

Full Paper

UV-Visible and Electrochemical Monitoring of Carbon Monoxide Release by Donor Complexes to Myoglobin Solutions and to Electrodes Modified with Films Containing Hemin

Joseph C. Obirai,^{a,b} Sarah Hamadi,^a Aurélie Ithurbide,^a Corinne Wartelle,^a Tebello Nyokong,^b José Zagal,^c Siden Top,^d Fethi Bedioui^{a*}

^a Ecole Nationale Supérieure de Chimie de Paris, Unité de Pharmacologie Chimique et Génétique, UMR CNRS 8151 / U INSERM 640, 11 Rue Pierre et Marie Curie, 75231, Paris Cedex 05, France

*e-mail: fethi-bedioui@enscp.fr

^b Department of Chemistry, Rhodes University, Grahamstown 6140, South Africa

^c Facultad de Química y Biología, Universidad de Santiago de Chile, Casilla 40, Correo 33, Santiago, Chile

^d Ecole Nationale Supérieure de Chimie de Paris, Laboratoire de Chimie et Biochimie des Complexes Moléculaires, UMR CNRS 7576, 11 rue Pierre et Marie Curie, 75231 Paris cedex 05, France

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Abstract

This study reports on the evaluation of the CO donating behavior of tricarbonyl dichloro ruthenium(II) dimer ($[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$) and 1,3-dimethoxyphenyl tricarbonyl chromium ($\text{C}_6\text{H}_3(\text{MeO})_2\text{Cr}(\text{CO})_3$) complex by UV-visible technique and electrochemical technique. The CO release was monitored by following the modifications of the UV-visible features of MbFe(II) in phosphate buffer solution and the redox features of reduced Hemin, HmFe(II), confined at the surface of a vitreous carbon electrode. In the latter case, the interaction between the hemin-modified electrode and the released CO was seen through the observation of an increase of the reduction current related to the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ redox process of the immobilized porphyrin. While the ruthenium-based complex, $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$, depended on the presence of Fe(II) species to release CO, it was found that the chromium-based complex released spontaneously CO. This was facilitated by illuminating and/or simple stirring of the solution containing the complex.

Keywords: Carbon monoxide, Ruthenium complex, Chromium CO-releasing complex, Hemin modified electrode, Cyclic voltammetry, UV-visible spectrophotometry, Myoglobin

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1. Introduction

It has been known for a long time that carbon monoxide (CO) is generated in the human body [1] but its biological functions have been explored only in recent years. CO is released endogenously, principally from heme oxygenase (HO) which exists in one inducible (HO-1) and two constitutive (HO-2 and HO-3) isoforms [2]. The physiological activities of CO parallel those of nitric oxide (NO). Indeed, it has been reported that HO-derived CO intervenes in physiological processes such as neurotransmission [3–5] and inhibition of platelets aggregation [6]. Also, exogenous CO has been shown to prevent endothelial cell apoptosis [7] and reduce vascular relaxation and moderate both coronary vasoconstriction and acute hypertension [8]. Contrary to NO, very rare studies have been reported on the investigation of organic or organometallic molecules capable of releasing CO. Motterlini et al. [9] reported on one of the rare example of transition metal carbonyls, namely: iron pentacarbonyl ($[\text{Fe}(\text{CO})_5]$), dimanganese decacarbonyl ($[\text{Mn}_2(\text{CO})_{10}]$) and tricarbonyl dichlororuthenium(II) dimer ($[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$), as potential CO-releasing molecules.

Specifically, the authors showed by developing spectrophotometric and NMR analysis that $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ releases CO in a concentration-dependent manner and causes sustained vasodilatation in precontracted rat aortic rings and significantly reduced acute hypertension in vivo.

In this work, we propose a physico-chemical study to further evaluate the CO donating behavior of $[\text{Ru}(\text{CO})_3\text{Cl}_2]_2$ (noted as **1**, see structure Fig. 1) by UV-visible and electrochemical techniques, using reduced Met-myoglobin (MbFe(II)) and hemin (HmFe(III)) based chemically modified electrode, respectively. The CO release was monitored by following the modifications of the UV-visible features of MbFe(II) in phosphate buffer solution and redox features of reduced HmFe(II) confined at the surface of a vitreous carbon electrode. In the latter case, the interaction between the hemin-modified electrode and the released CO was seen through the observation of an increase of the reduction current related to the $\text{Fe}^{\text{III}}/\text{Fe}^{\text{II}}$ redox process of the immobilized porphyrin. The second part of this work was devoted to evaluate the CO donating effect of a chromium carbonyl complexes (1,3-dimethoxyphenyl chromium tri-