of all the Pt-complexes studied reflect the susceptibility to reduction of all the olefinic groups conceivably *via* electron-transfer to their empty π^* orbitals. Moreover, the electron-withdrawing ability of the cyclophosphazene ring stabilises those orbitals, which explains the anodic shift of the reduction potential.

Anodic processes are observed if Pt(0) metal centres are present, and the strong electron-withdrawing capacity of the cyclophosphazene unit stabilises the metal ***d*** orbitals and shifts anodically the oxidation potential.

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