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# Probing the electronic factors responsible for the cyclic electron-transfer induced isomerism $fac \rightleftharpoons mer$ : Synthesis, electrochemical and spectroscopic studies of fac-[Mn(CO)<sub>3</sub>(L'-L')L]<sup>0/+</sup> complexes

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## Abstract

Spectroscopic (IR, <sup>31</sup>P NMR and UV–Vis) and electrochemical studies on fac-[Mn(CO)<sub>3</sub>(L'–L')(L)]<sup>0/+</sup>, where L'–L' = 1,2bis(diphenylphosphino)ethane (dppe) or 1,10-phenanthroline (phen) and L = bromide, triflate, imidazole (im), isonicotinamide (isn) or N-(2-hydroxyethyl)isonicotinamide (heisn), were undertaken to understand the effect of various ligands on the CO–Mn– L and CO–Mn–(L'–L') bonding characteristics of these complexes. Crystal structures for L = triflate/L'–L' = dppe, L = triflate/ L'–L' = phen and L = isn/L'–L' = phen are reported and they show that the two Mn–O(OSO<sub>2</sub>CF<sub>3</sub>) and Mn–N(isn) distances are similar. The tricarbonyl complexes exhibit two major bands in the 250–300 and 350–450 nm region of the UV–Vis spectrum. The lowest energy bands have been assigned as a contribution from both the metal-centered (MC) and metal to ligand ( $d_{\pi} \rightarrow L'-L'$ ) charge transfer (MLCT) transitions. The energy of this maximum absorption decreases in the order Br<sup>-</sup> ~ triflate > im > isn ~ heisn. The cyclic four-component mechanism fac-Mn(I)  $\rightarrow$  fac-Mn(II)  $\rightarrow$  mer-Mn(II)  $\rightarrow$  mer-Mn(I)  $\rightarrow$  fac-Mn(I) was observed at room temperature by voltammetric techniques for all the cases. On the basis of d metal orbital splitting, an electronic molecular orbital diagram is proposed. In this model, the ligands along the z-axis play a relevant role in the reverse of the HOMO energies of the fac/mer isomers by stabilizing the metal  $d_{z^2}$  orbital relative to  $d_{xy}$  in mer-Mn(II). © 2005 Elsevier B.V. All rights reserved.

Keywords: Cyclic induced isomerism; Mn(I); Tricarbonyl complexes; Diphosphine; a-Diimine

## 1. Introduction

Previous reports have shown that substitution of methyl, phenyl or nitro in the imidazole  $\sigma$ -donor ligand

in fac-[Mn(CO)<sub>3</sub>(phen)(im-Z)](SO<sub>3</sub>CF<sub>3</sub>) complexes produces significant changes in the electrochemical behavior without significantly altering their fundamental electronic structure [1]. In this study, voltammetry measurements of both facial and meridional isomers at room temperature gave rise to a cyclic process involving *fac*to *mer*-oxidation induced isomerization [1]. Although cyclic processes have been well reported for related transition metal complexes, such as Cr, Mo and W [2,3], as

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far as we know, this was the first reported cyclic scheme for Mn(I) tricarbonyl complex.

For studies defining the nature and magnitude of these processes, the preparation of metal carbonyl derivatives of varying electronic and steric properties is necessary. Therefore, as the  $\pi$ -bonding abilities of the metal center should be affected by the ligand field strength, it would be interesting to extend the range of ligands investigated to those with varying  $\pi$ -acceptor abilities.

In this paper, we report the synthesis, structural characterization and spectroscopic and electrochemical properties of a series of mononuclear manganese compounds of *fac*-[Mn(CO)<sub>3</sub>(L'-L')(L)]<sup>0/+</sup>, (L'-L' = 1, 10-phenanthroline (phen), 1,2-bis(diphenylphosphino)ethane (dppe); L = bromide (Br<sup>-</sup>), triflate (SO<sub>3</sub>CF<sub>3</sub><sup>-</sup>), imidazole (im), isonicotinamide (isn) and *N*-(2-hydroxyethyl)isonicotinamide (heisn)), aimed especially to establish both the similarities and differences in the properties of homologous systems. The basicity of the axial ligand *trans* to CO was chosen in such a way as to modulate the  $\pi$ -acidity of the manganese center. The studies described here illustrate the interplay between steric and electronic effects in determining the spectroscopic and electrochemical behavior of Mn(I) tricarbonyl complexes.

# 2. Experimental

#### 2.1. Materials

 $[Mn(Br)(CO)_5]$  was from Strem. 1,2-Bis(diphenylphosphine)ethane (dppe), 1,10-phenanthroline (phen), silver triflate (Ag(SO<sub>3</sub>CF<sub>3</sub>), imidazole (im), isonicotinamide (isn) and *N*-(2-hydroxyethyl)isonicotinamide (heisn) were from Sigma. Methylene chloride, acetonitrile, methanol, ethanol and acetone, HPLC grade, were distilled from the appropriate drying agents immediately prior to use. Tetrabutylammonium perchlorate (TBAP) from Eastman Kodak used as supporting electrolyte for electrochemical experiments was dried overnight under vacuum at 50 °C and stored under vacuum before use.

## 2.2. Physical measurements

Unless otherwise specified, all manipulations were carried out under argon atmosphere at room temperature (RT;  $24 \pm 1$  °C).

Elemental analyses were performed on an EA 1110 CHNS-O Carlo Erba Instrument. IR spectra were obtained in KBr disks on a Bomem FT-IR MB 102 spectrometer in the range of 4000–400 cm<sup>-1</sup>. UV–Vis spectra were measured at RT in dichloromethane solution with a Varian mod. Cary 5G UV–Vis NIR spectrophotometer using quartz cuvettes (10 mm). <sup>31</sup>P{<sup>1</sup>H} NMR spectra were obtained in CH<sub>2</sub>Cl<sub>2</sub> solution at 25.0  $\pm$  0.1 °C using a Brucker AC 200 spectrometer.

The obtained chemical shifts are reported in ppm relative to high frequency of 85% H<sub>3</sub>PO<sub>4</sub>. EPR measurements were carried out at 77 K using a Brucker ESP 300C apparatus (X-band) equipped with a TE102 cavity and HP 52152A frequency counter. Cyclic voltammetry was performed using an EG&G Princeton Applied Research model 264A polarographic analyzer/stripping voltammeter. Voltammograms were obtained in CH<sub>2</sub>CL<sub>2</sub> (0.1 mol L<sup>-1</sup> TBAP) at RT in a light-protected voltammetric cell with a platinum 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 concentration of the complexes was always kept at 1 mmol L<sup>-1</sup>.

## 2.3. Syntheses

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

<sup>31</sup>P NMR data for dichloromethane solutions of the compounds showed no evidence for either free or oxidated phosphine molecule. EPR was used to confirm the absence of Mn(II) species.

## 2.3.1. Preparation of fac- $[Mn(Br)(CO)_3(dppe)]$

The halo complex was prepared by reacting  $[Mn(CO)_5Br]$  (0.20 g; 0.73 mmol), freshly sublimated, with dppe (0.10 g; 0.90 mmol) in 40 mL CH<sub>2</sub>CL<sub>2</sub>. The mixture was stirred for 4 h at RT, after which the complex was precipitated by addition of cold degassed n-hexane, yielding a yellow-orange powder that was filtered off and dried under vacuum. Yield = 88%. Elemental analysis: Calc. C, 56.8; H, 3.9. Found: C, 56.4; H, 3.9%.

# 2.3.2. Preparation of fac- $[Mn(SO_3CF_3)(CO)_3(dppe)]$

The complex fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(dppe)] was prepared by a procedure different from that previously published for fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(dppe)] [4]. Ag (SO<sub>3</sub>CF<sub>3</sub>) (0.083 g; 0.324 mmol) was added to a solution of fac-[MnBr(CO)<sub>3</sub>(dppe)] (0.20 g; 0.324 mmol) in 40 mL CH<sub>2</sub>Cl<sub>2</sub>. The mixture was stirred for 1 h at RT. During this time a white precipitate was formed. The reaction mixture was filtered and the resulting solution was concentrated in a vacuum to ca. 10 mL. Yield = 78%. Elemental analysis: Calc. C, 52.4; H, 3.6. Found: C, 52.3; H, 3.9%.

# 2.3.3. Preparation of fac- $[Mn(CO)_3(dppe)(L)]$ (SO<sub>3</sub>CF<sub>3</sub>)

The following procedure, described for fac- $[Mn(CO)_3(dppe)(im)](SO_3CF_3)$ , is representative of the

synthesis of the other substituted triflate complexes (L = isn or heisn). Imidazole (0.02 g; 0.29 mmol) was added to a solution of *fac*-[Mn((SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(dppe)] (0.20 g; 0.29 mmol) in CH<sub>2</sub>CL<sub>2</sub> (40 mL) and the mixture was stirred for 24 h at RT. The solution was concentrated to ca. 10 mL, mixed with cold ethyl-ether, filtered and vacuum dried. A yellow crystalline solid was obtained. Elemental analyses: L = im; yield = 85%: Calc. C, 52.3; H, 3.8; N, 4.8. Found: C, 52.2; H, 3.8; N, 4.7%. L = isn; yield = 85%: Calc. C, 53.5; H, 3.7; N, 3.5. Found: C, 52.2; H, 3.7; N, 3.5%. L = heisn; yield = 85%: Calc. C, 53.5; H, 4.0; N, 3.3. Found: C, 52.3; H, 4.1; N, 3.5%.

# 2.3.4. Preparation of fac- $[Mn(Br)(CO)_3(phen)]$

The *fac*-[Mn(Br)(CO)<sub>3</sub>(phen)] was prepared from [Mn(Br)(CO)<sub>5</sub>], freshly sublimated, by a RT reaction with 1-10-phenanthroline in CH<sub>2</sub>CL<sub>2</sub> as described elsewhere [5]. Yield = 85%. Elemental analysis: Calc. C, 45.1; H, 2.0; N, 7.0. Found: C, 45.9; H, 2.2; N, 7.3%.

# 2.3.5. Preparation of fac- $[Mn(SO_3CF_3)(CO)_3(phen)]$

The *fac*-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(phen)] complex was synthesized by the direct reaction of *fac*-[Mn(Br)(CO)<sub>3</sub> (phen)] with Ag(SO<sub>3</sub>CF<sub>3</sub>) [1]. Yield = 90% Elemental analysis: Calc. C, 39.5; H, 2.1; N, 5.8. Found: C, 39.5; H, 2.2; N, 5.7%.

# 2.3.6. Preparation of fac- $[Mn(CO)_3(phen)(L)]$ (SO<sub>3</sub>CF<sub>3</sub>)

They were prepared by reacting *fac*-[Mn(SO<sub>3</sub>CF<sub>3</sub>) (CO)<sub>3</sub>(phen)] (0.20 g; 0.427 mmol) with L = im or isn (0.29 mmol) in CH<sub>2</sub>CL<sub>2</sub> (40 mL). Elemental analyses: L = im; yield = 90%: Calc. C, 42.5; H, 2.2; N, 10.4. Found: C, 43.0; H, 2.2; N, 10.6%. L = isn; yield = 85%: Calc. C, 44.7; H, 2.4; N, 9.5. Found: C, 43.6; H, 2.5; N, 9.2%. L = heisn; yield = 85%: Calc. C, 45.4; H, 2.9; N, 8.8. Found: C, 45.1; H, 2.8; N, 8.5%.

## 2.4. Crystal structure analyses

Single crystals of *fac*-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(dppe)] (1) were obtained by the diffusion of cold degassed *n*-hexane into a dichloromethane solution. An orange-yellow crystal (0.10 mm × 0.08 mm × 0.05 mm) was mounted and placed in the beam of a CAD4 diffractometer. Unit cell data and diffraction intensities were collected at 273K using Mo K $\alpha$  radiation ( $\lambda = 0.71073$ ).

Single crystals of *fac*-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(phen)] (2) were obtained from a dichloromethane solution maintained in the refrigerator for 4 days, under argon atmosphere. An orange-yellow crystal (0.15 mm × 0.25 mm × 0.50 mm) was mounted and placed in the beam of a CAD4 diffractometer. Unit cell data and diffraction intensities were collected at 263 K using Mo K $\alpha$  radiation ( $\lambda = 0.71073$ ).

Single crystals of *fac*-[Mn(CO)<sub>3</sub>(phen)(isn)](SO<sub>3</sub>CF<sub>3</sub>) (3) were obtained from a dichloromethane solution maintained in the refrigerator for 7 days, under argon atmosphere. A yellow crystal (0.10 mm × 0.08 mm × 0.08 mm) was mounted in a Lindemann capillary and placed in the beam of an Enraf-Nonius Kappa CCD diffractometer. Unit cell data and diffraction intensities were collected at 296K using Mo K $\alpha$  radiation ( $\lambda = 0.71073$ ).The optimized cell parameters were obtained using 25 reflections. The intensity data were reduced using WinGX [6] and the PSISCAN absorption correction was applied [7]. The crystal structure was solved by siR-92 [8] and refined by SHELXL-97 [9]. The geometrical analyses were applied using PLATON [10].

The crystal parameters and refinement conditions are shown in Table 1.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.

## 3. Results and discussion

#### 3.1. Description of structure

The molecular structures of fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>) (CO)<sub>3</sub>(dppe)], fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(phen)] and fac-[Mn(CO)<sub>3</sub>(phen)(isn)](SO<sub>3</sub>CF<sub>3</sub>) are shown in Figs. 1 and 2. Selected bond distances and angles are listed in Tables 2–4.

In fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(dppe)], the metal is in a distorted octahedral configuration. Phosphorous atoms from dppe ligand and the carbon atoms from two carbonyl groups define the equatorial plane. Another carbonyl carbon and an oxygen atom from a triflate ligand complete the coordination sphere in apical positions, forming an angle of 174.8 (3)°. The three carbonyls are in facial position and the triflate ligand is trans to a carbonyl. The Mn-P [2.337(2) and 2.348(2) Å] and Mn-C(CO) distances [1.814(9) and 1.815(8) A] in the equatorial plane are in agreement with those in the trans OC-Mn-P moiety in the bromide complex fac-[Mn(Br)(CO)<sub>3</sub>(dppe)], [2.314(3) and 2.327(3) A; 1.81(1) and 1.83(1) A] [11] and in the aqua complex  $fac-[Mn(CO)_3(dppe)(H_2O)](BF_4)$ , [2.347(1) and 2.354(2) Å; 1.835(2) and 1.836(2) Å], respectively [4]. The P–Mn–P bite angle of 83.14(8)° agrees with the values of  $84.14(10)^{\circ}$  for  $fac-[Mn(Br)(CO)_3(dppe)]$ [11], 84.6(1)° for fac-[Mn(CO)<sub>3</sub>(dppe)(OC(O)OCH<sub>3</sub>)] [12] and  $83.73(3)^{\circ}$  for fac-[Mn(CO)<sub>3</sub>(dppe)(H<sub>2</sub>O)](BF<sub>4</sub>) [4].

In fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(phen)], the metal is in an approximate octahedral configuration similar to that in fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(dppe)]. The phen ligand and

Table 1

Crystal data and X-ray experimental parameters for fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(dppe)] (1), fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(phen)] (2), and fac-[Mn(CO)<sub>3</sub>(phen) (isn)](SO<sub>3</sub>CF<sub>3</sub>) (3)

Complex	1	2	3
Empirical formula	$C_{30}H_{24}F_3MnO_6P_2S$	$C_{16}H_8F_3MnN_2O_6S$	C <sub>22</sub> H <sub>14</sub> F <sub>3</sub> MnN <sub>4</sub> O <sub>7</sub> S
Formula weight	686.43	468.25	590.37
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_{1}/c$	$P2_1/n$	$P2_1/n$
a (Å)	15.646(4),	6.917(2)	11.508(1)
b (Å)	10.031(8)	13.137(3)	14.006(1)
<i>c</i> (Å)	19.324(3)	19.867(5)	15.186(1)
β (°)	102.219(10)	99.55	99.464(2)
$V(\text{\AA}^3)$	2964.1(9)	1780.3(8)	2414.38(8)
Z	2	4	4
$D_{\rm calc} ({\rm Mg}\;{\rm m}^{-3})$	1.538	1.747	1.624
Absorption coefficient, $\mu$ (mm <sup>-1</sup> )	0.686	0.928	0.708
<i>F</i> (000)	1400	936	1192
Crystal size (mm)	$0.10 \times 0.08 \times 0.05$	$0.15 \times 0.25 \times 0.50$	$0.10\times0.08\times0.08$
$T\left(\mathbf{K}\right)$	273(2)	263(2)	296(2)
Limiting indices	$0 \leq h \leq 20, 0 \leq k \leq 13,$	$0 \leq h \leq 8, \ 0 \leq k \leq 16,$	$-13 \leqslant h \leqslant 13, -16 \leqslant k \leqslant 16,$
	$-25 \leqslant l \leqslant 24$	$-25 \leqslant l \leqslant 25$	$-17 \leqslant l \leqslant 18$
$\theta$ Range for minimum to maximum (°)	2.28-27.63	2.59-26.99.0	1.99-25.00
Reflection collected/unique $(R_{int})$	7139/6896 (0.0886)	4377/3868 (0.0648)	33008/4245 (0.1263)
Completeness to $\theta$ maximum (%)	100.0	99.9	99.9
Maximum and minimum transmission	0.9665 and 0.9346	0.7391 and 0.8016	0.9442 and 0.9326
Refinement method	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$	full-matrix least-squares on $F^2$
Data/restraints/parameters	6896/0/388	3868/0/262	4245/0/352
$R_1, wR_2, S$	0.0339, 0.1710, 0.895	0.0534, 0.143, 0.945	0.0441, 0.1140
Largest difference in peak and hole (e $Å^{-3}$ )	0.583 and -0.767	0.345 and -0.379	0.322 and -0.480

two carbonyl groups are in the equatorial plane, with the triflate ligand and a carbonyl forming an angle of 176.6  $(3)^{\circ}$  in apical positions.

In *fac*-[Mn(CO)<sub>3</sub>(phen)(isn)](SO<sub>3</sub>CF<sub>3</sub>), the Mn atom also exhibits octahedral coordination with the two N(phen) atoms and two terminal carbonyl groups in the equatorial positions, and one of the terminal C atom of the carbonyl group and the N(isn) occupy the apical positions forming an angle of 178.27(10)°. The distances and angles are the expected ones for this kind of compounds as [{*fac*-Mn(CO)<sub>3</sub>(phen)}<sub>2</sub> ( $\mu$ -CN)]PF<sub>6</sub> [13] or *fac*-[Mn(CO)<sub>3</sub>(phen)(1,8-naphthyridine)]ClO<sub>4</sub> [14].

Whereas for fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(L'–L')], the mean interatomic distances Mn–CO and Mn– O(SO<sub>3</sub>CF<sub>3</sub>) are not sensitive to the substitution of phen for dppe (see Tables 2 and 3), the Mn–L distance in *fac*-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub>(dppe)] (2.109(5) Å) is significantly shorter than those found in *fac*-[Mn(Br)(CO)<sub>3</sub>(dppe)] (2.504(2) Å [11]) and *fac*-[Mn(I)(CO<sub>3</sub>)(bpy)] (2.724(2) Å [15]) in which the coordinated halides are a substantially better  $\pi$  donors than triflate.

The Mn–C(CO) distance in the axial plane for *fac*-[Mn(CO)<sub>3</sub>(phen)(isn)](SO<sub>3</sub>CF<sub>3</sub>), 1.812(3) Å, is somewhat longer than that found in *fac*-[Mn(SO<sub>3</sub>CF<sub>3</sub>) (CO)<sub>3</sub>(phen)] (1.783(7) Å) and *fac*-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub> (dppe)] (1.797(8) Å). This may be attributed to the moderated  $\pi$ -acceptor nature of the isn increasing the  $\pi$ -electron competition. In the triflate coordinated complexes, the Mn–N(phen) distances of 2.062(4) and 2.053(4) Å are shorter than the Mn–P in the dppe complex (2.337(2) and 2.348(2) Å). Further, the angle L'-Mn–L' in the case with phen (79.9(2)°) is smaller than in the case with dppe (83.14(8)°), reflecting the small hole size of the phenan-throline. This comparison is also similar for the isn derivative (79.85(8)°) and for other *fac*-Mn(I) complexes with phen [13,14].

Relative to bonds involving sp<sup>2</sup> nitrogen atoms, the Mn–N(im) distance in *fac*-[Mn(CO)<sub>3</sub>(dppe)(im)] (SO<sub>3</sub>CF<sub>3</sub>) is expected to be close to that found in *fac*-[Mn(CO)<sub>3</sub>(phen)(isn)](SO<sub>3</sub>CF<sub>3</sub>) (Mn–N(isn), 2.107(2) Å) since this value is close to that found in *fac*-[Mn(CO)<sub>3</sub>(dppe)(H<sub>2</sub>O)](PF<sub>6</sub>) (Mn–O(H<sub>2</sub>O), 2.075(2) Å [4]), a weaker  $\sigma$ -donor ligand than im and isn. Consequently, it can be inferred that the Mn–L distances follow the sequence Br<sup>-</sup> > trif ~ im ~ isn ~ heisn, so that variations in bonding between the three latter ligands are not structurally dominant.

# 3.2. <sup>31</sup>P and <sup>13</sup>C NMR spectroscopy

The compounds fac-[Mn(CO)<sub>3</sub>(dppe)(L)](SO<sub>3</sub>CF<sub>3</sub>) show a single resonance in their <sup>31</sup>P NMR spectra, consistent with the facial configuration (Table 5). The small <sup>31</sup>P NMR downfield shift when compared to the neutral bromo precursor complex is attributed to charge migration from the axial ligand via  $\sigma$ -donation or  $\pi$ -back-







Fig. 2. ORTEP projection of *fac*-[Mn(CO)<sub>3</sub>(phen)(isn)](SO<sub>3</sub>CF<sub>3</sub>).

Table 2 Selected bond distances (Å) and angles (°) for fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>) (CO)<sub>3</sub>(dppe)] (1)

( )5(11)5()	
Bond distances (Å)	
Mn-C1	1.814(9)
Mn-C2	1.815(8)
Mn-C(3)	1.797(8)
Mn-O(4)	2.109(5)
Mn-P(1)	2.337(2)
Mn–P(2)	2.348(2)
C(1)–O(1)	1.150(8)
C(2)–O(2)	1.157(8)
C(3)–O(3)	1.133(8)
Bond angles (°)	
P(1)-Mn-P(2)	83.14(8)
C(1)-Mn-P(1)	173.7(2)
C(3)-Mn-P(1)	90.3(2)
C(2)-Mn-P(1)	93.3(2)
O(4)-Mn-P(1)	86.5(1)
C(1)-Mn-P(2)	90.6(2)
C(2)-Mn-P(2)	176.0(2)
C(3)-Mn-P(2)	94.3(2)
O(4)-Mn-P(2)	81.2(1)
C(3)-Mn-O(4)	174.8(3)

Table 3

Selected bond distances (Å) and angles (°) for *fac*-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub> (phen)] (2)

Bond distances $(\mathring{A})$	
Mn–C(1a)	1.783(7)
Mn–C(2a)	1.813(6)
Mn–C(3a)	1.805(6)
Mn–O(3)	2.096(4)
Mn-N(1)	2.062(4)
Mn–N(2)	2.053(4)
O(1a)–C(1a)	1.141(8)
O(2a)–C(2a)	1.141(8)
O(3a)–C(3a)	1.159(8)
N(2)–C(11)	1.372(7)
C(11)-C(12)	1.413(7)
S–O(1)	1.423(4)
S-O(2)	1.422(4)
S–O(3)	1.459(4)
S-C(13)	1.805(7)
Bond angles (°)	
O(3)-Mn-N(1)	84.1(2)
O(3)-Mn-N(2)	82.1(2)
O(3)-Mn-C(1)a)	176.3(2)
O(3)–Mn–C(2a)	91.7(2)
O(3)–Mn–C(3a)	95.4(2)
N(1)-Mn-N(2)	79.9(2)
N(1)-Mn-C(1a)	93.9(2)
N(1)-Mn-C(2a)	172.5(2)
N(1)-Mn-C(3a)	96.9(2)
N(2)-Mn-C(1a)	94.6(2)
N(2)-Mn-C(2a)	93.4(2)
N(2)-Mn-C(3a)	176.0(2)
C(1a)-Mn- $C(2a)$	89.9(3)
C(1a)-Mn-C(3a)	87.9(3)
C(2a))-Mn-C(3a))	89.8(3)
O(1)–S–O(2)	117.9(3)
Mn–O(3)–S	132.7(2)

Table 4

Selected bond distances (Å) and angles (°) for fac-[Mn(CO)<sub>3</sub> (phen)(isn)](SO<sub>3</sub>CF<sub>3</sub>) (**3**)

Bond distances $(\mathring{A})$	
Mn-C(21)	1.812(3)
Mn-C(20)	1.819(3)
Mn-C(19)	1.810(3)
Mn-N(1)	2.051(2)
Mn-N(2)	2.059(2)
Mn-N(3)	2.107(2)
O(15)-C(18)	1.227(3)
O(19)–C(19)	1.145(3)
O(20)-C(20)	1.142(4)
O(21)–C(21)	1.141(3)
Bond angles (°)	
C(21)-Mn-C(20)	87.83(13)
C(21)-Mn-C(19)	90.34(12)
C(20)-Mn-C(19)	88.01(13)
C(21)-Mn-N(1)	90.91(10)
C(19)-Mn-N(2)	173.71(10)
C(19)–Mn–N(1)	94.35(10)
C(21)-Mn-N(1)	90.91(10)
C(20)-Mn-N(1)	177.33(11)
C(19)–Mn–N(1)	94.35(10)
N(1)-Mn-N(2)	79.85(8)
C(21)-Mn-N(3)	178.27(10)

Table 5

Selected IR and NMR spectral data for fac-[Mn(CO)<sub>3</sub>(L'-L')(L)]<sup>0/+</sup> complexes

L'-L'	L	v <sub>CO</sub> <sup>a</sup>	${}^{31}P{}^{1}H{} NMR^{b}$	<sup>13</sup> C NMR
dppe	$Br^{-}$	2014; 1944; 1911	70.0	
	triflate	2027; 1959; 1932	72.0	
	im	2026; 1955; 1936	76.1	
	heisn	2029; 1957; 1940	76.3	
	isn	2029; 1965; 1947	76.4	
phen	$\mathrm{Br}^{-}$	2019; 1944; 1919		153.4
-	triflate	2042; 1953; 1922		
	im	2037; 1941; 1921		153.3
	heisn	2042; 1952; 1936		
	isn	2042; 1951; 1943		153.4

<sup>a</sup> In KBr; v in cm<sup>-1</sup>.

<sup>b</sup> In CD<sub>2</sub>Cl<sub>2</sub>; in ppm; free dppe = 40.0 ppm.

<sup>c</sup> Ref. [1]; in CD<sub>2</sub>Cl<sub>2</sub>; in ppm; free imine = 150.3 ppm.

bonding without much compensation by the dishielding effect of  $\sigma$ -donation at the phosphorous ligand. Similar behavior is observed for the corresponding <sup>13</sup>C NMR of immine ligand phenanthroline substituted complexes (Table 5), which show that the molecule is fairly rigid and therefore consistent with the facial configuration.

# 3.3. Infrared spectroscopy

The infrared spectrum of fac-[Mn(CO)<sub>3</sub>(L'-L')(L)]<sup>0/+</sup> complexes in the terminal carbonyl region shows three strong bands between 2050 and 1950 cm<sup>-1</sup> (Table 5). This is consistent with the facial arrangement of the three CO's in the coordination sphere shown from the

structure derived from the X-ray analyses as well as observed for similar *fac*-Mn(I) complexes with diphosphines [16,17]. Two bands arise from the symmetric and asymmetric stretching vibrations of the two equivalents *cis*-CO's C<sub>s</sub> symmetry) [16,17]. The remaining band at lowest frequency is assigned to the stretching mode of the CO *trans* to L since the greatest degree of Mn=CO  $\pi$  bonding is expected for *fac*-[Mn(Br)(L'-L')(CO)<sub>3</sub>], where Br<sup>-</sup> is a good  $\pi$ -donor. The increase of the lowest energy CO frequency in going from Br<sup>-</sup> to the isn ligand (Br<sup>-</sup>, triflate, im, heisn, isn) is consistent with the *trans*-influence of the axial ligands in agreement with the increased  $\pi$ -electron competition.

## 3.4. Electronic absorption spectra

Electronic absorption spectra for fac-[Mn(CO)<sub>3</sub>-(L'-L')(L)]<sup>0/+</sup> complexes in CH<sub>2</sub>Cl<sub>2</sub> solution are shown in Figs. 3 and 4. Table 6 summarizes the absorption positions and absorptivities for a number of complexes relevant to this investigation. In addition to ligand localized absorption bands (<300 nm), the electronic spectra of these complexes are dominated by relatively intense bands in the visible region (350–460 nm).

The spectrum of the fac-[Mn(Br)(CO)<sub>3</sub>(dppe)] complex is characterized by one low energy absorption band in the visible region  $\lambda_{max} = 388 \text{ nm}$ ,  $\varepsilon = 1300 \text{ mol}^{-1}$ L cm<sup>-1</sup>). This wavelength and intensity are comparable to those of MC in [Mn(Br)(CO)<sub>5</sub>] [18], and [Mn(Br)(CO)<sub>3</sub>-(CH<sub>3</sub>CN)<sub>2</sub>] [19] (Table 6); thus, a similar assignment would be sound for that band. This maximum absorption becomes a strong band in the corresponding triflate complex. In this case, the high  $\varepsilon$  value is most likely an MLCT band due to the Mn(d<sub> $\pi$ </sub>)  $\rightarrow$  dppe transition, as will be shown below. For L = im, the maximum absorption is shifted to higher energy as compared to the neutral precursor, as it should due to the greater ligand field strength



Fig. 3. Electronic absorption spectra of fac-[Mn(CO)<sub>3</sub>(dppe)L]<sup>0/+</sup> complexes in CH<sub>2</sub>Cl<sub>2</sub>. (a) L = Br<sup>-</sup>; (b) L = triflate; (c) L = im; (d) L = isn; (e) L = heisn.



Fig. 4. Electronic absorption spectra of fac-[Mn(CO)<sub>3</sub>(phen)L]<sup>0/+</sup> complexes in CH<sub>2</sub>Cl<sub>2</sub>. (a) L = Br<sup>-</sup>; (b) L = triflate; (c) L = im; (d) L = isn; (e) L = heisn.

 Table 6

 Electronic absorption data for a series of *fac*-Mn(I) complexes

Complex	$\lambda_{\rm max}/{\rm nm}~(\epsilon/{\rm mol}^{-1}~{\rm L~cm}^{-1})$
$[Mn(Br)(CO)_5]^a$	385 (1.700)
$[Mn(Br)(CO)_3(CH_3CN)_2]^b$	375 (1.500)
$[Mn(Br)(CO)_3(dppe)]$	388 (1.300)
$[Mn(SO_3CF_3)(CO)_3(dppe)]$	390 (3.050)
$[Mn(CO)_3(dppe)(im)]^+$	356 (2.700)
$[Mn(CO)_3(dppe)(isn)]^+$	329 (4.500) 360 <sup>sh</sup> (3.500)
$[Mn(CO)_3(dppe)(heisn)]^+$	329 (3.200) 360 <sup>sh</sup> (2.100)
$[Mn(Br)(CO)_3(phen)]$	380 (3.300) 425 (3.400)
$[Mn(SO_3CF_3)(CO)_3(phen)]$	356 (3.700) 405 (4.000)
$[Mn(CO)_3(phen)(im)]^+$	376 (4.200)
$[Mn(CO)_3(phen)(isn)]^+$	$350^{\text{sh}}$ (2.500) $400^{\text{sh}}$ (1.800)
[Mn(CO) <sub>3</sub> (phen)(heisn)] <sup>+</sup>	400 <sup>sh</sup> (2.100)
<sup>a</sup> <b>P</b> of [20]	

<sup>&</sup>lt;sup>a</sup> Ref. [20]. <sup>b</sup> Ref. [21].

of im versus that of Br<sup>-</sup> and to the concomitant rise in energy of the metal d orbitals. Consequently, the MC absorptions in  $fac-[Mn(CO)_3(dppe)(L)]^{0/+}$ , where L = triflate or im, are obscured by the more intense  $Mn(d_{\pi}) \rightarrow dppe CT$  absorption. But, since the immediate coordination sphere is the same for all complexes, it is assumed that the MC states are at nearly the same energy in all cases. Curiously, for L = isn or heisn, the 330 nm maximum appears to be split into two components, with a weaker component appearing at  $\sim 2700 \text{ cm}^{-1}$  towards the red of the actual maximum. Considering that the isn/heisn groups may act as  $\sigma$ -donor and  $\pi$ -acceptor, these results suggest that the transition around 360 nm has a MLCT (Mn  $\rightarrow$  dppe) character and, therefore, the 330 nm absorption is assigned as MC transition. Similar behavior has been observed for the MLCT transition in  $[W(CO)_4(phen)][20].$ 

In these complexes, the large intensity of the MC transition is attributed to the high metal-ligand contri-

bution. In fact, the position and intensity of the higher energy absorption in *fac*-[Mn(CO)<sub>3</sub>(dppe)L]<sup>0/+</sup> are sensitive to the nature of L, but are not solvent dependent (CH<sub>3</sub>CN, CH<sub>3</sub>OH, CH<sub>2</sub>CL<sub>2</sub>, CHCl<sub>3</sub> or DMSO). These data are best rationalized by considering the  $\sigma$ -charge densities on the metal center. Going from L = Br<sup>-</sup> to triflate and im, more charge will be donated to the metal, thus increasing the metal contribution to the highest filled orbital. As a result, the intensity of the lowest energy absorption band will increase. The energy of the transition between 390 and 320 nm decreases in the order Br<sup>-</sup> ~ triflate > im > isn ~ heisn in accord to increases in the spectrochemical series of ligands. The energetic dependence of the first band in dppe with respect to L is as found in [Re(CO)<sub>5</sub>X] [21].

Changing the equatorial ligand from dppe to phen results in a shift of the absorption maxima to longer wavelengths in all cases, indicating that the transitions are directed to the  $\pi^*$  (phen) orbital. This may be related to the well-defined structural organization of the phen ligand and its small hole size compared to that of the phosphine, which is a non-rigid molecule. This behavior suggests an MLCT band in the visible region.

By analogy with the fac-[Mn(CO)<sub>3</sub>(dppe)L]<sup>+</sup> ion complexes, the two well-separated bands in fac-[Mn(Br)(CO)<sub>3</sub>(phen)] and fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>)(CO)<sub>3</sub> (phen)] are assigned to MLCT and MC transitions. The increased intensity obtained for L = triflate with respect to that of the bromo complex is explained by the increased metal character in the metal-triflate bonding combination. Going from triflate to im, a better  $\sigma$ -donor ligand, it will increase the metal contribution to the highest filled orbital and consequently the intensity of the first band will increase overlapping the MC band.

It is interesting to note that for all the complexes studied, MC and MLCT bands dominated the UV–Vis absorption spectrum in the 350–460 nm region, while a very small and solvatochromic behavior was only observed for *fac*-[Mn(CO)<sub>3</sub>(phen)(im)]<sup>+</sup>. This finding leads to the conclusion that the energy of the MLCT transition is almost entirely due to overlap stabilization and in going from  $L = Br^-$  to heisn, the MLCT state moves to higher energy by a greater amount than do the MC states. Thus, in the case of bromide, triflate and imidazole, the MC and MLCT transitions are overlapping as in the isoelectronic [Mo(CO)<sub>5</sub>L] [21] but for [Mn(CO)<sub>3</sub> (L'–L')L]<sup>+</sup>, L'–L' = dppe or phen and L = isn or heisn, the MLCT transitions are well below the MC bands.

## 3.5. Cyclic voltammetry at a Pt electrode

Cyclic voltammograms for complexes fac-[Mn(SO<sub>3</sub> CF<sub>3</sub>)(CO)<sub>3</sub>(dppe)] and fac-[Mn(Br)(CO)<sub>3</sub> (phen)] are depicted in Fig. 5. The electrochemical behavior observed for these two complexes is representative of the other Mn(I)-(L'-L') complexes substituted with ligands



Fig. 5. Cyclic voltammograms for the oxidation of fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>) (CO)<sub>3</sub>(dppe)] (a) and fac-[Mn(Br)(CO)<sub>3</sub>(phen)] (b) in CH<sub>2</sub>CL<sub>2</sub> (0.1 mol L<sup>-1</sup> TBPA); vs. Ag/AgCl, scan rate 100 mV/s.

L. Similar electrochemical behavior of the *fac*- $[Mn(CO)_3(phen)(L)]^+$ , where L = im or triflate, has been previously reported [1]. The potential values are summarized in Table 7.

Taking the voltammogram of fac-[Mn(SO<sub>3</sub>CF<sub>3</sub>) (CO)<sub>3</sub>(dppe)] as example for discussion (Fig. 5(a)), it is observed that it displays on the first oxidative scan the process I and on the reverse scan the cathodic processes I' and II'. On the second and subsequent scans, the redox couples II/II' and I/I' are observed and the cyclic voltammogram attains a steady state response. These observations indicate that the cathodic process observed at ~0.8 V (process II') results from the reduction of a Mn(II) species produced in the first oxidation step. Thus, after the first oxidative process there are two Mn(II) carbonyl species in solution and, probably, they have the same stability on the electrochemical time scale. In general, when *fac*-Mn(I) complexes are oxidized at the electrode surface they cause electrode processes I/I'

Table 7

Cyclic voltammogram data (V) for oxidation of fac-[Mn(CO)<sub>3</sub>(L'-L')(L)]<sup>0/+</sup> complexes<sup>a</sup>

L'–L'	L	$E_{a}$ (I)	$E_{c}$ (I')	<i>E</i> <sub>1/2</sub> ( <b>I</b> / <b>I</b> ′)	<i>E</i> a ( <b>II</b> )	$E_{c}$ (II')	<i>E</i> <sub>1/2</sub> ( <b>II/II</b> ')
dppe	Br <sup>–</sup>	1.26	1.16	1.21	0.86	0.79	0.83
	triflate	1.22	1.12	1.17	0.82	0.74	0.78
	im	1.32	1.16	1.24	0.87	0.79	0.83
	isn	1.42	1.20	1.31	0.67	0.57	0.62
phen	Br <sup>-</sup>	1.18	1.00	1.09	0.97	0.71	0.84
	triflate	1.29	1.26	1.27	1.06	1.02	1.04
	im <sup>b</sup>	1.22	1.00	1.11	0.66	0.28	0.47
	isn	1.40	1.18	1.29	0.68	0.60	0.64

 $^{a}$  At a platinum electrode at room temperature in  $CH_{2}Cl_{2}$  (0.1 mol  $L^{-1}$  TBPA) vs. Ag/AgCl.

<sup>b</sup> Ref. [1].

and II/II' to happen in a cyclic way, even after repeated scans, indicating that these species are never exhausted and do not cause changes in the coordination sphere compositions. On the basis of these data, processes I/I'and II/II' are all associated with electrochemical and interconversion reactions of the isomeric species *fac*-Mn(I/II) and *mer*-Mn(I/II). The overall reaction scheme is shown in Fig. 6.

The only other characterized example of a similar induced isomerization observed for Mn(I) tricarbonyl



Fig. 6. Qualitative diagram showing the energy level of the d orbitals for the Mn(I/II) tricarbonyl isomers for the electrochemical–chemical– electrochemical–chemical process. The numbers in parentheses show the numbers of CO ligands that can interact with a given metal  $d_{\pi}$ orbital (adapted from [23]). For clarity, only the subscripts of the d orbitals are shown.

complexes is that of *fac*-[Mn(Cl)(CO)<sub>3</sub>(dppm)], which differs from our example by exhibiting a thermodynamically stable oxidized *mer*-Mn(Cl)(CO)<sub>3</sub>(dppm)]<sup>+</sup> isomer which was isolated [22].

In the present case of the *fac*-Mn(II/I) complexes, the factors responsible for determining the thermodynamically preferred forms of the isomers are not entirely clear. But it is clear that upon oxidation to fac-Mn(II), the *mer*-Mn(II) isomer becomes thermodynamically favored. This could happen if steric repulsion between ligands is important or if the *fac*-Mn(II) complex undergoes a Jahn-Teller distortion as has been suggested for other isomerization reactions [2]. The former effect, if it exists, would be small since no steric repulsion has been observed when dppe is replaced by phen in fac-Mn(I) as shown from the crystal data discussed in Section 3.1. Thus, the cyclic scheme behavior can be interpreted qualitatively by considering the ligand field splitting of the  $d_{\pi}$  ( $d_{xv}$ ,  $d_{xz}$  and  $d_{vz}$ ) and  $d_{\sigma}$  ( $d_{x^2-v^2}$ ) and  $d_{z^2}$ ) manifold orbitals involved in the change in oxidation states, which leads to the prediction of an electronic preference in each species (Fig. 6).

Notice that the present facial isomers are characterized by three good  $\pi$ -acceptor ligands (the CO molecules) that are well bonded to the filled  $d_{\pi}$  orbitals. Further, in each case, the arrangement of the molecules along the *z*-axis presents ligands exhibiting different  $\sigma/\pi$ donor/acceptor abilities in sight of a synergic  $L \rightarrow$ Mn  $\rightarrow$  CO bonding effect.

According to the MO diagrams (Fig. 6), after the oxidative process, the high oxidation state of the metal and its small size favor a shortness along the x-y-axes and an elongation along the z-axis, reducing the energies of both  $d_{xz}$  and  $d_{yz}$  orbitals with respect to the  $d_{xy}$ . The  $d_{\sigma}$  set will also be reorganized: the  $d_{z^2}$  will be stabilized and the  $d_{x^2-v^2}$  destabilized. Hence, if the ligands along the z are further from the metal, the  $d_{z^2}$  orbital will be stabilized relative to the  $d_{xy}$ . Dealing with an inert sixcoordinated complex, on populating the fifth d electron in  $d_{z^2}$  it will show a tendency to weaken the bonds along the z-axis and so it will also favor rearrangements which places a weaker  $\sigma$ -composite axis along z, i.e., CO–Mn– CO, favoring the *mer*-Mn(II) isomer. By the same token, upon reduction to an 18 e<sup>-</sup> system, which temporarily places 2 e<sup>-</sup> in  $d_{z^2}$ , increasing a distortion due to the great  $\sigma$ -labilizing effect, the d<sub>xy</sub> orbital will be stabilized relative to the  $d_{z^2}$ . Thus, the filled  $d_{\pi}$  orbitals favor rearrangement back to the fac-Mn(I) isomer when they present equal number of ligands CO that can interact with the metal  $d_{\pi}$  orbitals [23]. Furthermore, the different number of ligands CO that can interact with the metal  $d_{\pi}$  orbitals explains the lower anodic potential of the *mer* species in relation to the *fac* ones.

In this interpretation, the ligand field energy order of the  $d_{x^2-y^2}$  and  $d_{z^2}$  orbitals explains why the change in oxidation state promotes the isomerization. This is to be expected if we consider that the  $d_{\pi}$  orbitals lie between the ligands and they are not so sensitive to changes in M-L distances as the X-ray results showed. Furthermore, compared to the *fac*-[Mn(CO)<sub>3</sub>(dppe)(L)] (SO<sub>3</sub>CF<sub>3</sub>) complexes series, the redox potentials in *fac*-[Mn(CO)<sub>3</sub>(phen)(L)](SO<sub>3</sub>CF<sub>3</sub>) complexes are only slightly shifted, reflecting the small difference in donor strength of the dppe and phen ligands. Then, the equatorial ligand substitutions affect reduction potential less than the changes in axial ligands, a finding that is consistent with electron transfer to  $d_{r^2}$  in forming *mer*-Mn(II).

It is interesting to note that light irradiation of the MLCT/MC manifold in *fac*-[Mn(CO)<sub>3</sub>(phen)(im)] (SO<sub>3</sub>CF<sub>3</sub>), which weaken metal–ligand bonds, has the effect of removing an electron from a  $d_{\pi}$  level, decreasing  $\pi$ -bonding stabilization [24]. In a sense, the excited state from which *fac*- to *mer*-photoisomerization occurs resembles the oxidized *fac*-Mn(II) isomer. Similar factors may govern the isomeric distributions in both the oxidative and the photoisomerization reaction.

## 4. Conclusion

Comparison of the series of complexes *fac*-Mn(I) revealed similar bonding properties and redox reactivity independent of the ligand field strength of the axial or bidentate equatorial ligands. The electrochemical model proposed for *fac*-Mn(I)  $\xrightarrow{-e}$  *fac*-Mn(I)  $\rightarrow$  *mer*-Mn(II)  $\xrightarrow{+e}$  *mer*-Mn(I)  $\rightarrow$  *fac*-Mn(I) cyclic-induced isomerism, to the light of several spectroscopic, crystallographic and voltammetric measurements, is consistent with the ligand rearrangement in the Mingos model [25]. Moreover, the present study shows that the electron-transfer induced isomerization process in *fac*-[Mn(CO)<sub>3</sub>(L'-L')(L)]<sup>0/+</sup> is governed by the relative energy order of the d<sub>2<sup>2</sup></sub> orbital; that is, electron population along the *z*-axis leads to ligand repulsion and a switch to a weaker  $\sigma$ -field in that direction for the oxidation step.

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