

Figure 2. Plot of experimental (●) and simulated (—) i_c/i_0 vs $-\log(v)$ (v = scan rate in $V s^{-1}$), for $\gamma = 1$. Simulated values were obtained by considering k_1 and k_2 values of $1.2 \times 10^3 M^{-1}s^{-1}$ and $2.5 s^{-1}$, respectively.

Acknowledgements

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Redox Properties of Carbene Complexes of Chromium and Tungsten

Annette Limberg, M. Amélia N. D. A. Lemos and Armando J. L. Pombeiro

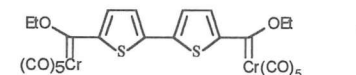
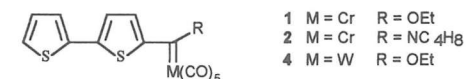
Centro de Química Estrutural, Complexo I, Instituto Superior Técnico, Av. Rovisco Pais, 1096 Lisboa codex, Portugal

Stefano Maiorana, Antonio Papagni and Emanuela Licandro

Dipartimento di Chimica Organica e Industriale, Università degli studi di Milano, via Golgi 19, 20133 Milano, Italy

Abstract

The electrochemical behaviour of the following carbene complexes of chromium and tungsten (1-4), was investigated by cyclic voltammetry (CV) and controlled-potential electrolysis (CPE), in 0.2 M $[NBu_4][BF_4]/MeCN$, thf or CH_2Cl_2 , at Pt-electrodes.



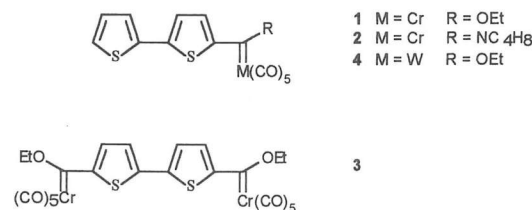
They all show a single anodic wave with $E_{p/2}^{ox}$ in the range +0.88 V to +1.12 V (vs. S.C.E.). For the chromium compounds (1-3) this wave presents a partially reversible character, whereas the oxidation wave of the tungsten compound (4) is irreversible at all the scan rates investigated. These processes correspond to the expected $M^0 \rightarrow M^I$ oxidations. However, CPE carried out for complexes 1, 2 and 4 indicate the participation of more than one electron in the overall anodic process. For the chromium compounds (1-3), the values of the ligand P_L parameter were estimated for the carbene ligands, as follows: -0.62 V (1), -0.56 V (2) and -0.38 V (3). The complexes also present cathodic waves and the first one is reversible for 1, 3 and 4 [$E_{1/2}^{red}$ in the range from -0.70 V to -1.02 V (vs. S.C.E.)]. CPE carried out for 1 and 3 show that only a single electron is involved in this process. However, compound 2 shows an irreversible cathodic wave at a

remarkably more negative potential ($E_{p/2}^{\text{red}} = -1.54 \text{ V}$).

Introduction

The extensive investigation of carbene complexes has involved only very few studies of their redox properties, in spite of the promising redox-induced chemistry of their multiple metal-carbon bonded ligands.

Following our interest on the investigation of the electrochemical behaviour of rhenium [1], platinum and palladium [2] complexes with multiple metal carbon bonds, we are presently extending this study to the following Fischer-type carbene complexes of chromium and tungsten (1-4) [3], with a bithiophenyl as the organic group and an alkoxy or an amino function as the hetero-organic group.



In this work we compare the potentials for the redox reactions presented by these different types of compounds, aiming the study of the influence of the metal (chromium and tungsten), of the organic group (ethoxy and pyrrolidine) and of a second carbene group attached to the bithiophene ligand.

The electrochemical studies were carried out by cyclic voltammetry (CV) and controlled-potential electrolysis (CPE), at a Pt-wire, or Pt-gauze electrode, respectively, in 0.2 M [NBu₄][BF₄]/NCMe, thf or CH₂Cl₂.

Results and Discussion

Anodic Processes

Each of the studied compounds shows a single anodic wave at a potential in the range of +0.9 V to +1.1 V (vs. S.C.E). (see table I). For the chromium complexes (1-3) this wave presents a partially reversible character, its reversibility decreasing with a decrease of the scan rate. For the tungsten compound (4) the anodic process is irreversible in the

investigated range of scan rates (30 mVs⁻¹ to 800 mVs⁻¹).

Table I - Oxidation and reduction potentials (versus SCE) measured at 200 mVs⁻¹ at a Pt-wire electrode in 0.2 M [NBu₄][BF₄]/NCMe, thf or CH₂Cl₂, using ferrocene as internal reference ($E_{1/2}^{\text{ox}} = 0.40 \text{ V versus S.C.E.}$, in 0.2 M [NBu₄][BF₄]/NCMe and 0.54 V versus S.C.E. in 0.2 M [NBu₄][BF₄]/thf or CH₂Cl₂).

Compound	$E_{1/2}^{\text{ox}}/\text{V}$	$E_{1/2}^{\text{red}}/\text{V}$
	+0.88	-1.02
	+0.94	(-1.68) ^(a)
	+1.12	-0.70
	(+1.03) ^(a)	-0.95

^(a) Irreversible process; value of $E_{p/2}$ is given

The current-functions for the anodic processes show, for all the compounds, a considerable increase with decreasing scan rates, *e.g.* almost duplicating its value with a tenfold decrease in the scan rates investigated, for compound (2).

These facts suggest that a chemical reaction is occurring after the electron-transfer step and the product is further oxidized at the electrode process.

In order to get more data about these processes, CPE was attempted, but since the measurements were complicated by adsorption problems the number of electrons

involved in the process could not be given accurately. Nevertheless, the CPE confirmed that more than one electron is transferred in the overall oxidation process.

The oxidation potential of the tungsten compound (**4**) is slightly higher than that of the corresponding chromium compound (**1**), thus following the $M^0 \rightarrow M^I$ ionisation potential in the gas phase [4].

For the discussion of the influence of the hetero-organic group and the second carbene group at the bithiophene function we have estimated the P_L ligand parameters for the carbene ligands of the chromium compounds, according to the expression (1).

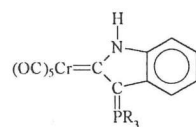
$$P_L = E_{1/2}^{OX} [Cr(CO)_5L] - E_{1/2}^{OX} [Cr(CO)_6] \quad (1)$$

$$\text{with } E_{1/2}^{OX} [Cr(CO)_6] = 1.5 \text{ V}$$

The P_L parameter is considered as a measure of the net π -acceptor minus donor electron ability of the ligand [5], meaning that a less negative P_L value corresponds to a higher electron withdrawing ability of the ligand.

In contrast with the similarity of the P_L values for the carbene ligands in compounds **1** and **2** (-0.62 V and -0.56 V, respectively), that for **3** (-0.38 V) is significantly less negative. That suggests that the two carbene functions interact even though they are quite far away from each other, and that the second carbene group attached to the ligand possesses a significant electron withdrawing ability.

Comparing the P_L values obtained in this work with those for the known [6] neutral carbene compounds



we find ours to be significantly less negative, thus meaning that the investigated carbene ligands carrying the bithiophene group have a stronger net electron withdrawing ability. This agrees with the extended conjugated system of the bithiophene.

Cathodic Processes

The cyclic voltammograms show several cathodic waves, but only the first ones are

discussed here. For compounds **1**, **3** and **4** these first reduction waves are reversible and are found in the -0.70 V to -1.02 V (vs. S.C.E.) range (table I).

Controlled-potential electrolysis carried out for the compounds **1** and **3** confirmed that only a single electron is involved in this process. However, compound **2** shows an irreversible cathodic wave at a remarkably more negative potential (-1.68 V). This large potential shift may be due to the electron donating character of the amine group and can possibly indicate that the energy of the LUMO is much influenced by the carbene substituent, as expected for a significant contribution of the carbene carbon to that orbital as observed [7] for related carbene complexes.

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