

**STUDY OF THE ELECTROCHEMICAL BEHAVIOUR OF
CAMPHOR(+) DERIVATIVES AND SOME OF THEIR PALLADIUM
COMPLEXES**

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Summary

The electrochemical behaviour of some camphor(+) derivatives (L) is reported and their electronic properties discussed. The redox properties of some new palladium(II) complexes, $[\text{PdCl}_2\text{L}_2]$, $[\text{PdCl}_2(\text{NCMe})\text{L}]$ and $[\text{PdCl}_2\text{L}]$, with such ligands, are also discussed. This study was done by cyclic voltammetry at a Pt electrode in an aprotic medium, commonly 0.2M $[\text{Bu}_4\text{N}][\text{BF}_4]/\text{CH}_2\text{Cl}_2$. In a few cases, controlled potential electrolysis was performed at a Hg pool or a Pt gauze electrode, for cathodic or anodic processes, respectively.

Introduction

Enantiomeric pure camphor(+) derivatives are convenient ligands to the synthesis of chiral complexes which can be used [1] to induce optical activity in organic substrates through asymmetric synthesis. The activity and selectivity displayed by a system are dependent on the electronic properties of the ligands and their metal centre. In order to have an insight into such properties we underwent a study, by cyclic voltammetry and controlled potential electrolysis, of camphor(+) derivatives and of some of their palladium complexes.

Results and discussion

Within our interest on the synthesis of chiral organic compounds using low oxidation state complexes [2] as intermediates, we started the study of the redox properties of camphor-type compounds and of new Pd complexes obtained from them. The camphor-type species studied can be grouped into two categories, those having the sulphonimine ($>C=N-SO_2-$) moiety and those without it. Although SO_2 reduction does not appear to be observed, by cyclic voltammetry, within the range of potentials available, the electron withdrawing ability of the $-SO_2$ group is probably responsible for the considerably high reduction potentials (see below) of the adjacent $-N=C$ moiety (which conceivably undergoes reduction in our complexes), when compared with other imino groups [3].

Table 1 - Redox potentials for camphor(+) derivatives, in V vs. s.c.e. (a)

Ligand	$E_{1/2}^{red}$	E_p^{ox}	Ligand	$E_{1/2}^{red}$	$E_{1/2}^{ox}$
	-1.42 ^b	1.54 1.80			1.48
	-0.72 -1.72 ^b			-1.70	1.62
	-0.78 -1.10 ^b -1.34 ^b			-1.62	
	-1.20 ^b	1.74			

(a)-Values measured in 0.2M $[Bu_4N][BF_4]/CH_2Cl_2$; ferrocene was used as internal standard. (b)-Irreversible.

All, but LV, camphor(+) derivatives (table 1) display at least one cathodic process, which is attributed either to the reduction of the imino group ($-0.72V > E_p^{red} > -1.42V$), or, at a lower potential ($-1.62V > E_p^{red} > -1.72V$), of

the ketone group, in view of the known [3] common relative behaviour of these functional groups in organic compounds (ketones being harder to reduce than imines).

Compounds LII and LIV exhibit the first cathodic wave at identical potentials (-0.72 and $-0.78V$, respectively), which is believed to correspond to the reduction of the sulphonimine group. However, ligand III (racemic mixture of the *syn* with the *anti* isomer) presents two other cathodic processes, attributed to the reduction of the hidroxoimino group.

Table 2- Redox potentials for palladium complexes, in V vs. s.c.e. (a)

Complex	E_p^{red}	E_p^{ox}
<i>cis</i> - $[PdCl_2(LI)_2]$ (IA)	-1.48	1.52 1.81
$[PdCl_2(NCMe)(LIV)]$ (IVA)	-1.26	1.94
$[PdCl_2(LV)]$ (VA)		1.70

(a)-Values measured in 0.2M $[Bu_4N][BF_4]/CH_2Cl_2$; ferrocene was used as internal reference

Some of the ligands also display anodic processes in the range 1.54V to 1.80V which can occur at the imino or other functional groups (such as the dimethylamino or the diazo moieties). Controlled potential electrolysis at the potential of the first anodic wave of LI shows a multielectron process probably involving chemical reaction of the amine or the imino group during the period of the electrolysis.

Using the camphor(+) derivatives LI, LIV and LV as ligands, the palladium complexes IA, IVA and VA have been obtained (table 2) and their redox properties also investigated by cyclic voltammetry and compared with those exhibited by the free ligands. The cyclic voltammogram of *cis*- $[PdCl_2(LI)_2]$ (IA) is displayed on the figure.

The anodic behaviour of compound IA follows that observed for the corresponding LI ligand, thus pointing to the occurrence of the oxidation processes mainly at the ligand. However, for complexes (IVA) and (VA), the anodic processes occur at considerably higher (by *ca.* 0.20V) potentials than those presented by the corresponding ligands.

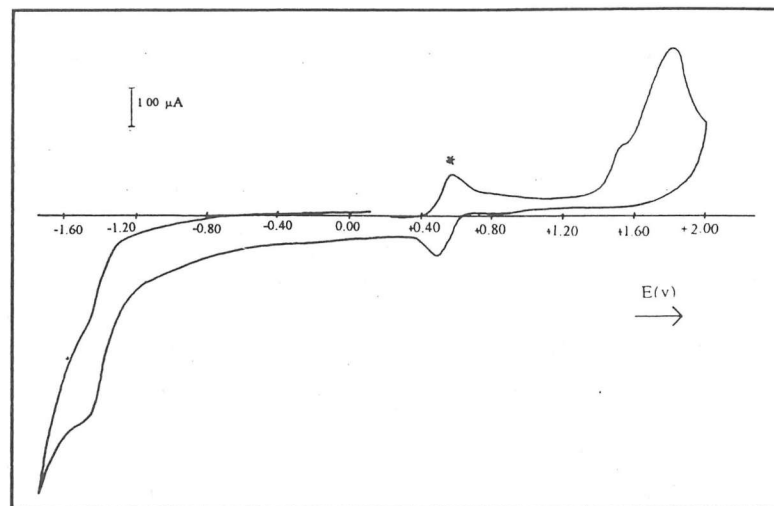


Figure-Cyclic voltammogram of *cis*-[PdCl₂(LI)₂] in 0.2M [Bu₄N][BF₄]/CH₂Cl₂.
* Ferrocene (internal reference).

The palladium compounds (IA) and (IVA) also display cathodic processes at reduction potentials which are very close to those observed in the free ligands, again suggesting their occurrence at such sites. In agreement with this, no cathodic process has been detected either for complex (VA) or for the corresponding free ligand.

Controlled potential electrolysis at the potential of the cathodic wave of *cis*-[PdCl₂(LI)₂] (IA) appears to involve the transfer of 8 electrons and precipitation of palladium metal from the electrolysed solution was observed to occur.

Unlike the other palladium compounds, an influence of the solvent was observed on the behaviour of complex (VA) in solution and an equilibrium between the complex and the free ligand was detected in acetonitrile, possibly corresponding to the competition of this solvent for the metal centre.

Although ligand LV can be considered as binding the metal through the ketone and/or the imino groups, probably coordination through only one of them occurs as suggested by an X-ray diffraction analysis of *cis*-[PdCl₂(LI)₂] [4] where LI behaves as a monodentate ligand. Furthermore controlled potential electrolysis at the oxidation wave of (VA) shows the involvement of only half of an electron *per* metal atom, although in the free ligand one electron *per* molecule is transferred, thus pointing to the dimeric nature of the complex.

Acknowledgements

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