

delocalization along the aromatic π -system, the aromatic diolate acting as an efficient electron withdrawing ligand.

Each of the complexes $[\text{ReO}\{\eta^2\text{-B}(\text{pz})_4\}(\text{OMe})\text{L}']$ (9-11) with the dihapto ($\text{B}(\text{pz})_4$) ligand displays, by cyclic voltammetry, an irreversible oxidation and a partially reversible reduction wave at the values of potential indicated in table 2.

Although a smaller number of $\eta^2\text{-B}(\text{pz})_4$ complexes have been studied, one observes that they exhibit higher oxidation potentials than those of the $\eta^3\text{-B}(\text{pz})_4$ compounds, possibly suggesting that the $\eta^2\text{-B}(\text{pz})_4$ pyrazolylborate has a stronger stabilizing effect on the HOMO than the η^3 -ligand.

Controlled potential electrolysis performed at the potential of the anodic and the cathodic waves of the complex (2) allowed the determination of one and two electrons per molecule, respectively. Furthermore, chemical reactivity is induced by anodic electrolysis, in spite of the reversible character of the anodic wave observed in the time scale of cyclic voltammetry. The characterization of the products is under way.

Acknowledgements

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STUDY OF THE REDOX PROPERTIES OF IRON (III), COPPER (II) AND PALLADIUM (II) CAMPHOR COMPLEXES

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Summary

The redox properties of complexes of general formulæ $[\{\text{FeCl}_3\text{L}\}_2]$, $[\{\text{CuCl}_2\text{L}\}_2]$ and $[\text{PdCl}_2\text{L}_2]$ (L=camphor-type ligand) were studied by cyclic voltammetry and controlled potential electrolysis. As a general behaviour, the complexes display at least one cathodic wave which has a marked metal character. The potentials are discussed on the basis of the electronic properties of the camphor-type ligands. Extensive reductive controlled potential electrolysis of one of the diiron complexes allowed the electrosynthesis of a mononuclear product. The electrochemical behaviour of the L ligands [L=A (R=Ph or Prⁱ) and L=B (R=NH₂)] is also reported.

Introduction

Within our interest on the coordination chemistry of camphorimine ligands we have prepared some palladium complexes with such ligands [1]. Their electrochemical behaviour, studied by cyclic voltammetry, showed that there is a marked effect of the characteristics of the camphorimine ligand on the redox potential of the metal site, *i.e.* the ketone-type ligands (A) strongly influence the redox potentials in contrast with a slight effect observed for the sulfonimide-type ligands (B). In order to further investigate that effect we now extend the study to other camphor type (A) or (B) ligands. Moreover, camphorimine iron(III) and copper(II) complexes were prepared and the study of their redox properties show that a metal centred reduction process takes place.



(A)



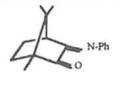
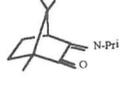
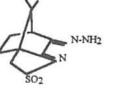
(B)

Results and discussion

The electrochemical behaviours of camphorimine ligands [type (A), R=Ph or Prⁱ and type (B) R=NH₂] and the corresponding palladium complexes [PdCl₂L₂] as well as the dinuclear compounds [{FeCl₃L}₂] [L=A (R=OH, NMe₂, OMe); L=B (R=NMe₂)] and [{CuCl₂L}₂] [L=A (R=OH, OMe)] were studied by cyclic voltammetry and whenever convenient by controlled potential electrolysis, at platinum wire or platinum gauze electrodes in 0.2M [NBu₄][BF₄] / CH₂Cl₂ or THF solutions. Potentials are quoted versus S.C.E. and were measured at 200 mVs⁻¹ using ferrocene ($E_{1/2}^{ox} = 0.54$ V) as internal standard.

Commonly the camphorimine ligands display one cathodic and one anodic process at potentials dependent on the nature of the substituents [2]. As a general trend [2] the camphor sulfonimide (type B) species display higher oxidation and reduction potentials than the camphor ketone imine (type A) species, Table 1.

Table 1 - Cyclic voltammetric data^(a) for camphor species (L) and [PdCl₂L₂] complexes.

L	L		Complex [PdCl ₂ L ₂]	
	E_p^{red}	E_p^{ox}	E_p^{red}	E_p^{ox}
 (1)	-1.54 ^(b)	1.86	-1.01	1.96
 (2)	-2.12	1.59	-1.24	1.76
 (3)	-1.46	1.98	-1.42	1.92

^(a) In 0.2 M [NBu₄][BF₄] / CH₂Cl₂, values in Volt (±20 mV) measured at 200 mV s⁻¹ using [Fe(η⁵-C₅H₅)₂] ($E_{1/2}^{ox} = 0.54$ V) as internal reference. ^(b) Partially reversible wave ($E_{1/2}^{red}$).

The palladium complexes also present, by cyclic voltammetry, one anodic and one cathodic wave, Figure 1. The potential of the anodic wave is close to that of the free ligand and the oxidation of the complex is believed to be mainly centred at the ligand. However, the potential measured for the reduction process is considerably less cathodic for complexes (1 and 2) derived from (A) type ligands, than for the corresponding free ligands (Table 1), and is within the range observed [3] for related isocyanide complexes of the type *cis*-[PdCl₂(CNR)₂] in which the cathodic

process is believed to correspond to the reduction of the metal. On the contrary, for complex (3) with a (B) type ligand, just a very slight increase of the cathodic potential, relative to that of the free ligand, is observed (Table 1), thus suggesting that, in this case, the reduction process should involve at least a substantial contribution of the ligand. Such a type of behaviour has already been detected [1] for related complexes with camphorsulfonimide-type ligands.

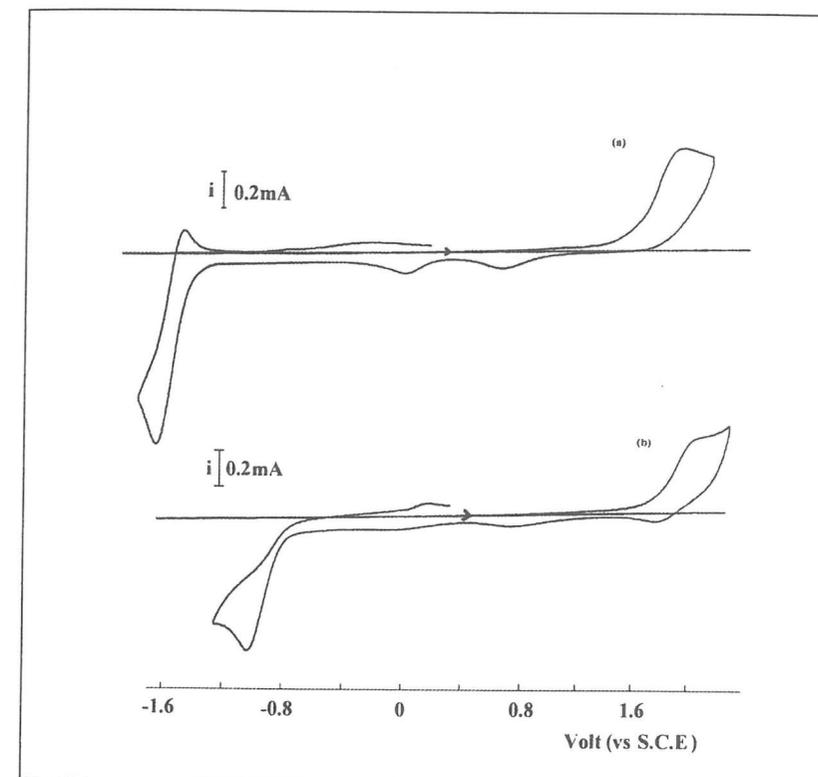
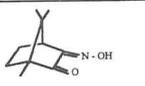
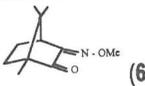
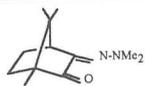
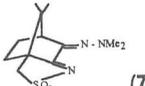


Figure 1 Cyclic voltammograms of the (A, R=Ph) camphorimine ligand (a) and of the derived palladium complex [PdCl₂L₂] (b), obtained in 0.2 M [NBu₄][BF₄] / CH₂Cl₂ solution at 200 mVs⁻¹.

In order to evaluate the influence of the transition metal on the redox characteristics of camphorimine complexes we studied the electrochemical behaviour of some iron(III) compounds of general formula [{FeCl₃L}₂] (4-7). In contrast with the palladium(II) complexes the iron(III) compounds display cathodic processes within the narrow potential range of 0.08 to 0.10 V, Table 2.

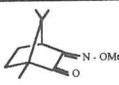
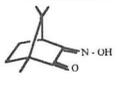
Table 2 -Cyclic voltammetric data^(a) for the iron complexes $[\{FeCl_3L\}_2]$.

L	$E_{1/2}^{red}$ [$\{FeCl_3L\}_2$]	L	$E_{1/2}^{red}$ [$\{FeCl_3L\}_2$]
 (4)	0.08	 (6)	0.08
 (5)	0.08	 (7)	0.10

^(a) In 0.2 M $[NBu_4][BF_4]$ / CH_2Cl_2 , unless stated otherwise, potentials measured at 0.2 Vs^{-1} , in Volt (± 20 mV) versus S.C.E. using $[Fe(\eta^5-C_5H_5)_2]$ as internal reference.

Hence, the cathodic processes are apparently unaffected by the electronic characteristics of the coordinated ligand. Moreover, the cathodic potentials are close to that measured for the $Fe(III) \rightleftharpoons Fe(II)$ reduction process of the trichloride salt, $FeCl_3 \cdot 6H_2O$ ($E_{1/2}^{red} = 0.06$ V) using similar conditions. The observed behaviour suggests an essentially metal centred reduction process, similarly to the behaviour observed for the palladium type (A) complexes.

Table 3 -Cyclic voltammetric data^(a) for complexes $[\{CuCl_2L\}_2]$

L	$E_{1/2}^{red}$	E_p^{red}	E_p^{ox}
 (8)	0.70	-1.91	1.11
 (9)	0.70	-2.11	

^(a) In 0.2 M $[NBu_4][BF_4]$ / THF, potentials measured at 0.2 Vs^{-1} , in Volt (± 20 mV) versus S.C.E. using $[Fe(\eta^5-C_5H_5)_2]$ as internal reference.

Controlled potential electrolysis performed at the cathodic wave of complexes (4 and 5) is consistent with two electrons being transferred *per* molecule at the cathodic process, possibly one *per* metal atom, in agreement with a $Fe(III) \rightarrow Fe(II)$ reduction process. Analysis of the current intensity *versus* time plot points to an electrolysis process involving a sequence of two single-electron processes. Furthermore, electro-synthesis of the iron(II) species $[FeCl_2L_2]$ [$L=A$ ($R=OH$)]

was achieved by extensive cathodic controlled potential electrolysis of complex (4) the product being isolated and characterized by conventional techniques [4].

The redox properties of the dimeric $Cu(II)$ complexes were also studied by cyclic voltammetry, the complexes displaying two reduction and one oxidation waves, Table 3.

The higher potential cathodic wave occurs at 0.70 V, a value similar to that measured for the $Cu(II) \rightarrow Cu(I)$ process ($E_{1/2}^{red} = 0.70$ V) in a copper dichloride ($CuCl_2 \cdot 2H_2O$) solution, using experimental conditions similar to those of the study of the complexes. This behaviour is consistent with that observed for the $Fe(III)$ system, thus pointing to the cathodic process having considerable metal character. The lower potential cathodic process of the $Cu(II)$ complexes occurs at potentials not far from those measured for the corresponding free ligands, pointing to a ligand based reduction process. The anodic process of complex (8) occurs at a potential slightly lower than that observed [1] for the corresponding free ligand. For complex (9) no oxidation wave is detected in agreement with the behaviour observed for the free ligand.

Conclusions

In spite of their different nature, all the three families of complexes show, by cyclic voltammetry, cathodic processes at potentials which are strongly dependent on the transition metal, the effect of the electronic properties of the ligand being almost negligible for the $Fe(III)$ and $Cu(II)$ species. Although no chemical synthesis of complexes $[FeCl_2L_2]$, from the corresponding iron(II) salt, was possible, the electro-synthesis of $[FeCl_2L_2]$ [$L=A$ ($R=OMe$)] was achieved in this study by cathodic reduction of the iron(III) complex $[\{FeCl_3L\}_2]$.

Acknowledgements

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