ELSEVIER

www.elsevier.nl/locate/ica

Inorganica Chimica Acta 299 (2000) 231–237

Inorganica Chimica Acta

# Spectroscopic and electrochemical properties of $[Mn(phen)(CO)_3(imidazole)](SO_3CF_3)$ complexes

Rose Maria Carlos [a], Ivani Ap. Carlos [b], Benedito S. Lima Neto [a], Miguel G. Neumann [a,*]

[a] *Instituto de Química de São Carlos, Universidade de São Paulo, Caixa Postal 780, 13560-970 São Carlos, SP, Brazil*
[b] *Departamento de Química, Universidade Federal de São Carlos, Caixa Postal 676, 13565-905 São Carlos, SP, Brazil*

Received 11 March 1999; accepted 5 November 1999

---

## Abstract

The spectroscopic and electrochemical properties of $[Mn(phen)(CO)_3(L)]^+$ type complexes where L is an imidazole or an imidazole derivative containing a methyl, phenyl or $NO_2$ group, have been investigated. Introduction of the substituents to the σ-donor ligand has been found to produce significant changes in the electrochemical behaviour without significantly altering the fundamental electronic structure of the complexes. The oxidation potentials of the *fac*-$[Mn(phen)(CO)_3L]^+$ and *mer*-$[Mn(phen)(CO)_3L]^+$ isomers are very different, allowing detailed electrochemical studies to be made. Cyclic voltammetry of both the *fac* and *mer* isomers provides a complete description of a cyclic process involving the following reactions.

$$\begin{tikzcd}
fac\text{-}[Mn(phen)(CO)_3L]^+ \arrow[r, "-e^-"] & fac\text{-}[Mn(phen)(CO)_3L]^{2+} \arrow[d] \\
mer\text{-}[Mn(phen)(CO)_3L]^+ \arrow[u] & mer\text{-}[Mn(phen)(CO)_3L]^{2+} \arrow[l, "+e^-"']
\end{tikzcd}$$

*Keywords:* Electrochemistry; Manganese complexes; Phenanthroline complexes; Imidazole complexes; Carbonyl complexes

---

## 1. Introduction

Mn(I) tricarbonyl complexes, containing bidentate heterocyclic ligands have been a source of continuous interest for several years [1–10]. One goal of these studies has been the systematic investigation of complexes with different ligand combinations in order to establish both the generalities and discontinuities in the excited state behaviour of homologous systems [1–8]. Whereas, most work has grown around *N*,*N*-chelating pyridine bases [5] and related species like $MnX(CO)_3$(α-diimine) [1,3,5–8], only the influence of π-donating 'spectator' ligands X (halides) was investigated [1,4–13], although alkyl complexes have also been studied [3,6]. Therefore, as the ligand field strength of the ligands should affect significantly the physical and chemical properties of the complex it seems of interest to extend the range of ligands investigated to those with strong σ donors properties.

Since imidazole ligands contain a number of possible bridging sites, the spectroscopic and electrochemical properties of a series of monometallic Mn(I) tricarbonyl complexes containing $CH_3$-, $C_6H_5$-, $NO_2$-substituted imidazole ligands were examined with the goal of manipulating the basicity of the imidazole ligand, and consequently the π-acidity of the compound. The studies described illustrate how structural features can modify the bonding properties and the excited state dynamics of the Mn(I) complexes. Understanding the

---

* Corresponding author. Tel.: + 55-16-273 9940; fax: + 55-16-273 9952.

*E-mail address:* neumann@iqsc.sc.usp.br (M.G. Neumann)

0020-1693/00/$ - see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0020-1693(99)00505-8

consequences of such molecular perturbations is essential in the design of chemical systems for practical applications.

## 2. Experimental

### 2.1. Materials

$Mn(CO)_5Br$ was from Strem, 1,10-phenanthroline, imidazole, 2-methyl-imidazole and 2-phenyl-imidazole were from Aldrich and Metroimidazole (2-methyl-5-nitroimidazole-1-ethanol) was from Sigma. Methylene chloride, acetonitrile, methanol, ethanol, tetrahydrofuran and acetone were HPLC grade. Tetrabutylammonium perchlorate (TBPA) from Eastman Kodak used as supporting electrolyte for electrochemical experiments was dried overnight under vacuum at 50°C and stored under vacuum before use. The ligands were phenanthroline (phen), trifluoromethanesulfonic ion (trif), imidazole (Im), 2-methyl-imidazole ($CH_3$-Im), 2-phenyl-imidazole ($C_6H_5$-Im), and 2-methyl-5-nitroimidazole-1-ethanol (Metro-Im).

### 2.2. Syntheses

All syntheses and preparations for electrochemical experiments were carried out under purified $N_2$ atmosphere, using Schlenk techniques. The solutions were carefully handled in the dark before the experiments were performed.

#### 2.2.1. $MnBr(CO)_3(phen)$

The halo complex was prepared by reacting $Mn(CO)_5Br$ (1.0 g, 3.65 mmol) with phenanthroline (0.65 g, 3.60 mmol), as described by Riera and coworkers [14] but using 40 ml $CH_2Cl_2$ (freshly distilled and dried under $P_2O_5$) instead of benzene. The mixture was left in the dark overnight at room temperature, after which the complex was precipitated by addition of cold ethyl ether. Yield: 1.31 g (90%).

#### 2.2.2. $Mn(trif)(CO)_3(phen)$

Ag(trif) (0.27 g, 1 mmol) was added to a solution of $MnBr(CO)_3(phen)$ (0.30 g, 0.75 mmol) in 40 ml $CH_2Cl_2$ (freshly distilled and dried under $P_2O_5$). The mixture was stirred overnight at room temperature in the dark. During this time a white precipitate was formed. The reaction mixture was filtered and the resulting solution was concentrated in vacuo to ca. 10 ml. Addition of cold ethyl ether (2 ml) with stirring precipitated a dark yellow crystalline solid, that was recrystallized from $CH_2Cl_2$/ethyl ether. Yield: 0.31 g (90%)

#### 2.2.3. $[Mn(CO)_3(phen)L](trif)$

The following procedure, described for $[Mn(CO)_3(phen)(Im)](trif)$, is also representative of the synthesis of the other substituted imidazole complexes (L: $CH_3$-Im, $C_6H_5$-Im, Metro-Im). Imidazole (0.044 g, 0.51 mmol) was added to a solution of $Mn(trif)(CO)_3(phen)$ (0.15 g, 0.32 mmol) in $CH_2Cl_2$ (40 ml) and the mixture was stirred for 24 h at room temperature in the dark. The solution was concentrated to ca. 10 ml, mixed with cold ethyl ether (5 ml), filtered and vacuum dried. The product was recrystallized from $CH_2Cl_2$/ethyl ether to give a bright yellow microcrystalline powder. Yield: 90%. The yield for $[Mn(CO)_3(phen)(Metro\text{-}Im)](trif)$ is usually smaller ( ~ 60%).

The elemental analyses of the final compounds were consistent with the composition of the anhydrous complexes: $[Mn(CO)_3(phen)(Im)](trif)$. Calc.: C, 42.55; H, 2.24; N, 10.44. Found: C, 43.02; H, 2.18; N, 10.64%. $[Mn(CO)_3(phen)(CH_3\text{-}Im)](trif)$. Calc.: C, 43.65; H, 2.55; N, 10.18. Found: C, 45.60; H, 2.75; N, 10.7%. $[Mn(CO)_3(phen)(Metro\text{-}Im)](trif)$. Calc.: C, 50.03; H, 2.92; N, 9.13. Found: C, 49.02; H, 2.61; N, 9.15%. $[Mn(CO)_3(phen)(C_6H_5\text{-}Im)](trif)$. Calc.: C, 41.08; H, 2.63; N, 10.95; S, 5.01. Found: C, 40.82; H, 2.62; N, 10.76; S, 4.90%.

### 2.3. Instruments and procedures

Microanalyses (C,H,N) were performed on a Eager 200 elemental analyzer. Infrared spectra were obtained on a Bomen MB spectrometer using KBr pellets. UV–Vis spectra were obtained with a U2000 Hitachi spectrophotometer. $^{13}C$ NMR spectra were recorded on a Bruker DRX 400 spectrometer using $CD_2Cl_2$ solutions.

Cyclic voltammetry was performed using an EG&G Princeton Applied Research Model 173 potentiostat/galvanostat in conjunction with a three-electrode cell. Voltammograms were obtained in $CH_2Cl_2$ (1 mM TBPA) at 22°C in a light-protected voltammetric cell with a platinum cylinder for both the working and the auxiliary electrodes. A silver wire coated with silver chloride was used as reference electrode, connected to the bulk of the solution by a Luggin capillary filled with the same solvent and electrolyte. The area of the working electrode was 0.30 $cm^2$ as determined by the Cottrell equation using $K_4[Fe(CN)_6]$ in aqueous 1 mM KCl. The platinum electrodes were prepared by carefully polishing with 0.3 μm alumina (in water suspension) followed by cleaning with $HNO_3$ 1 mM, and rinsed with distilled water. Solutions were deoxygenated with a stream of $N_2$ and maintained under a positive pressure of $N_2$ during the measurements. The concentration of the complexes was kept always at 1 mM. A 1.0 mM ferrocene (Fc) solution in $CH_2Cl_2$ (0.1 mM TBPA) was used as voltammetric reference redox couple.

## 3. Results and discussion

### 3.1. Preparation and characterization of $[Mn(CO)_3(phen)(L)](trif)$

The Mn complexes were prepared by the reaction of a halo derivative with Ag(trif), which leads to the precipitation of the silver halide and the formation of a trifluoromethanesulfonate complex. The application of this process was used as a general method for the synthesis of the cationic organocomplexes. Owing to its poor donor capacity [15] the triflate group in $Mn(trif)(CO)_3(phen)$ may readily be replaced by a variety of substituted imidazole ligands even at room temperature. These ligand substitutions were monitored by the changes in the UV–Vis spectra as a function of time. The solid complexes are soluble in organic solvents, slightly soluble in water and stable in air at room temperature. In solution they are sensitive to light and air.

### 3.2. $^{13}C$ NMR spectra

The $^{13}C$ NMR chemical shifts of the phenanthroline and its complexes are listed in Table 1. The chemical shifts of the imine carbon atoms are indicative of the structure of the complexes and electronic distribution in the imine structure. The equivalence of both phenanthroline ligand halves as indicated by the presence of a single set of lines in the spectra indicates that the phen ligand is in the σ,σ-bidentate coordination mode and that only the facial isomer is formed (Fig. 1).

Table 1
$^{13}C$ NMR and infrared stretching frequencies ($cm^{-1}$) for manganese carbonyl complexes and phenanthroline

| Compound | $\nu$(CO) | C (imine) (ppm) |
|---|---|---|
| Phenanthroline (phen) | | 150.3 |
| $MnBr(CO)_3(phen)$ | 2020(vs); 1922(s) | |
| $[Mn(CO)_3(phen)(CH_3\text{-Im})](trif)$ | 2029(vs); 1942(s); 1916(s) | 153.7 |
| $[Mn(CO)_3(phen)Im](trif)$ | 2037(vs); 1941; 1921(s) | 153.3 |
| $[Mn(CF_3SO_3)(CO)_3(phen)]$ | 2037(vs); 1946(s); 1921(s) | |
| $[Mn(CO)_3(phen)(C_6H_5\text{-Im})](trif)$ | 2038(vs); 1932(s); | 155.9 |
| $[Mn(CO)_3(phen)(Metro\text{-Im})](trif)$ | 2044(vs); 1949(s); 1929(s) | 154.5 |

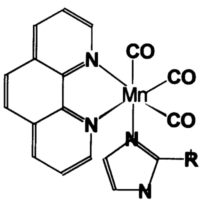

Fig. 1. Structure of $[Mn(CO)_3(phen)(L)]^+$ complexes.

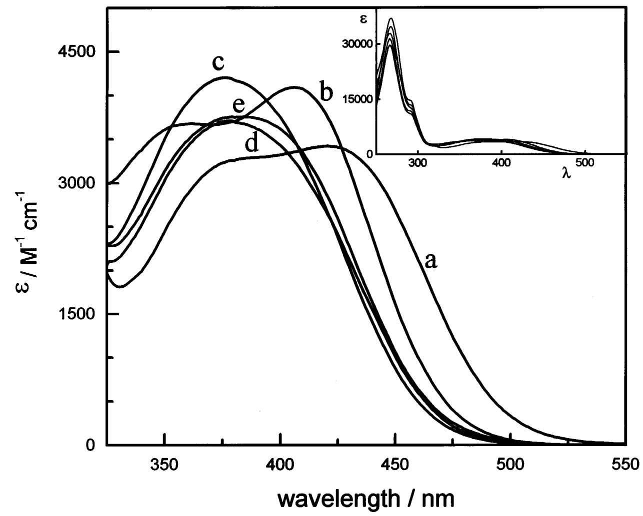

Fig. 2. Absorption spectra of *fac*-$[Mn(CO)_3(phen)(L)](trif)$ complexes in dichloromethane. (a) L = Br; (b) L = trif; (c) L = Im; (d) L = $CH_3$-Im; (e) L = $C_6H_5$-Im.

### 3.3. Infrared spectra

The carbonyl bands of the complexes show a noticeable frequency shift towards higher frequencies when compared to the $Mn(Br)(CO)_3(phen)$ precursor (Table 1). This effect is expected from the increase of the positive charge on the manganese ion that reduces the *d*-electron back-bonding to the CO resulting in a larger triple bond character of the coordinated carbonyls. This pattern of three strong bands between 2050 and 1950 $cm^{-1}$ is consistent with the facial arrangement [16] of the three COs in the coordination sphere, confirming the structure derived from the NMR spectra.

Table 2
Electronic absorption maxima for *fac*-$[Mn(CO)_3(phen)(L)]^{0/+}$ complexes in dichloromethane solution, at 22°C

| L | $\lambda$, nm ($\varepsilon$, $M^{-1}$ $cm^{-1}$) |
|---|---|
| Br | 382(3300); 422(3400); 267(34 000) |
| $CF_3SO_3$ | 366(3700); 395(4000); 269(37 000) |
| Im | 376(4200); 266(35 000) |
| $CH_3$-Im | 380(3700); 266(37 000) |
| $C_6H_5$-Im | 384(3700); 266(33 000) |
| Metro-Im | 400(3800); 268(32 000) |

Table 3
Solvatochromism of the absorption bands of *fac*-[Mn(CO)$_3$(phen)(L)](trif)

| L | Solvent | $\lambda_{max}$, nm ($\varepsilon$, M$^{-1}$ cm$^{-1}$) |
|---|---|---|
| Im | CHCl$_3$ | 378(3900); 266(32 000) |
| | THF | 371(4000); 267(29 000) |
| | MeOH | 369(3500); 266(27 000) |
| | CH$_3$CN | 369(4000); 267(29 000) |
| CH$_3$-Im | CHCl$_3$ | 383(3400); 266(30 000) |
| | THF | 376(3300); 266(29 000) |
| | MeOH | 372(2800); 266(26 000) |
| | CH$_3$CN | 372(3000); 266(29 000) |
| C$_6$H$_5$-Im | CHCl$_3$ | 387(3000); 267(30 000) |
| | THF | 378(3500); 266(27 000) |
| | MeOH | 376(2600); 266(27 000) |
| | CH$_3$CN | 374(2800); 266(28 000) |
| Metro-Im | CHCl$_3$ | 400(2700); 266(25 000) |
| | THF | 400(2800); 268(22 000) |
| | MeOH | 400(2800); 266(23 000) |
| | CH$_3$CN | 400(2600); 269(20 000) |

### 3.4. Electronic absorption spectra

Absorption properties of the *fac*-[Mn(CO)$_3$(phen)(L)]$^{0/+}$ complexes in dichloromethane are shown in Fig. 2. The absorption maxima and extinction coefficients in dichloromethane and various other solvents are collected in Tables 2 and 3, respectively. Each of the complexes shows absorption maxima in the range 370–400 nm with molar extinction coefficients between 2000 and 4000 M$^{-1}$ cm$^{-1}$. In addition, all the complexes present also an intense transition in the UV region ($\varepsilon \sim 35\,000$ M$^{-1}$ cm$^{-1}$).

Fig. 2 clearly shows that the change of the ligand has a strong influence on the positions and relative intensities of the absorption maxima of the Mn complexes. When changing from bromide to the poor π-acceptor triflate ligand, both absorption shoulders shift to higher energies. At the same time the intensity of the first band increases, and the intensity of the second one decreases. For imidazole, the shifts are so large that both shoulders merge into an unique absorption band at 370 nm.

The wavelength shift of the visible absorption band for the complexes with imidazole derivatives compared to that with unsubstituted imidazole was smaller than expected from the range of the donor/acceptor substituents used on the imidazole ring [17,18]. Although the methyl and phenyl groups do not produce large shifts of the absorption maximum, the electronic spectrum of Metro-Im substituent is seen to be very different from those of the other imidazole complexes, presenting the band at 400 nm as a shoulder of the high energy absorption.

The energies of the absorption bands in the visible region were found to be solvent-dependent. For all complexes, the position of the longer wavelength band is shifted by 700–800 cm$^{-1}$ when changing the solvents (Table 3). In contrast, the shorter wavelength band is solvent-independent. On the basis of the solvent and ligand dependencies of those bands and their rather large intensities, the lower energy absorption band is assigned to a metal-to-ligand (Mn → phen) charge transfer transition. The analogous [Re(CO)$_3$(phen)(Im)]$^+$ complex [19] also presents a MLCT transition which corresponds to the lowest energy absorption. This Re complex shows an intense absorption band near the free ligand phenanthroline absorption which is assigned to an intra-ligand (IL) transition. Therefore, the corresponding band in [Mn(CO)$_3$(phen)(L)]$^+$ is also assigned to an IL transition.

The first ligand field absorption band [20] for [Mn(CO)$_6$]$^+$ occurs at 24 000 cm$^{-1}$. Substitution of three of the CO ligands by Im and two nitrogen donors should substantially lower the average ligand field (LF) strength and yield lower lying LF states for [Mn(CO)$_3$(phen)(L)](trif). Therefore, the LF transitions are expected to appear above 26 000 cm$^{-1}$ based on the [Mn(CO)$_6$]$^+$ spectra. However, this region is obscured by the strong MLCT absorption. The MLCT band is strongly solvatochromic, and the MLCT states are stabilized in nonpolar solvents. On the other hand, the energy of the LF states is generally solvent-independent [21,22]. Therefore, using the information obtained from the electronic spectra, the LF-MLCT energy gap in CHCl$_3$ can be estimated to be 650, 800, and 900 cm$^{-1}$ larger than in CH$_3$CN for L = H-Im, CH$_3$-Im and C$_6$H$_5$-Im, respectively.

These results show that replacement of the bromide ligand by a strong σ-donor ligand as imidazole, is an effective way of altering the energy states of [Mn(CO)$_3$(phen)(L)](trif) complexes. The imidazole groups are merely σ donors to Mn(I), whereas in Ru(III) complexes they act as σ + π donors [23]. Thus, in the case of imidazole complex the lowest energy transitions will be MLCT in character in contrast to XLCT/MLCT for L = Br$^-$. Due to the change in the XLCT/MLCT character, the attraction between the metal and the phenanthroline ligand increases, strengthening this bond. As a consequence, the intensity of the visible absorption increases and shifts to shorter wavelengths, as shown in Fig. 2.

On the other hand, altering the substituents on the imidazole ligand will affect the complex mainly by destabilizing the $e_g$ orbitals (considering an $O_h$ microsymmetry). However, the MLCT states arise from the promotion of an electron from a $t_{2g}$ orbital, which is only affected slightly by the imidazole ligand basicity. For this reason, the energy of the intense MLCT band ($\sim 10^4$ M$^{-1}$ cm$^{-1}$) does not change significantly with the substituents on the imidazole ring. This argument

Table 4
Oxidation and reduction potentials (in V) of *fac*-[Mn(CO)$_3$-(phen)(L)](trif) in dichloromethane [a]

| L | Process | $E_{ox}$ | $E_{red}$ |
|---|---|---|---|
| Im | I,I′ | +0.80 | +0.60 |
| | II,II′ | +0.26 | −0.12 |
| $CH_3$-Im | I,I′ | +0.92 | +0.52 |
| | II,II′ | +0.28 | −0.06 |
| $C_6H_5$-Im | I,I′ | +0.78 | +0.48 |
| | II,II′ | +0.18 | −0.42 |
| Metro-Im | I,I′ | +0.78 | +0.68 |
| | II,II′ | +0.58 | −0.22 |

[a] Potentials are vs. Fc/Fc$^+$ couple in TBPA 0.1 mM, $t = 22$°C, conc. 1.0 mM, $v = 200$ mV s$^{-1}$

also accounts for the values of the Mn(I/II) oxidation potentials, which measures the easiness of the removal of $t_{2g}$ electron, as discussed below.

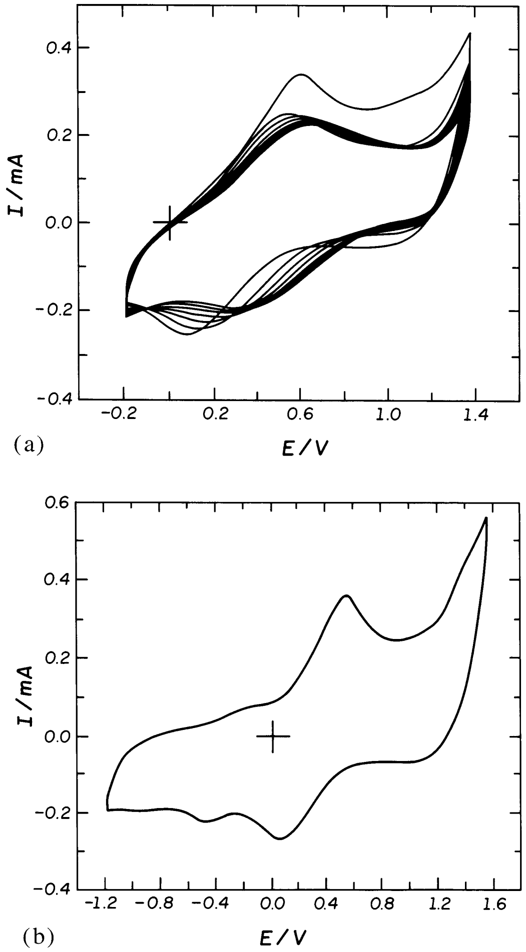

Fig. 3. Cyclic voltammograms of *fac*-[Mn(CO)$_3$(phen)(CH$_3$-Im)](trif) in CH$_2$Cl$_2$ (TBPA 0.1 M) at a platinum electrode vs. Fc/Fc$^+$; scan rate 200 mV s$^{-1}$. (a) range between 0.2 and 1.8 V; (b) range between −0.2 and 1.8 V.

### 3.5. Electrochemical studies

The voltammetric data are summarized in Table 4. The electrochemical behaviour observed for *fac*-[Mn(CO)$_3$(phen)(CH$_3$-Im)]$^+$ is representative of the other substituted imidazole Mn(I) complexes studied.

Fig. 3a shows a cyclic voltammogram (scan rate 200 mV s$^{-1}$) for a 1 mM solution of the *fac*-[Mn(CO)$_3$(phen)(CH$_3$-Im)](trif) complex over the range 0.2–1.8 V (vs. Fc$^+$/Fc) in dichloromethane (TBPA 0.1 M). On the first positive-going potential scan an oxidative response (electrode process I) is observed and the corresponding reduction response (process I′) is seen on the reverse scan. Second and subsequent scans, under these conditions, show a small shift towards more positive potentials for both the oxidation and reduction responses. Whereas the current associated with the oxidative response decreases with successive scans, the ic current increases. Processes I and I′ become time-independent after seven cycles, when $E_{ox}$ and $E_{red}$ reach values of + 1.00 and + 0.72 V versus Fc$^+$/Fc, respectively. These results suggest that interactions between the complex and the solvent during the redox cycle produce changes in the nature of the complex that are more pronounced during the initial stages of the voltammetric experiments. In tetrahydrofuran, a coordinating solvent, although the oxidative response was not very intense, the cyclic voltammetry showed reduction processes that are virtually unaltered even after repeated cycles, supporting the above arguments. Cyclic voltammetry was therefore carried out only in CH$_2$Cl$_2$, where better defined and more informative electrochemistry was obtained.

Fig. 3b shows a cyclic voltammogram in dichloromethane (TBPA 0.1 M, scan rate 200 mV s$^{-1}$) over a wider potential range. A second reductive response at 0.08 V versus Fc$^+$/Fc can be observed on the first scan (process II′), with the corresponding reduction response at 0.24 V (process II). Multiple scans resulted in superposable cyclic voltammograms, thereby showing the marked stability of the Mn species involved in the electrochemical cycle.

The reversible couple II, II′ is not observed when the potential is switched to the − 0.6 to 0.4 V range, proving that the electrode processes II and II′ are derived from a product formed in the first oxidation step. Thus, the electrode processes I and I′ can be summarized as

$$fac\text{-}[\mathrm{Mn(CO)_3(phen)(CH_3\text{-}Im)}]^{+} \xrightarrow{-e^-} fac\text{-}[\mathrm{Mn(CO)_3(phen)(CH_3\text{-}Im)}]^{2+} \quad (1)$$

When *fac*-[Mn(CO)$_3$(phen)(CH$_3$-Im)]$^+$ is oxidized at the electrode surface it rapidly causes electrode processes II and II′ to happen in a cyclic way, even after repeated scans, indicating that the oxidizable species is never exhausted.

Extensive studies have been made on the electrochemical behaviour of many carbonyl complexes of Mn(I), Cr(III), Mo(I) and W(I) transition metals [2,24–28]. The *fac–mer* isomerization induced by oxidation has already been observed for several complexes. In the case of Mn(I) complexes [2,24–26], it was shown that after chemical or electrochemical oxidation the 17-electron *fac*-compound isomerizes to the *mer*-configuration which, in turn, is readily reduced to the 18-electron *mer*-configuration. Using a series of similar Mo complexes [27] it was demonstrated that the 18-electron reduction product isomerizes back to the starting species in a cyclic process.

Based on those studies, it is suggested that at room temperature *fac*-$[Mn(CO)_3(phen)(CH_3\text{-}Im)]^{2+}$ isomerizes to the *mer*-$[Mn(CO)_3(phen)(CH_3\text{-}Im)]^{2+}$ isomer, which suffers the electrode processes II and II′

$$mer\text{-}[Mn(CO)_3(phen)(CH_3\text{-}Im)]^{2+} \xrightarrow{+e^-} mer\text{-}[Mn(CO)_3(phen)(CH_3\text{-}Im)]^{+} \quad (2)$$

The generated *mer*-$[Mn(CO)_3(phen)(CH_3\text{-}Im)]^+$ reverts back to *fac*-$[Mn(CO)_3(phen)(CH_3\text{-}Im)]^+$ closing the cycle.

Although all the components of the cyclic scheme can be detected voltammetrically at the electrode surface, attempts to isolate the *mer*-$[Mn(CO)_3(phen)(CH_3\text{-}Im)]^+$ intermediate by potential-controlled oxidation have failed indicating that the *fac*-$[Mn(CO)_3(phen)(CH_3\text{-}Im)^+$ isomer is electronically favoured. These studies also show that the back reaction or isomerization $mer^{2+} \rightarrow fac^{2+}$ is negligible.

## 4. Conclusions

Synthesis of $[Mn(phen)(CO)_3(imidazole)]^+$ type complexes was achieved with relatively high yields.

Modifying the 'spectator' ligand (from $Br^-$ to Im) is a better way of changing the characteristics of the transitions than substitution on the chromophore (imidazole ligand). Not only the XLCT/MLCT character can be modified, but the energy gap between MLCT and LF states can be varied, affecting the electronic absorption and electrochemical properties of the complex as well as the properties of the lowest energy excited state.

The *fac*-$[Mn(CO)_3(phen)L]^+$ isomer is the preferred configuration for the complex of Mn(I), whereas after electrochemical oxidation to Mn(II) the *mer*-isomer is favoured. This gives place to an electrochemical cycle involving

$$fac^+ \xrightarrow{-e^-} fac^{+2} \rightarrow mer^{+2} \xrightarrow{+e^-} mer^+ \rightarrow fac^+$$

## Acknowledgements

R.M.C. thanks FAPESP for a Post-Doctoral Fellowship (Proc. 97/10047-0). We thank Professor Nabil El Murr (Université de Nantes, France) for helpful discussions.

## References

[1] A. Rosa, G. Ricciardi, E.J. Baerends, D.J. Stufkens, Inorg. Chem. 37 (1998) 6244.
[2] (a) A.M. Bond, R. Colton, R.W. Gable, M.F. Mackay, J.N. Walter, Inorg. Chem. 36 (1997) 1181. (b) A.M. Bond, R. Colton, Coord. Chem. Rev. 166 (1997) 161.
[3] B.D. Rossenaar, F. Hartl, D.J. Stufkens, C. Amatore, E. Maisonhaute, J.N. Verpeaux, Organometallics 16 (1997) 4675.
[4] C.J. Cleverlaan, F. Hartl, D.J. Stufkens, J. Photochem. Photobiol. A 103 (1997) 231.
[5] P. Giordano, M.S. Wrighton, Inorg. Chem. 16 (1977) 160.
[6] B.D. Rossenaar, D.J. Stufkens, A. Oskan, J. Fraanje, K. Goubitz, Inorg. Chim. Acta 247 (1996) 215.
[7] A. Rosa, G. Ricciardi, E.J. Baerends, D.J. Stufkens, J. Phys. Chem. 100 (1996) 15346.
[8] G. Stor, D.J. Stufkens, P. Vernooijs, E.J. Baerends, J. Fraanje, K. Goubitz, Inorg. Chem 34 (1995) 1588.
[9] K. Finger, C. Daniel, J. Am. Chem. Soc. 117 (1995) 12322.
[10] (a) G.A. Carriedo, P.G. Elipe, F.J.G. Alonso, L.F. Catuxo, M.R. Díaz, S.G. Granda, J. Organomet. Chem. 498 (1995) 207. (b) S.K. Mandal, J.A. Krause, M. Orchin, J. Organomet. Chem. 467 (1994) 113.
[11] F. Hartl, B.D. Rossenaar, G.J. Stor, D.J. Stufkens, Recl. Chim. Pays-Bas 114 (1995) 565.
[12] C. Daniel, T. Matsubara, G. Stor, Coord. Chem. Rev. 132 (1994) 63.
[13] T. Van der Graaf, R.M.J. Hofstra, P.G.M. Schilder, M. Rijkhoff, D.J. Stufkens, J.G.M. Van der Linden, Organometallics 10 (1991) 3668.
[14] R. Uson, V. Riera, J. Gimeno, M. Laguna, Transition Met. Chem. 2 (1977) 123.
[15] J. Nitschke, S.P. Schmidt, W.C. Trogler, Inorg. Chem. 24 (1985) 1972.
[16] F.J.G. Alonso, A. Llamazares, V. Riera, M. Vivanco, S.G. Granda, M.R. Diaz, Organometallics 11 (1992) 2826.
[17] J.A. Winter, D. Caruso, R.E. Shepherd, Inorg. Chem. 27 (1988) 1086.
[18] (a) E.M. Sabo, R.E. Shepherd, M.S. Rau, M.G. Elliot, Inorg. Chem. 26 (1987) 2897. (b) W.W. Henderson, R.E. Shepherd, J. Abola, Inorg. Chem. 25 (1986) 3157.
[19] W.B. Connick, A.J. DiBilio, M.G. Hill, J.R. Winkler, H.B. Gray, Inorg. Chim. Acta 240 (1995) 169.
[20] N.A. Beach, H.B. Gray, J. Am. Chem. Soc. 90 (1968) 5713.
[21] S. Wreland, K. Bal Reddy, R. van Eldik, Organometallics 9 (1990) 1802.
[22] J. Vichová, F. Hartl, A. Vleck Jr., J. Am. Chem. Soc. 114 (1992) 10903.
[23] M. Fazlul Hoq, R.E. Shepherd, Inorg. Chem. 23 (1984) 1851.
[24] N.C. Brown, G.A. Carriedo, N.G. Connelly, F.J. Garcia Alonso, I.C. Quarmby, A.L. Rieger, P.H. Rieger, V. Riera, M. Vivanco J. Chem. Soc., Dalton Trans. (1994) 3745.
[25] (a) A.M. Bond, R. Colton, M.E. McDonald, Inorg. Chem. 17 (1978) 2842. (b) A.M. Bond, B.S. Grabaric, Z. Grabaric, Inorg. Chem. 17 (1978) 1013. (c) A.M. Bond, R. Colton, M.J. McCormick, Inorg. Chem. 16 (1977) 155. (d) F.L. Wimmer, M.R. Snow, A.M. Bond, Inorg. Chem. 13 (1974) 1617.

[26] (a) A.M. Bond, R. Colton, F. Daniels, D.R. Fernando, F. Marken, Y. Nagaosa, R.F.M. Van Steveninck, J.N. Walter, J. Am. Chem. Soc 115 (1993) 9556. (b) A.M. Bond, R. Colton, J.E. Keverkordes, Inorg. Chem. 25 (1986) 749

[27] F.L. Winner, M.R. Snow, A.M. Bond, Inorg. Chem. 13 (1974) 1617.

[28] R.N. Bagchi, A.M. Bond, G. Brain, R. Colton, T.L.E. Henderson, J.E. Keverkordes, Organometallics 31 (1984) 4.