Elucidation of the Wide Range of Reaction Pathways That Accompany the Electrochemical Oxidation of *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)X] (dpm = Ph$_2$PCH$_2$PPh$_2$; X = Cl, Br)

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The electrochemical oxidation of *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br] (dpm = Ph$_2$PCH$_2$PPh$_2$), or (*cis,mer*)^0, has been examined in dichloromethane (0.1 M Bu$_4$NPF$_6$) by voltammetric, bulk electrolytic, in situ and ex situ spectroelectrochemical and simulation techniques. On the voltammetric time scale at 20 °C, the neutral 18-electron *cis,mer* Mn(I) species is oxidized to the corresponding 17-electron cation which at slow scan rates isomerizes to the trans cation. Simulations are consistent with a rate constant of 3.1 ± 0.3 s^{-1} for this isomerization process. Monitoring the reaction by in situ IR spectroscopy at low-temperature enables the identification of the ν(CO) bands of all four species ((*cis,mer*)^0; (*cis,mer*)$^+$; (*trans*)^0; (*trans*)$^+$) in the resultant square reaction scheme that is operative under these thin layer electrolysis conditions. Additionally, 17-electron *cis,fac*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]$^+$ and its 18-electron (*cis,fac*)^0 counterpart, generated by a redox-induced catalytic isomerization reaction, are detected and characterized by IR spectroscopy (ν(CO)). Room-temperature bulk oxidative electrolysis experiments reveal that the trans cation, generated in bulk solution from the (*cis,mer*)$^+$ and (*cis,fac*)$^+$ isomers, slowly ejects bromide with a rate constant of 1.6×10^{-3} s^{-1} to form *trans*-[Mn(CO)$_2$(η^2-dpm)$_2$]$^+$. The equivalent voltammetry in acetonitrile is complicated by an additional competing kinetic step which is attributed to reaction of this cation with the solvent. However, the major product formed upon oxidation at room temperature is still the *trans* cation. Less detailed studies on the oxidation of *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Cl] only show significant differences under conditions of bulk electrolysis after *trans*-[Mn(CO)$_2$(η^2-dpm)$_2$]$^{2+}$ is formed via expulsion of Cl$^-$.

Introduction

Electrochemical oxidation of neutral 18-electron transition metal organometallic complexes containing combinations of carbon monoxide and phosphine ligands has received much attention.[1−10] Upon one-electron oxidation, a number of reaction routes for the initially formed isostructural 17-electron cation are possible on either the voltammetric (short) or bulk electrolysis (long) time scales:

(a) The resulting cation is highly stable. In this case a chemically reversible one-electron process is observed.[6−9]

(b) The cation may isomerize to give the well-known square reaction scheme.[3,5,9]

(c) The cationic species may react to form an entirely new class of product.[9,11]

In this present study we have examined in detail the electrochemical oxidation of *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br] (Chart 1, **1A**) in dichloromethane and acetonitrile by voltammetric, bulk electrolytic and spectroelectrochemical techniques. As noted above, in principle on oxidation of **1A**, the resulting isostructural cation (**1A**$^+$) may isomerize, eject a ligand and/or undergo internal nucleophilic attack by the pendant phosphorus atom associated with the η^1-dpm ligand or external attack by the solvent. We show that all of these processes and also cross redox reactions occur during the course of oxidation of **1A** so that the electrochemistry is unusually complex. To obtain kinetic parameters and verify postulated mechanisms, the commercial package, DigiSim,[12] is used to simulate the cyclic voltammetric response in both dichloromethane and acetonitrile. Less detailed studies are reported on the *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Cl] (**1B**) system to examine the influence of the halide ligand on the redox chemistry.

Experimental Details

Reagents, Compounds, and Solvents. Acetonitrile (Mallinckrodt, Biolab Scientific Pty Ltd. (HPLC grade, 99.9%)) and dichloromethane (Mallinckrodt. (HPLC grade, 99.9%)) were dried for at least 12 h over molecular sieves. The electrolytes were tetrabutylammonium hexafluorophosphate (Bu$_4$NPF$_6$)[13] and Bu$_4$NClO$_4$ (South Western Analytical,

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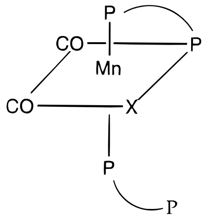
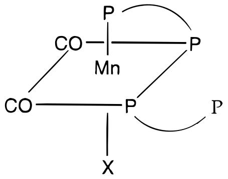
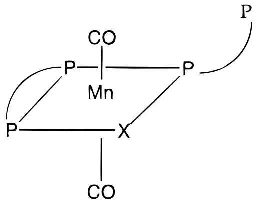
Chart 1[a]



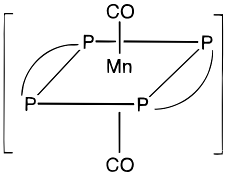
1A, **1B** *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)X]



2A, **2B** *cis,fac*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)X]



3A, **3B** *trans*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)X]



4$^+$ *trans*-[Mn(CO)$_2$(η^2-dpm)$_2$]$^+$

[a] For compounds above, X = Br (**A**), Cl (**B**).

electrometric grade). Compounds **1A** and **1B** were prepared by standard literature procedures.[14,15] The assignment of the *cis,mer* isomeric form was made on the basis of IR and ^{31}P NMR data.[14,15] All solutions were thoroughly purged of oxygen by outgassing with nitrogen that had been presaturated with solvent. The absence of incident irradiation[16] was ensured by wrapping all solution vessels in aluminum foil. Experiments were conducted at either 20 (±1) or −40 (±1)°C.

Instrumentation and Procedures. Cyclic voltammetric experiments employed 1.0 or 3.0 mm diameter platinum or glassy-carbon macrodisk or 10 or 25 μm diameter platinum or 10 μm diameter glassy carbon microdisk working electrodes in conjunction with Ag/Ag$^+$ (0.01 M AgNO$_3$, 0.1 M Bu$_4$NClO$_4$ in acetonitrile) or Ag/AgCl (saturated LiCl, 0.1 M Bu$_4$NPF$_6$ in dichloromethane) reference electrodes and a platinum wire counter electrode. All potentials are quoted relative to the reversible potential for the ferricenium/ferrocene couple (Fc$^{+/0}$). Rotating disk electrode experiments used a platinum macrodisk electrode (diameter, 3.0 mm) which was rotated by a variable speed rotator (Metrohm 628−10).

A Cypress Systems (model CYSY-1R) potentiostat in conjunction with a 386 personal computer or an ADI Instruments Maclab4e/potentiostat system controlled by a Macintosh Powerbook microcomputer were used for voltammetric measurements.

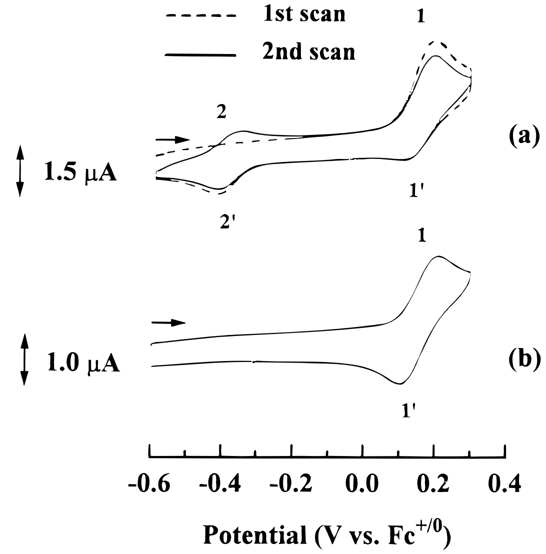


Figure 1. Cyclic voltammograms obtained at a scan rate, 200 mV s^{-1} for the oxidation of **1A** (1.0 mM) in dichloromethane (0.1 M Bu$_4$NPF$_6$) at a 1 mm diameter Pt macrodisk electrode; (a) 20 °C; (b) −40 °C.

Conventional bulk electrolysis experiments combined with coulometry were undertaken with either a PAR model 273 potentiostat or a BAS 100A electrochemical analyzer using a large platinum basket working electrode, a platinum gauze auxiliary electrode separated from the test solution by a salt bridge and the same reference electrodes used in the voltammetric studies.

^{31}P NMR spectra were recorded on a Bruker AM300 spectrometer operating at 121.4 MHz, and chemical shifts were referenced against an external aqueous solution of 85% H$_3$PO$_4$. Ex situ Infrared spectra were recorded on Perkin-Elmer FT-IR 1720X, Perkin-Elmer 1430 IR, or Bio-Rad FT-infrared spectrometers. In situ IR spectroelectrochemical experiments were carried out using a modified IR reflection−absorption spectroscopy (IRRAS) cell,[17,18] mounted on a specular reflectance accessory located in the sample compartment of a Bruker IFS 55 FTIR spectrometer. The electrode arrangement consisted of a polished platinum disk working electrode (r = 2.5 mm), a platinum gauze auxiliary electrode and a silver wire pseudo-reference electrode. Electrolyses were carried out by stepping the potential of the working electrode from a rest potential to a potential sufficient to cause electrolysis, and single scan IR spectra (resolution 1.0 cm^{-1}) were collected as a function of time. The cell was thoroughly flushed with nitrogen prior to addition of the sample and maintained under a nitrogen atmosphere throughout the experiments.

X-band EPR measurements were made with a Varian E-12 spectrometer. Positive ion electrospray mass spectroscopic experiments were conducted on a Micromass Platform II quadrupole spectrometer. Portions of the approximately 1 mM solutions used in dichloromethane experiments were diluted 1:10 with acetonitrile. The diluted solution was injected directly into the spectrometer and the solution was delivered to the vaporization nozzle of the electrospray ion source, via an acetonitrile mobile phase, at a flow rate of 5 μL min^{-1}. Voltages at the first skimmer electrode were the minimum necessary to maintain a stable spray (typically 10−25 V).

To simulate cyclic voltammetric responses DigiSim V2.1[12] was run on a 120 MHz Pentium PC.

Results and Discussion

A. Voltammetric Studies on *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br] (Chart 1, Compound 1A) in Dichloromethane. Figure 1 depicts a low scan rate, cyclic voltammogram (scan

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rate, 200 mV s^{-1}) obtained at 20 °C for oxidation of **1A** in dichloromethane (0.1 M Bu_4NPF_6). Over the potential range −0.60 to 0.40 V (vs $Fc^{+/0}$) and in the first cycle, an irreversible response is observed (process 1) with an oxidative peak potential ($E^{ox}{}_{P}$) of +0.20 (±0.02) V. In addition, a reductive feature (process 2′) is evident at $E^{red}{}_{P}$, −0.44 (±0.02) V, with its corresponding oxidation peak (process 2) being detected in second and subsequent cycles at $E^{ox}{}_{p}$, −0.36 (±0.02) V. As the scan-rate increases, a reduction peak current associated with process 1 (described as process 1′) is detected (Figure S1). Concurrently, the current magnitude of process 2′ decreases relative to that of process 1. The scan-rate dependence suggests that the product of process 1 reacts to form a new species that in turn undergoes a chemically reversible electron-transfer process at less positive potentials (i.e. to generate processes 2 and 2′ on second and subsequent cycles). If the reaction temperature is decreased to −40 °C, redox couple 1 becomes chemically reversible (see Figure 1), while processes 2 and 2′ disappear, indicating that the rate of the reaction following the initial charge-transfer process is slowed upon lowering the temperature.

Process 1 was further studied using rotating-disk electrode (RDE) which showed that the oxidation exhibits Levich behavior[19] over the rotation speed range of 500−3000 rpm to give a diffusion coefficient of $(7 \pm 1) \times 10^{-6}$ cm^2 s^{-1}. Analysis of the limiting current−mass transport behavior suggests that process 1 involves a one-electron charge-transfer process at all rotation rates. Fast scan-rate voltammetry using a 25 μm diameter platinum microdisk electrode enables the reversible potential ($E°_F$) to be determined for process 1 (assuming equal diffusion coefficients for reactant and product). In the scan rate range of 2000−5000 mV s^{-1} the measured half-wave potential ($E_{1/2} \approx E°_F$) is independent of scan rate, as expected when the homogeneous kinetics following the one-electron-transfer process are out-run. Thus, an $E°_F$ value for the formal reversible potential of +0.16 (±0.01) V is obtained at 20 °C. The same reversible potential ($E_{1/2} \approx 0.16$ V) was obtained under near steady-state conditions at platinum or glassy carbon microdisk electrodes. These microdisk data also imply that the homogeneous kinetics also may be out-run under these near steady-state conditions, implying that the value of the first-order rate constant (k_1, see below) must be of the order of 1 s^{-1}.[20]

An additional irreversible oxidative process is observed at $E^{ox}{}_{P}$ = +1.20 (±0.10) V (scan rate 100 mV s^{-1}). The process of interest in this paper is the first one-electron step, so no further detail on the suggested Mn^{II}/Mn^{III} oxidation process is presented.

B. Monitoring of Bulk Electrolysis Experiments on *cis,-mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br] Using a Combination of in Situ and ex Situ Voltammetric and Spectroscopic Techniques. Bulk oxidative electrolyses experiments on solutions of **1A** in dichloromethane (0.1 M Bu_4NPF_6) were conducted at 20 and −40 °C in both conventional and thin-layer IRRAS cells. Unless otherwise stated, the potential of the platinum working electrode was held at +0.25 V which is sufficiently positive to achieve oxidation at process 1. At both 20 and −40 °C process 1 was determined by coulometry (exhaustive electrolysis conditions at a platinum basket electrode) to be a one-electron process. The product(s) formed was examined by ex situ EPR measurements and found to contain six lines of equal intensity indicative of Mn(II) (^{55}Mn, $I = {}^5/_2$). The EPR spectrum is very similar to that found after oxidation of *fac*-[Mn(CO)$_3$(η^2-dpm)Cl][3−5] where six-line spectra were observed and attributed to the formation of low-spin Mn(II) species, *fac*-[Mn(CO)$_3$(η^2-dpm)Cl]$^+$ and *mer*-[Mn(CO)$_3$(η^2-dpm)Cl]$^+$.[4]

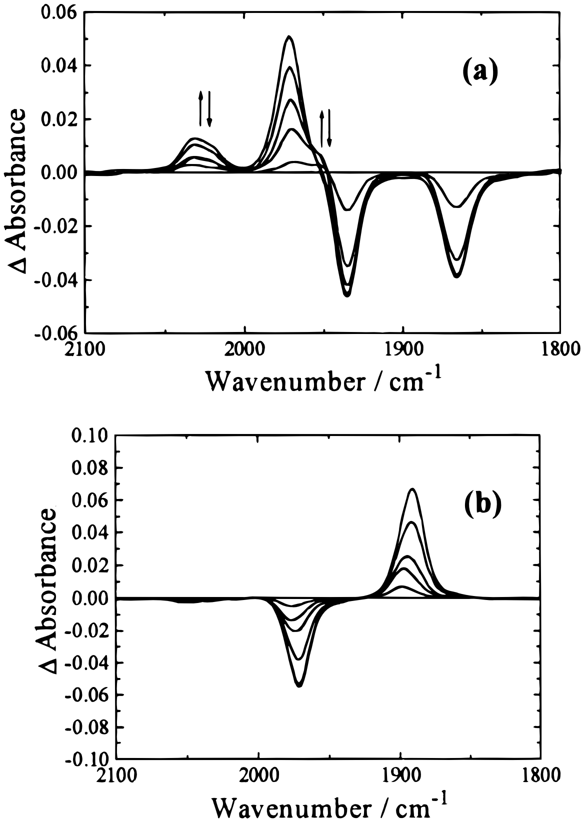

Figure 2. In situ IR spectra obtained during electrolysis experiments in an IRRAS cell commencing with **1A** (1.0 mM) in dichloromethane (0.1 M Bu_4NPF_6) at −40 °C. (a) Change in IR absorbance, relative to that of the initial IR spectrum of **1A** during oxidative electrolysis at +0.25 V (the ↑ and ↓ arrows signify that the IR intensity initially increases and then decreases). (b) Change in IR absorbance relative to that of the IR spectrum formed in (a) of **2A**$^+$ during reductive electrolysis at −0.55 V.

The oxidation of **1A** at −40 °C was monitored by IR spectroscopy using an IRRAS cell. Upon oxidation, the two ν(CO) bands from **1A** at 1936 and 1866 cm^{-1} decrease in intensity while unresolved bands initially grow at approximately 2031 and 2022 cm^{-1} and at 1960 and 1950 cm^{-1} (Figure 2a). These new ν(CO) bands are attributed to the generation of two cationic cis isomeric forms of oxidized **1A** since the difference in frequency of about 80 cm^{-1} relative to **1A** is consistent with this interpretation.[21−24] The two possible cis cationic isomers are the *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]$^+$ (1950 and 2022 cm^{-1}) and *cis,fac*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]$^+$ (1960 and 2031 cm^{-1}) species now referred to as compounds **1A**$^+$ and **2A**$^+$, respectively (Chart 1). After initially increasing with time (seconds) the intensity of the overlapping ν(CO) bands from compounds **1A**$^+$ and **2A**$^+$ eventually decreases. The intense single ν(CO) band observed to grow at 1971 cm^{-1} is assigned to the formation of the *trans*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]$^+$

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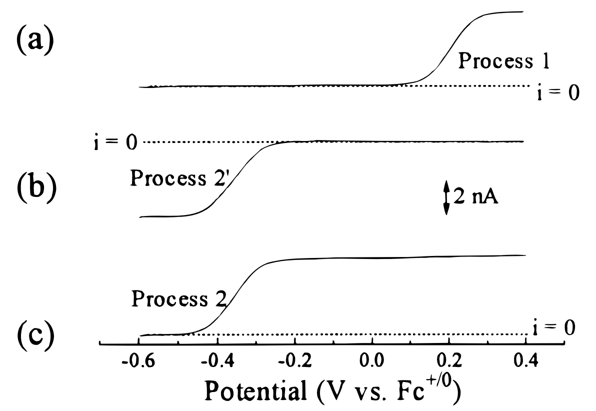

Figure 3. Microdisk near steady-state voltammograms obtained at −40 °C with a 25 μm diameter platinum electrode (scan rate 10 mV s^{-1}) from an initially 1.0 mM solution of **1A** in dichloromethane (0.1 M Bu_4NPF_6) (a) before electrolysis, (b) after electrolysis at + 0.25 V, and (c) after reduction of the solution formed in (b) at −0.55 V.

(compound **3A**$^+$, Chart 1). An additional minor product with ν(CO) bands at 1878 and 1945 cm^{-1} detected as an intermediate also disappeared upon complete electrolysis. Since **1A** (*cis,-mer*) has IR bands at 1866 and 1936 cm^{-1}, the transient species with a similar IR spectrum is attributed to the generation of a small amount of *cis,fac*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br] (compound **2A**). If only partial rather than exhaustive electrolysis is undertaken at −40 °C, then the IR spectrum shown in Figure S2 is observed. This spectrum implies that catalytic isomeric conversion of **1A** (*cis,mer*) to **2A** (*cis,fac*) occurs in good yield in the presence of only trace amounts of the **1A**$^+$ (*cis,mer*) cation.

Presumably the **2**$^{+/0}$ (*cis,fac*) redox couple has a similar reversible potential to that for the **1**$^{+/0}$ (*cis,mer*) process so that **2A** formed in a bulk electrolysis experiment is oxidized to **2A**$^+$ which like the *cis,mer* cation is also then isomerized to the trans cationic isomer (see above), as shown by the detection of the ν(CO) band at 1971 cm^{-1} (Figure S2). However, after only a small amount of electrolysis, all species required for catalytic isomeric conversion of **1A** (*cis,mer*) to **2A** (*cis,fac*) are present in bulk solution. The reactions summarizing the catalytic generation of **2A** after formation of small amounts of **1A**$^+$ from **1A** in bulk solution at early stages in the low-temperature oxidation in the thin-layer IR spectroelectrochemical cell are:

$$\mathbf{1A}^+\ (cis,mer) \rightarrow \mathbf{2A}^+\ (cis,fac) \qquad (1)$$

$$\mathbf{2A}^+\ (cis,fac) + \mathbf{1A}\ (cis,mer) \rightarrow \mathbf{2A}\ (cis,fac) + \mathbf{1A}^+\ (cis,mer) \qquad (2)$$

Under the conditions of electrolysis at −40 °C in a conventional cell, only reductive process 2′ was observed in the cyclic and steady-state (Figure 3) microdisk voltammetry after exhaustive electrolysis, and there was no spectroscopic or voltammetric evidence of liberated Br$^-$, CO or dpm. From steady-state microdisk electrode voltammetry, the magnitude of the reductive current associated with process 2′ is the same as the equivalent current associated with process 1 before bulk electrolysis (Figure 3c). Thus, all electrolysis data are consistent with the formation of an essentially quantitative yield of the trans cation (**3A**$^+$) with **1A**$^+$ (*cis,mer*) and **2A**$^+$ (*cis,fac*) cations and neutral **2A** (*cis,fac*) species being generated at earlier stages of the experiment.

On rereduction in the IRRAS cell at − 0.55 V and −40 °C, the IR signal at 1971 cm^{-1} for **3A**$^+$ (*trans*) decays with time and is replaced by a single ν(CO) band at 1891 cm^{-1} which is assigned to the formation of the neutral 18-electron **3A** (*trans*) species (Figure 2b).

The ^{31}P NMR spectrum of the product formed by the bulk oxidative-reductive electrolysis sequence obtained in a conventional cell was recorded at −40 °C with Bu_4NClO_4 being used instead of Bu_4NPF_6 as the supporting electrolyte. Four lines of equal intensity were observed as expected for formation of **3A** (Table 1). The ^{31}P NMR signal at −31.8 ppm (*trans*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]) is consistent with retention of the pendant phosphorus. In addition, steady-state microdisk voltammetry after this electrolysis sequence produced only one wave with an identical half-wave potential and limiting current (now for process 2) to that observed prior to reduction. However, importantly the position of zero current indicates that the species in solution is now in the reduced form (Figure 3c). When this reduced solution was warmed to 20 °C, steady-state voltammograms indicate that concomitantly the limiting current for process 2 decreases and that for process 1 grows until process 2 is not observed. In addition the ν(CO) band at 1891 cm^{-1}, assigned to **3A** (*trans*), decreases and two new bands grow at 1936 and 1866 cm^{-1} as expected for formation of **1A** (*cis,-mer*), which must therefore be the thermodynamically favored 18-electron form of [Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br].[25]

When bulk electrolysis experiments were conducted at 20 °C in the conventional cell the pink color associated with the formation of **3A**$^+$ gradually disappeared when the oxidized solution was left to stand (no applied potential) and the solution became pale yellow. Cyclic voltammetric monitoring of this experiment after completion of the electrolysis (Figure S3) reveals that the major response detected is associated with redox couple **2**. However, a previously undetected reversible process (couple 3) is also observed with a half-wave potential of 0.37 (±0.02) V. Further monitoring by cyclic voltammetry shows that couple **3** continues to grow until 30 min post-bulk electrolysis, redox couple **2** is not detected while couple **3** is extremely well defined. The ^{31}P NMR spectrum from bulk electrolysis in dichloromethane (0.1 M Bu_4NClO_4) obtained at this time shows a single resonance having a chemical shift of 35.3 ppm. In situ IR spectroelectrochemical oxidation experiments in the IRRAS cell at room temperature lead to a decrease in the intensity of the **1A** (*cis,mer*) ν(CO) bands at 1937 and 1866 cm^{-1} and concomitant growth of a single sharp band at 1971 cm^{-1} due to formation of **3A**$^+$ (*trans*), whereas the IR spectrum of the solution oxidized in a conventional cell, collected some 30 min after oxidation, exhibits a single carbonyl stretch at 1916 cm^{-1}. The IR and NMR data of this latter species are similar to that reported[14] for the *trans*-[Mn(CO)$_2$(η^2-dpm)$_2$]$^+$ cation or compound **4A**$^+$ (*trans*) (1916 cm^{-1} and 33 ppm, respectively) which suggests that this compound is formed slowly from **3A**$^+$. This assignment was supported by the positive-ion electrospray mass spectrum obtained from the bulk electrolyzed solution which produced a strong signal at 879 (*m*/*e*), as expected for the **4A**$^+$ cation. The simulated and experimental mass spectra for this formulation of the cation were in excellent agreement.

On the basis of all the above evidence, it is therefore postulated that redox couple 3 corresponds to the reaction

$$E \qquad \mathbf{4}^+\ (trans) \rightleftarrows \mathbf{4}^{2+}\ (trans) + e^- \qquad (3)$$

This process is analogous to that of the reversible [Mn(CO)$_2$(η^2-dpe)$_2$]$^{0/+}$ reaction which has a half-wave potential of +0.60

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Table 1. IR and ^{31}P NMR Spectroscopic Data Obtained for the Species Associated with the Electrochemical Oxidation of *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br] in Dichloromethane

	ν(CO)/cm^{-1}		δ (^{31}P)/ppm			
cis,mer-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]	1866	1936	50.3	35.0	0.3	−28.1
cis,fac-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]	1878	1945				
cis,mer-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]$^+$ [a]	1950	2022				
cis,fac-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]$^+$ [a]	1960	2031				
trans-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]	1891		53.2	49.3	19.0	−31.8
trans-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]$^+$	1971					
trans-[Mn(CO)$_2$(η^2-dpm)$_2$]$^+$	1916		35.3			

[a] Deduced by reference to ν(CO) data obtained for the isostructural neutral analogues.

($\pm$0.10) V (vs Fc$^{+/0}$).[10] The significantly more positive potential for the dpe analogue (+0.60 vs +0.37 V) is in line with the general observation that dpe species are oxidized at more positive potentials than their dpm counterparts.[6,26,27]

Analysis of the rate of increase of ν(CO) at 1916 cm^{-1} (**4A**$^+$) and decrease of ν(CO) 1971 cm^{-1} (**3A**$^+$) using the IRRAS cell by a first-order rate law gave a rate constant of 1.6 ($\pm$0.2) $\times$ 10^{-3} s^{-1} at 20 °C (k_2, see below) for the conversion **3A**$^+$ to **4A**$^+$.

All of the evidence obtained from these bulk electrolysis experiments imply that process 1, at short voltammetric time domains, must correspond to the oxidation of **1A** (*cis,mer*) to the isostructural 17 electron cationic manganese(II) species **1A**$^+$ (*cis,mer*) and that process 1′ is the reverse reduction process, so that couple 1 is the reaction:

$$\text{E}\qquad \mathbf{1A}\ (cis{,}mer) \rightleftarrows \mathbf{1A}^+\ (cis{,}mer) + \text{e}^- \tag{4}$$

However, **1A** apparently is unstable on longer time scales so that under slow scan rate cyclic voltammetric conditions, **1A**$^+$ (*cis,mer*) isomerizes to **3A**$^+$ (*trans*). This result is analogous to oxidation of *cis*-[Cr(CO)$_2$(η^2-dpe)$_2$]$^+$ which yields the cis cation at short times, but the *trans*-[Cr(CO)$_2$(η^2-dpe)$_2$]$^+$ isomer on long time-scale experiments.[28] Thus, if processes 2 and 2′ are associated with the redox couple:

$$\text{E}\qquad \mathbf{3A}\ (trans) \rightleftarrows \mathbf{3A}^+\ (trans) + \text{e}^- \tag{5}$$

then it follows that the slow scan rate voltammetric oxidation of **1A** occurs in dichloromethane via an EC scheme:

$$\text{E}\qquad \mathbf{1A}\ (cis{,}mer) \rightleftarrows \mathbf{1A}^+\ (cis{,}mer) + \text{e}^- \tag{4}$$

$$\text{C}\qquad \mathbf{1A}^+\ (cis{,}mer) \xrightarrow{k_1} \mathbf{3A}^+\ (trans) \tag{6}$$

This EC reaction scheme assumes that the catalytic process which generates **2A** (*cis,fac*) under bulk electrolysis conditions is too slow to be significant on the voltammetric time scale. Additionally, the reaction **1A**$^+$ (*cis,mer*) → **2A**$^+$ (*cis,fac*) may occur more rapidly than reaction 6 and hence not be detected under these conditions (not rate determining) or else it may not be detectable because of lack of resolution of the [**1A**]$^{+/0}$ and [**2A**]$^{+/0}$ processes.

Since the 18-electron **4**$^+$ compound is the final stable product of bulk electrolysis, it can be concluded that the 17-electron **3A**$^+$ slowly releases bromide to give **4A**$^{2+}$. However, this trans dication is a strong oxidant and can oxidize bromide to bromine, so that steps 4−6 may be followed by:

$$\text{C}\qquad \mathbf{3A}^+\ (trans) \xrightarrow{k_2(\text{slow})} \mathbf{4A}^{2+}\ (trans) + \text{Br}^- \tag{7}$$

$$\text{C}\qquad \mathbf{4A}^{2+}\ (trans) + \text{Br}^- \xrightarrow{k_3(\text{fast})} \mathbf{4A}^+\ (trans) + {}^1\!/_2\text{Br}_2 \tag{8}$$

where reaction 7 is the rate-determining step and k_2 has a value of 1.6 ($\pm$0.2) $\times$ 10^{-3} s^{-1}.

Thus, at 20 °C the overall oxidation of *cis,mer*-[Mn(CO)$_2$-(η^1-dpm)(η^2-dpm)Br] on the time scale of bulk electrolysis is represented by the reaction

$$cis{,}mer\text{-[Mn(CO)}_2(\eta^1\text{-dpm})(\eta^2\text{-dpm})\text{Br]} \rightarrow trans\text{-[Mn(CO)}_2(\eta^2\text{-dpm})_2]^+ + {}^1\!/_2\text{Br}_2 + \text{e}^- \tag{9}$$

C. Simulation of the Room-Temperature Voltammetric Oxidation of *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br]. The cyclic voltammetric response obtained at 20 °C was simulated according to the square reaction scheme described by eqs 4−6 in combination with the slow bromide expulsion step described by eq 7 using the DigiSim voltammetric simulation package.[12] The formal potentials for the redox processes 1/1′ (0.16 $\pm$ 0.02 V) and 2/2′ (−0.40 $\pm$ 0.03 V) were obtained as described above. Double-layer capacitance values of 25 μF cm^{-2} and uncompensated resistances of 2000 Ω were used in the simulations which are typical of the solvent/electrolyte system of interest.[29−31] The isomerization process was assumed to be completely irreversible. Thus, solely for the purposes of the simulation, a very high (10^{10}), but chemically insignificant value of the equilibrium constant was used for the C step. The kinetic parameter (k_2) used for the debromination of *trans*-[Mn(CO)$_2$-(η^1-dpm)(η^2-dpm)Br]$^+$ was the value obtained from IR experiments, although it eventuated that this rate constant is too slow to be significant at the scan rates employed in experimental studies. The diffusion coefficients of all the species in the electrode reaction mechanism were set to 7 $\times$ 10^{-6} cm^2 s^{-1} (the value determined for compound **1A** using microdisk and rotating disk voltammetry).

As can be seen in Figure 4 excellent agreement is obtained between experiment and theory at scan rates of 100 and 1000 mV s^{-1} for the proposed mechanism in dichloromethane when the heterogeneous charge-transfer rate constants for electron-transfer in steps 4 and 5 were both set at 0.06 ($\pm$0.03) s^{-1} and when a k_1 value of 3.1 ($\pm$0.3) s^{-1} is used. Similarly good fits

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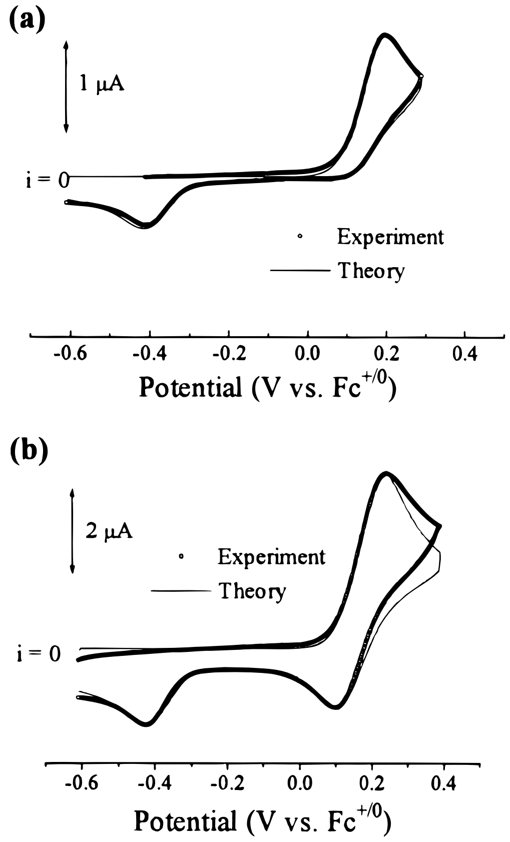

Figure 4. Comparison of experimental and simulated (according to the mechanism described by eqs 4−7 and the parameters given in the text) voltammograms obtained at a 1 mm diameter platinum macrodisk electrode for the oxidation of 0.92 mM **1A** at 20 °C in dichloromethane (0.1 M Bu_4NPF_6). (a) Scan rate, 100 mV s^{-1} ($k_1 = 2.9$ s^{-1}), (b) scan rate, 1000 mV s^{-1} ($k_1 = 3.4$ s^{-1}).

were obtained for other scan rates in the range of 100−2000 mV s^{-1} and concentrations of **1A** (0.2−1.0 mM).

D. Voltammetry and Bulk Electrolysis in Acetonitrile. Qualitatively, the voltammetry of **1A** in acetonitrile is similar to that in dichloromethane. Thus, (i) the reversible $E_{1/2}$ value for the $[\mathbf{1A}]^{+/0}$ couple is +0.26 (±0.02) V (vs $Fc^{+/0}$) as determined from fast scan rate cyclic voltammetric measurements at a microdisk electrode, (ii) the $E_{1/2}$ value for the $[\mathbf{3A}]^{+/0}$ couple is −0.26 (±0.02) V (slow scan rate voltammetry at a macrodisk electrode), and (iii) the irreversible Mn(II) to Mn(III) oxidation process has a peak potential of +0.53 (±0.05) V at a scan rate of 100 mV s^{-1}.

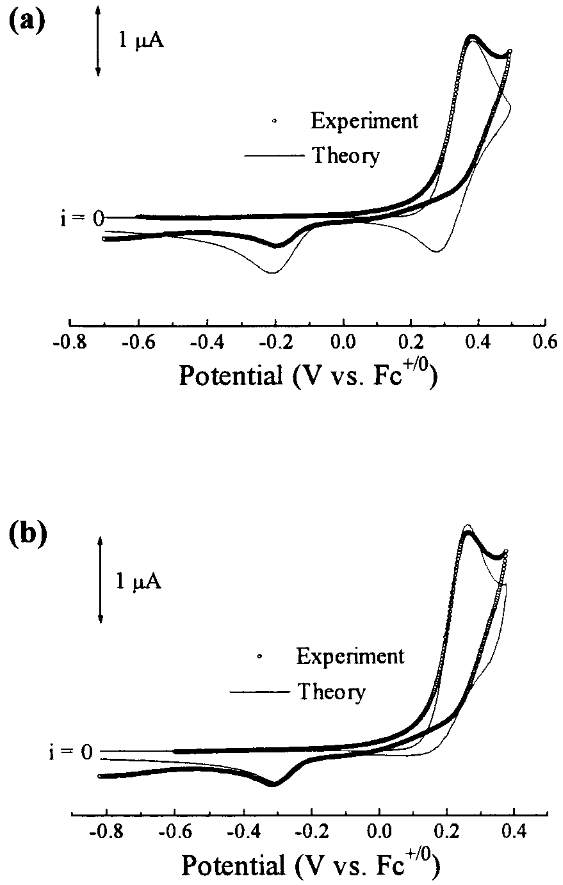

Figure 5. Experimental and simulated (according to the mechanism described by eqs 4−6 and 10 and the parameters given in the text) voltammograms obtained at a 1 mm diameter platinum macrodisk electrode using a scan rate of 100 mV s^{-1} for the oxidation of 1.04 mM **1A** at 20 °C in acetonitrile (0.1 M Bu_4NPF_6). (a) $k_1 = 0.5$ s^{-1}; single C step (eq 6) EC mechanism, (b) $k_1 = 2$ s^{-1} and $k_4 = 4$ s^{-1}; two parallel C steps (eqs 6 and 10) mechanism.

However, it can be seen (Figure 5a) that poor agreement between experiment and simulation is observed in acetonitrile when the reaction scheme represented by eqs 4−6 is used because the experimentally observed peak current values for both processes 2′ and 1′ are both lower than the simulated values. Furthermore, these peak currents cannot be simulated because if the value of k_1 (the only variable parameter in the simulation) is increased, the peak currents for processes 1′ and 2′ will decrease and increase, respectively. In this solvent, the parameters utilized in the dichloromethane voltammetric simulations were used to calculate theoretical voltammograms, except for the diffusion coefficient of 1.0 (±0.1) × 10^{-5} cm^2 s^{-1} obtained from rotating-disk experiments, an uncompensated resistance of 500 Ω, the reversible potentials given above and the debromination step (eq 7) was neglected. It is suggested that the failure to simulate the peak currents associated with both processes 1′ and 2′, with the mechanism found in dichloromethane, results from the presence of a homogeneous process (additional to the isomerization step), C′ (eq 10), which removes $\mathbf{1A}^+$ from near to the electrode surface:

$$C' \qquad \mathbf{1A}^+ \ (cis,mer) \xrightarrow{k_4} \text{products} \qquad (10)$$

If this additional homogeneous chemical step is included into the simulations with a first-order or pseudo-first-order rate constant, k_4, of 4 s^{-1}, reasonable agreement is obtained between the experimental and theoretical voltammograms (Figure 5b). Due to the substantial nucleophilicity of acetonitrile,[15] it is suggested that the $\mathbf{1A}^+$ (*cis*,*mer*) cation may react with this solvent at a similar rate to that for the isomerization process in an analogous manner to that of voltammetrically generated $[Cr(CO)_3(\eta^6\text{-arene})]^+$ [32] or $[Cr(CO)_4(\eta^2\text{-dpm})]^+$ [33] or chemically generated $[Cr(CO)_4(\eta^2\text{-dpe})]^+$ [34] 17-electron cations which undergo nucleophilic attack by CH_3CN and elimination of CO ligands.

In situ IR oxidative spectroelectrochemical experiments at 20 °C on **1A** in acetonitrile (0.1 M Bu_4NPF) at +0.35 V, reveal that the ν(CO) bands at 1935 and 1867 cm^{-1} are replaced by a

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strong single band at 1973 cm^{-1} and a weak band at 1874 cm^{-1}. The band at 1973 cm^{-1} corresponds to the formation of $\mathbf{3A}^+$ as deduced by comparison with IR data obtained in dichloromethane (1971 cm^{-1}). It is postulated that the weak band at 1874 cm^{-1} results from a carbonyl ligand of $\mathbf{1A}^+$ being replaced by acetonitrile in a pseudo-first-order process. However, the identity of this finally formed acetonitrile substituted species or any intermediates has not been determined.

E. Electrochemical Oxidation of *cis,mer*-[Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Cl] in Dichloromethane (Chart 1, Compound 1B). Comparative voltammetric and electrolysis experiments also were conducted on **1B** in dichloromethane at 20 °C. This species exhibits a voltammetric response that is closely related to the bromo-anologue. Thus, while the potentials of the processes for **1B** are slightly more positive ($E^{ox}{}_p = +0.20$ V (process 1); $E^{ox}{}_p = -0.34$ V, $E^{red}{}_p = -0.42$ V (processes 2 and 2′), scan-rate = 200 mV s^{-1}) than for **1A**, bulk oxidative electrolysis at 0.30 V also led to $\mathbf{4}^+$ (*trans*) being detected as the final stable product by voltammetric, IR, and electrospray mass spectroscopic measurements. However, since released chloride is much more difficult to oxidize than bromide,[35] $\mathbf{4}^{2+}$ does not convert chloride to chlorine. In this case, it was therefore necessary to maintain the electrode potential at 0.30 V until the solution had changed color from pink to pale yellow in order to obtain a quantitative yield of the $\mathbf{4}^+$ cation. At the potential of +0.30 V any $\mathbf{4}^{2+}$, formed by expulsion of Cl^- from the $\mathbf{3B}^+$ (*trans*) produced via isomerization of $\mathbf{1B}^+$ (*cis,mer*), is immediately reduced at the electrode surface to $\mathbf{4}^+$ to give the overall reaction:

$$\mathbf{1B}\ (cis,mer) \rightarrow \mathbf{4}^+\ (trans) + Cl^- \tag{11}$$

A possible alternative mechanistic description to explain the long time-scale bulk oxidative electrolysis of **1A** would be to propose that $\mathbf{3A}^+$ undergoes an oxidatively induced reductive elimination reaction (akin to those observed for [Cp_2MoCl_2][36,37] and [Cp_2TiCl_2][38]) in which a bromine atom rather than the bromide anion is ejected and replaced by the pendant phosphine arm of the η^1-dpm ligand. However, for the chloride analogue, the Mn(II) unit is not a sufficiently strong oxidant to induce elimination of $Cl^\bullet$, so that Cl^- must be ejected, leaving the central manganese atom in oxidation state II. In this case, the reduction of *trans*-[Mn(CO)$_2$(η^2-dpm)$_2$]$^{2+}$ to the Mn(I) *trans*-[Mn(CO)$_2$(η^2-dpm)$_2$]$^+$ complex must occur heterogeneously at the electrode surface.

Conclusions

At 20 °C, slow scan rate cyclic voltammetry and bulk electrolysis experiments suggest that $\mathbf{1A}^+$ (*cis,mer*) formed upon oxidation of **1A** (*cis,mer*) rapidly isomerizes to $\mathbf{2A}^+$ (*trans*), the overall first-order rate constant for this isomerization reaction being 3.1 (±0.3) s^{-1}. On standing in solution after bulk electrolysis experiments, $\mathbf{2A}^+$ slowly reacts at 20 °C to give $\mathbf{4}^+$ (*trans*) and bromine, the rate constant for the expulsion of bromide being $1.6\ (\pm 0.2) \times 10^{-3}\ s^{-1}$. Under conditions of bulk electrolysis at −40 °C, IR evidence for the 17-electron **1A** cation is obtained. Additionally, at this temperature IR evidence for catalytic generation of **2A** (*cis,fac*) as well as its isostructural cation, $\mathbf{2A}^+$, have been obtained. This appears to be the first time that evidence has been obtained for the *cis,fac* isomeric forms in [Mn(CO)$_2$(η^1-dpm)(η^2-dpm)Br] type systems. In the thermodynamic sense, *cis,mer* is the favored isomeric form in the 18-electron configuration, whereas the trans geometry is the favored form in the oxidized 17-electron system. However, interconversions between the two thermodynamically favored states may occur via the *cis,fac* geometric configuration.

In acetonitrile, the isomerization processes are complicated by what is believed to be a parallel reaction of the oxidized cations with the solvent.

The oxidation of **1B** in dichloromethane parallels that of the bromine analogue on the voltammetric time scale. However, the lower redox reactivity of released Cl^- leads to differences in the reaction mechanism on the bulk electrolysis time scale.

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Supporting Information Available: Figures S1−S3 are available as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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