

## Optical metal-to-metal charge transfer in [Fe<sup>III</sup>(C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Re<sup>I</sup>(CO)<sub>3</sub>Cl]<sup>+</sup>

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### Abstract

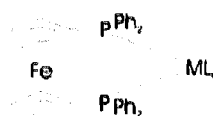
The electronic spectrum of the binuclear complex ion [Fe<sup>III</sup>(C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Re<sup>I</sup>(CO)<sub>3</sub>Cl]<sup>+</sup> in CH<sub>2</sub>Cl<sub>2</sub> shows a long-wavelength absorption at λ<sub>max</sub> = 700 nm (ε = 206 M<sup>-1</sup>cm<sup>-1</sup>) which is assigned to a Re<sup>I</sup> → Fe<sup>III</sup> MMCT transition. An analysis according to the Hush model confirms the assumption that the complex contains weakly coupled metal centers and is thus a type II compound (Robin and Day classification). © 1997 Elsevier Science S.A.

**Keywords:** Ferrocenium; Rhenium carbonyl complex; Charge transfer

### 1. Introduction

Binuclear ligand-bridged heterometallic transition metal complexes have attracted much attention in recent years. This interest is related to the importance of such compounds in biochemistry, catalysis and other potential applications. These functions depend on several effects including steric, electrostatic and electronic interactions. The electronic coupling of both metal centers could be quite significant but is largely unknown in most cases.

A series of rather interesting binuclear complexes are of the type [1]



Since the organometallic compound 1,1'-bis(diphenylphosphino)ferrocene Fe(C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub> is easily accessible and commercially available a variety of binuclear or polynuclear complexes incorporating this ferrocene-substituted phosphine as bidentate ligand has been prepared and characterized [1]. However, the existence and

extent of electronic coupling between both metals has not yet been studied in any detail.

Binuclear complexes which simultaneously contain a reducing and an oxidizing metal center show optical metal-to-metal charge transfer (MMCT) which provides important information on metal-metal interaction [2–7]. Typical examples are mixed-valence complexes which contain bridging ligands such as cyanide or pyrazine. Ferrocenes are also known to participate in optical Fe<sup>II</sup> → Fe<sup>III</sup> MMCT when ferrocene and ferrocenium are linked by a carbon-carbon bond. However, it is not yet known if the electronic communication between two metals is also mediated by phosphine bridges in general and the phosphine function of Fe(C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub> in particular. In the case of [Co<sup>III</sup>(C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Re<sup>I</sup>(CO)<sub>3</sub>Cl]<sup>+</sup> the possible appearance of a MMCT absorption was pointed out but clear evidence was missing [8]. As a suitable candidate for the detection of a MMCT band in the electronic spectrum of this type of complex we selected the cation [Fe<sup>III</sup>(C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Re<sup>I</sup>(CO)<sub>3</sub>Cl]<sup>+</sup>. It is easily prepared and has been described before [9]. The expectation to observe a MMCT band at relatively low energies is based on the following considerations. Ferrocenium is a rather strong oxidant and its reduction is not associated with a large reorganization energy since the electron is accepted in the a<sub>1g</sub> orbital which is not involved in strong σ-bonding [10]. The Re<sup>I</sup>(CO)<sub>3</sub>X moiety is a well known donor. Complexes of the type (1,2-diimine)Re(CO)<sub>3</sub>X (e.g. diimine = bipy) display

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long-wavelength  $\text{Re}^I \rightarrow 1,2$ -diimine metal-to-ligand charge transfer (MLCT) bands [10,11]. Moreover, the participation of the  $\text{Re}^I(\text{CO})_3\text{X}$  fragment in optical MMCT has been recently suggested to take place in  $\text{S}_2\text{Re}^{\text{VII}}(\mu\text{-S})_2\text{Re}^I(\text{CO})_3\text{Cl}$  [12]. Accordingly, our target ion  $[\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^I(\text{CO})_3\text{Cl}]^+$  is anticipated to show a low-energy MMCT transition, if the bridging phosphine mediates a sufficient metal–metal interaction.

## 2. Experimental

### 2.1. Materials

The compounds  $\text{Fe}^{\text{II}}(\text{C}_5\text{H}_4\text{PPh}_2)_2$  (1,1'-bis(diphenylphosphino)ferrocene), diphos (1,2-bis(diphenylphosphino)ethane),  $\text{Re}(\text{CO})_5\text{Cl}$ , ferrocene (Aldrich), and  $\text{NO}(\text{BF}_4)$  (Strem) were commercially available and used as received. For spectroscopic measurements the solvents were spectrograde and argon-saturated. The binuclear complex  $\text{Fe}^{\text{II}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^I(\text{CO})_3\text{Cl}$  was prepared as described by Wrigton et al. [9]. The complex (diphos) $\text{Re}(\text{CO})_3\text{Cl}$  was also obtained according to a literature procedure [13].

### 2.2. Instrumentation

Absorption spectra were measured with a Uvikon 932 and a Bruins Instruments Omega 10 UV-VIS-NIR double-beam spectrophotometer.

## 3. Results

The oxidation of  $\text{Fe}^{\text{II}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^I(\text{CO})_3\text{Cl}$  with  $\text{NOBF}_4$  yields  $[\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^I(\text{CO})_3\text{Cl}]^+$  [9]. The electronic spectrum of this cation in  $\text{CH}_2\text{Cl}_2$  (Fig. 1) shows long-wavelength absorptions at  $\lambda_{\text{max}} = 609$  nm ( $\epsilon = 290 \text{ M}^{-1}\text{cm}^{-1}$ ) and 700 nm (shoulder,  $\epsilon = 206$

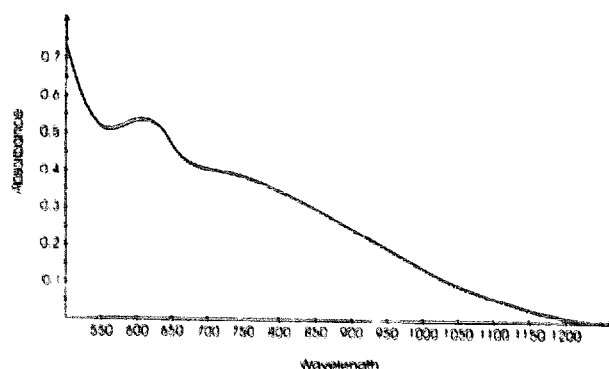


Fig. 1. Electronic spectrum of  $1.8 \times 10^{-4} \text{ M}$   $[\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^I(\text{CO})_3\text{Cl}]^+$  in argon-saturated  $\text{CH}_2\text{Cl}_2$ , 1 cm cell.

$\text{M}^{-1}\text{cm}^{-1}$ ). The band at 609 nm which was reported previously [9] is not solvent dependent. On the contrary, the lower-energy absorption is shifted to shorter wavelength with increasing solvent polarity. Owing to this blue shift in solvents such as  $\text{CH}_3\text{CN}$  the band maximum is not any more discernible since it is obscured by the 609 nm band. The absorption spectra of the mononuclear fragments which constitute the binuclear complex cation should be considered for comparison. Unfortunately they do not exist as separate entities. However, the ferrocenium cation and the complex (diphos) $\text{Re}(\text{CO})_3\text{Cl}$  (diphos = 1,2-bis(diphenylphosphino)ethane) may be taken as suitable substitutes.  $\text{Fe}(\text{C}_5\text{H}_5)_2^+$  shows a diagnostic band at  $\lambda_{\text{max}} = 617$  nm ( $\epsilon = 450 \text{ M}^{-1}\text{cm}^{-1}$ ) [7,10,14] while (diphos) $\text{Re}(\text{CO})_3\text{Cl}$  absorbs at  $\lambda_{\text{max}} = 329$  nm ( $\epsilon = 1100 \text{ M}^{-1}\text{cm}^{-1}$ ) and 299 nm ( $\epsilon = 3100 \text{ M}^{-1}\text{cm}^{-1}$ ).

## 4. Discussion

If both metals of  $[\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^I(\text{CO})_3\text{Cl}]^+$  are weakly coupled its absorption spectrum should consist of the spectra of its mononuclear components  $[\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{PPh}_2)_2]^+$  and  $[(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^I(\text{CO})_3\text{Cl}]^{2-}$ . Since both components are not existent the ferrocenium cation and (diphos) $\text{Re}(\text{CO})_3\text{Cl}$  serve as appropriate models. The diphos complex is colourless and absorbs only below 400 nm. Accordingly, the long-wavelength absorptions of the binuclear cation cannot be ascribed to the mononuclear  $\text{Re}^I$  complex. On the contrary, the shorter-wavelength absorption of  $[\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^I(\text{CO})_3\text{Cl}]^+$  at  $\lambda_{\text{max}} = 609$  nm is attributed to an internal transition of the ferrocenium moiety.  $\text{Fe}(\text{C}_5\text{H}_5)_2^+$  shows this characteristic ligand-to-metal charge transfer (LMCT) band at  $\lambda_{\text{max}} = 617$  nm [7,10,14]. These observations are consistent with the assumption that the binuclear ion contains both metals in trapped valencies. However,  $[\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^I(\text{CO})_3\text{Cl}]^+$  shows an additional long-wavelength band at  $\lambda_{\text{max}} = 700$  nm (Fig. 1) which does not belong to the separate components. This new absorption is logically assigned to a  $\text{Re}^I \rightarrow \text{Fe}^{\text{III}}$  MMCT transition. It follows that the binuclear ion should be a type II compound according to the Robin and Day classification of mixed-valence complexes [15]. This conclusion is confirmed and elaborated by the application of the Hush theory [2,4,16–19].

In distinction to delocalized systems the energy of the MMCT transition between weakly coupled metal centers depends on the solvent polarity. The longest-wavelength band of  $[\text{Fe}^{\text{III}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^I(\text{CO})_3\text{Cl}]^+$  shows indeed such a solvatochromic behaviour. Moreover, the energy of the MMCT transition  $E_{\text{op}}$  (or  $\bar{\nu}_{\text{max}}$  =

14290  $\text{cm}^{-1}$ ) is the sum of the reorganizational energy  $X$  and the energy difference  $\Delta E$  (or potential difference, respectively) between the redox couples  $\text{Fe}^{\text{III/II}}$  and  $\text{Re}^{\text{I/II}}$ :

$$E_{\text{op}} = X + \Delta E$$

While  $[\text{Fe}^{\text{II}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}]$  is reversibly oxidized to the  $\text{Fe}^{\text{III}}$  complex at  $E_{1/2} = 0.67$  V versus  $\text{Ag}/\text{Ag}^+$  [9] the redox potential for oxidation of  $\text{Re}^{\text{I}}$  is not known. However, for an approximation the potential for the irreversible oxidation of (diphos) $\text{Re}(\text{CO})_3\text{Cl}$  ( $E_{1/2} = 1.4$  V) may be taken [9]. The reorganizational energy is then calculated to be  $X = 8400$   $\text{cm}^{-1}$  (or 24 kcal). This is a reasonable value since the donor and acceptor orbital of the MMCT transition are not involved in strong  $\sigma$ -bonding interactions. The donor orbital at  $\text{Re}^{\text{I}}$  with  $d^6$  configuration is of the  $t_{2g}$  type (in  $O_h$  symmetry). This is also true for the  $a_{1g}^*$  acceptor orbital at  $\text{Fe}^{\text{III}}$  with a  $d^5$  configuration [7,10,14].

The theoretical half-bandwidth of the MMCT absorption should satisfy the equation

$$\Delta\bar{\nu}_{1/2} = [2310(E_{\text{op}} - \Delta E)]^{1/2}$$

The experimental half-width could not be measured precisely owing to the overlap of the MMCT and LMCT band, but was estimated to be  $\Delta\bar{\nu}_{1/2} = 5300$   $\text{cm}^{-1}$  by analyzing the band shape at the long-wavelength side. This half-width exceeds the theoretical value  $\Delta\bar{\nu}_{1/2} = 4400$   $\text{cm}^{-1}$ . However, a discrepancy of this magnitude is frequently observed for class II complexes.

The delocalization coefficient can be calculated according to the equation

$$\alpha^2 = 4.24 \cdot 10^{-4} \epsilon_{\text{max}} \Delta\bar{\nu}_{1/2} / \bar{\nu}_{\text{max}} \cdot R^2$$

Since the Fe–Re distance in the binuclear complex is  $R = 4.5$  Å [20] the delocalisation is  $\alpha^2 = 1.6 \cdot 10^{-3}$  and thus rather small as expected for weakly coupled metal centers.

In this context a comparison with  $[\text{Co}^{\text{III}}(\text{C}_5\text{H}_4\text{PPh}_2)_2\text{Re}^{\text{I}}(\text{CO})_3\text{Cl}]^+$  would be quite interesting. The possible existence of a  $\text{Re}^{\text{I}} \rightarrow \text{Co}^{\text{III}}$  MMCT transition has been indicated [8]. However, the detection of the corresponding absorption is probably hampered

by the interference with other bands of different origin since MMCT transitions with  $\text{Co}^{\text{III}}$  as acceptor are expected to occur at relatively high energies. This assumption which applies also to other cobalt complexes [5,6] is based on the small oxidizing strength of the cobaltocenium cation,  $\text{Co}^{\text{III}}(\text{C}_5\text{H}_5)_2^+$ , and the large reorganizational energy which is required for  $\text{Co}^{\text{III}}$  reduction. The electron is accepted into a strongly antibonding  $e_{1g}^*$  orbital [7].

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