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A Search for the Influence of the Electronic Characteristics of the Camphor Derived Ligands and Complexes on their Redox Properties

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Abstract

The electrochemical data obtained by cyclic voltammetry on several camphor-type (A, B and C) ligands and derived complexes are revised. A direct positive correlation is established between the redox potentials (anodic or cathodic) of the camphor species and the σp-Hammett parameter of the R group on the camphor skeleton. A study of the effect of the ligand on the redox properties of some Pd, Pt or Cu camphor complexes shows that the ligands influence either the anodic or cathodic processes but the characteristics of the metal drive the potential values.

Keywords**:** Camphor ligands, complexes, redox properties, electronic properties.

Introduction

Camphor derived species with imine, phosphine, thioether or other functionalities can act as suitable ligands for a variety of metals [1-6]. Within our work we prepared several transition metal (Pd, Pt, Fe, Cu, Re) complexes derived from camphorimine (type A) or camphorsulphonylimine (type B) [1,2], as well as a few complexes derived from di-alkyne (type C) ligands. In contrast with Pd(II),

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no Pt(II) di-alkyne complexes were obtained. In this case, ring opening / ring closure with ring expansion of the camphor skeleton was induced by Pt(II) [7]. Recently, we demonstrated that *trans*-[$PdCl_2L_2$] (**1**, L=**A11**) acts as an efficient catalyst for the cyclotrimerization of alkynes in contrast with the related complex derived from camphorsulphonylimine (**B2**) that shows no such an activity [8].

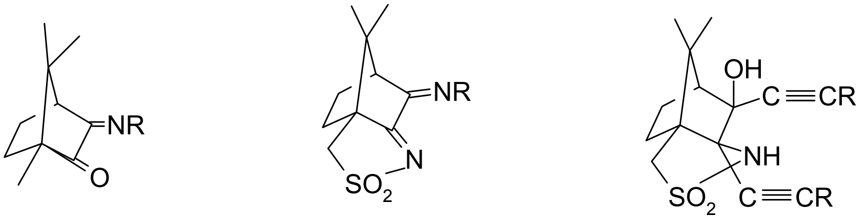
Experimental Section

The solvents were dried by standard methods before use. The preparation of the solutions was carried out under nitrogen using standard Schlenk glassware techniques.

The electrochemical studies were performed under nitrogen at an EG&G PAR 173 potentiostat / galvanostat and an EG&G PARC 175 universal programmer, using 0.2 M [NBu_4][BF_4] / THF, CH_2Cl_2 or CH_3CN solution and a Pt-wire as working electrode. The potential values were measured by using the $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ redox couple (E = 0.54 V *versus* SCE) as internal standard.

Results and Discussion

The redox properties of a considerable number of camphor derived compounds of types A, B or C, Fig. 1, have been studied by cyclic voltammetry and controlled potential electrolysis.



(A) (B) (C)

Figure 1. Camphor type ligands

As a general trend these organic species display at least one cathodic process that involves one electron *per* molecule as confirmed by controlled potential electrolysis. In addition, most of the camphorimine (A) or camphorsulfonylimine

(B) compounds but not the alkyne camphor derived species (C), display one anodic process. For most of the compounds the reduction or oxidation processes occur at potential values close to the observable limits, Table 1, in agreement with considerable high stability to reduction or oxidation.

A tentative search for the effect of the electronic characteristics of the R group on the redox properties of the camphor type compounds points to a direct relation between the oxidation or reduction potentials of the species and the σ_p Hammett constants for the R group, Fig. 2. The slopes of the two lines are identical and lower than one, conceivably due to a small effect of the R group on the redox properties of the camphorimine species. Hence, the potential values appear to be driven by the characteristics of the camphor skeleton.

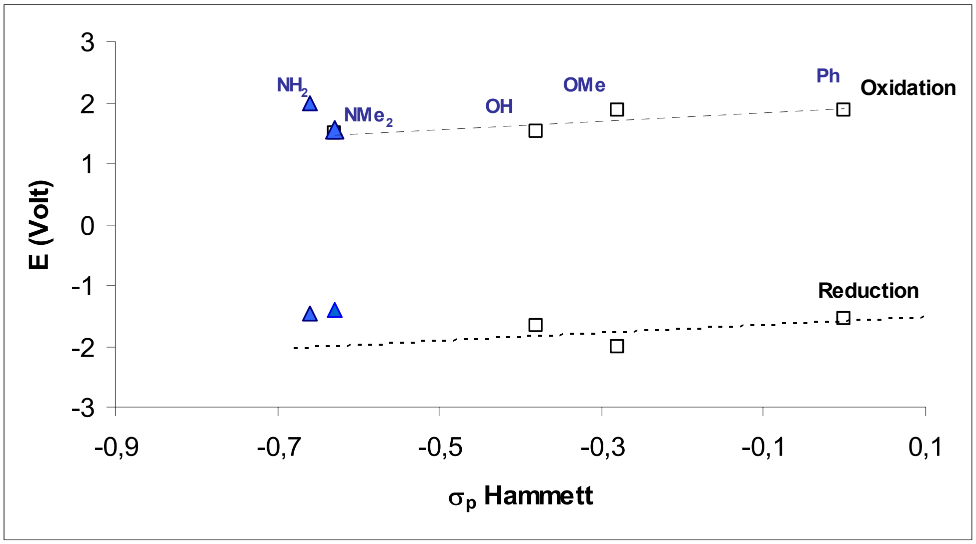
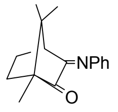
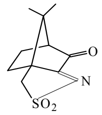
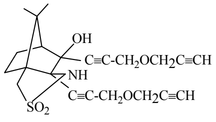
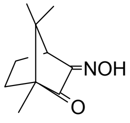
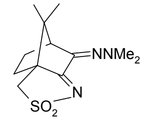
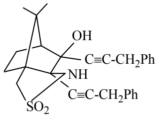
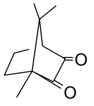
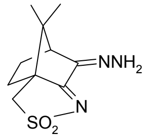
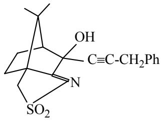
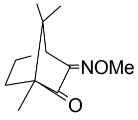
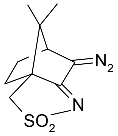
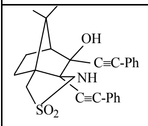
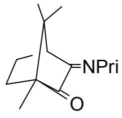
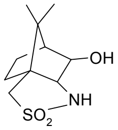
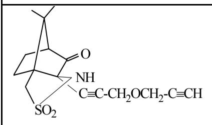
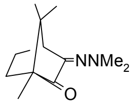
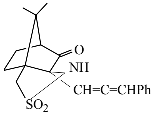


Figure 2. Effect of the σ_p-Hammett parameter on the oxidation (above) or the reduction (below) potential of camphor type (A, □) or (B, ▲) species.

Table 1- Cyclic voltammetry data for camphor derived ligands

COMPOUND	E_p^{red}	E_p^{ox}	Ref	COMPOUND	E_p^{red}	E_p^{ox}	Ref	COMPOUND	E_p^{red}	Ref
 (A**6**)	-1.54	1.86	3	 (B**1**)	-0.72^{b} -1.72		4	 (C**12**)	-1.80^{d}	6
 (A**7**)	-1.68	1.53	1	 (B**2**)	-1.42	1.54	1	 (C**13**)	-1.96^{d}	6
 (A**8**)	-1.62^{b}		4	 (B**3**)	-1.46	1.98	5	 (D**14**)	-2.10^{d}	6
 (A**9**)	-2.02	1.86	1	 (B**4**)	-1.20	1.62	1	 (C**15**)	-2.10^{d}	6
 (A**10**)	-2.12	1.59	5	 (B**5**)	-1.58^{c}		2	 (D**16**)	-2.26^{d}	6
 (A**11**)		1.48^{b}	1					 (D**17**)	-1.24^{c}	6

[a] Values in Volt (± 20 mV) measured in 0.2 M $[NBu_4][BF_4]$ /CH_2Cl_2, unless stated otherwise, using $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ (0.54 V *versus* SCE) as internal standard.
[b] Reversible wave. [c] In CH_3CN. [d] In THF.

Table 2. Cyclic voltammetry data[a] for camphorimine derived complexes.

Pd - Complexes		E_p^{red}	E_p^{ox}	Ref	**Pt** - Complexes		E_p^{red}	E_p^{ox}	Ref	**Fe** or **Cu** Complexes		$E_{1/2}^{red}$	E_p^{ox}	Ref
1	*trans*-$[PdCl_2L_2]$ (L=**A11**)	-1.2	1.76	1	**9**	$[PtCl_2L_2]$ (L=**A11**)	-1.10	1.34	3	**12**	$[FeCl_2L_2][FeCl_4]$ (L=**A11**)	0.08		9
2	$[PdCl_2L]$ (L=**A11**)	-0.84		1	**10**	$[PtCl_2L_2]$ (L=**A6**)	-1.00	1.45	3	**13**	$[FeCl_2L_2][FeCl_4]$ (L=**A7**)	0.08		9
3	*trans*-$[PdCl_2L_2]$ (L=**A9**)	-0.84		1	**11**	$[PtCl_2L]$ (L=**B2**)	-1.40	1.36	3	**14**	$[FeCl_2L_2][FeCl_4]$ (L=**A9**)	0.08		9
4	*trans*-$[PdCl_2L_2]$ (L=**A7**)	-1.52	1.81	1						**15**	$[FeCl_2L_2][FeCl_4]$ (L=**B2**)	0.10		9
5	$[PdCl_2L_2]$ (L=**A6**)	-1.01	1.96	3						**16**	$[\{CuCl_2L\}_2]$[b] (L=**A7**)	0.70 -2.11[c]	1.54	9
6	$[PdCl_2L_2]$ (L=**A10**)	-1.24	1.76	3						**17**	$[\{CuCl_2L\}_2]$[b] (L=**A9**)	0.70 -1.91[c]	1.11	9
7	*cis*-$[PdCl_2L_2]$ (L=**B2**)	-1.48	1.52 1.80	1						**18**	$[\{CuCl\}_2(\mu\text{-}L)_2]$ (L=double deprot **B5**)	-1.13	1.03	2
8	$[PdCl_2L_2]$ (L=**B3**)	-1.42	1.92	1										

[a] Values in Volt (± 20 mV) measured in 0.2 M $[NBu_4][BF_4]$ /CH_2Cl_2, unless stated otherwise, using $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ (0.54 V *versus* SCE) as internal standard.
[b] In THF.[c] Irreversible wave. [d] In CH_3CN. [e] Reversible wave.

Table 3. Cyclic voltammetry data[a] for camphorimine derived complexes

	Other Complexes	E_p^{red}	E_p^{ox}	Ref		**Other** Complexes	$E_{1/2}^{red}$	E_p^{ox}
19	$[\{FeCl_2(THF)\}(\mu\text{-}L)_2]^b$ (L=double deprot **B5**)	-0.09 -0.95	1.03	2	**22**	$[PdClL_2]^b$ (L=**C16**)	-1.06	1.10
20	$[\{CoCl(H_2O)\}_2(\mu\text{-}L)_2]^d$ (L=double deprot **B5**)	-1.04	1.03	2	**23**	$[\{PdClL\}_2]$ (L= **C16**)	-0.93 -1.60[c]	
21	$[\{Re(OMe)_2(NEt_3)\}_2(\mu\text{-}L)_2]^d$ (L=double deprot **B5**)	-0.92	0.56[e] 1.04	2	**24**	$[\{FeClL_2(H_2O)\}_2]$ (L= **C16**)	-0.12 -2.18[c] -2.60[c]	
					25	$[\{CuClL\}_2]^b$ (L= **C16**)	-1.40	0.70[e]

[a] Values in Volt (± 20 mV) measured in 0.2 M $[NBu_4][BF_4]$ /CH_2Cl_2, unless stated otherwise, using $[Fe(\eta^5\text{-}C_5H_5)_2]^{0/+}$ (0.54 V *versus* SCE) as internal standard. [b] In THF. [c] Irreversible wave. [d] In CH_3CN. [e] Reversible wave.

The electrochemical properties of Pd, Pt, Fe, Cu, Co and Re complexes derived from camphor type ligands (A, B, or C) were studied and the potential values are displayed on Tables 2 and 3. At the complexes, the cathodic processes occur at higher potential values than those at the corresponding free ligands, with the exceptions of palladium (**7**, **8**) and copper (**16**) complexes, Table 2. That behaviour was expected for systems with ligand centred reduction processes, even for weak ligands, since electron release from the ligand to the metal facilitates its reduction.

In what concerns the anodic processes, the palladium complexes (**1-6**) derived from type (A) ligands display higher potential values than the free ligands. This tendency is not verified for the complexes derived for type (B) ligands (**7**, **8**) that display similar values to those of the free ligands nor is observed on Pt complexes (**9-11**) that display oxidation potentials lower than the free ligands.

In order to evaluate the influence of the ligand on the redox properties of the complexes we plotted the cathodic and anodic potential values of the complexes *versus* the corresponding potential values of the ligands, Fig. 3.

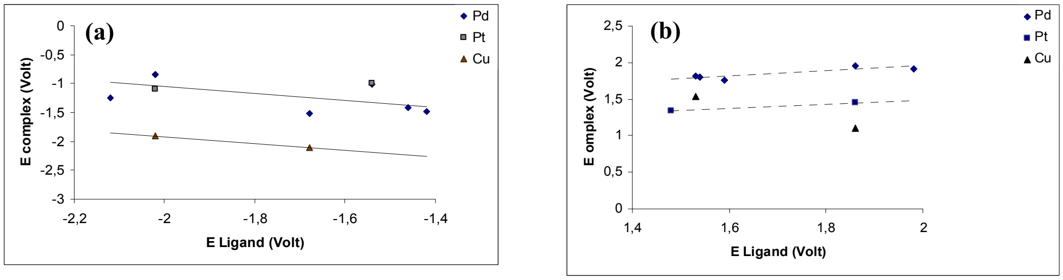


Figure 3. Plot of the reduction (a) or oxidation (b) potential of camphor derived complexes *versus* the corresponding potentials at the ligands.

Reasonable good linear correlations were obtained for palladium complexes on the two sets of data, although the slopes have different signs. In what concerns the cathodic potentials, the potential values for the Pt complexes approach the trend line obtained for the Pd complexes, Fig. 3(a), whether the anodic ones do not, Fig. 3(b). The anodic data for copper are completely out of the range of that one for Pd or Pt.

Further data are necessary for generalization but it seems that at these systems the characteristics of the metal play a more important role on the anodic than on the cathodic processes.

Acknowledgements

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