Spectroscopic Characterization of Some Unstable ortho-Semiquinone and ortho-Quinone Complexes of MnI by Variable-Temperature Thin-Layer Spectroelectro-chemistry at Optically Transparent Electrodes

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Spectroscopic characterization of some unstable ortho-semiquinone and ortho-quinone complexes of Mn(I) by variable-temperature thin-layer spectroelectrochemistry at optically transparent electrodes

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Abstract

Four carbonyl complexes of MnI containing 3,5-di-tert.butyl-1,2-semiquinone (DBSQ) and 3,5-di-tert.butyl-1,2-benzoquinone (DBQ) ligands, the radicals [Mn(CO)3(L)(DBSQ)] and the cationic complexes [Mn(CO)3(L)(DBQ)]+ (L=H2O, PPh3), have been characterized for the first time by UV-Vis spectroscopy. These compounds possess limited stability at room temperature with the exception of [Mn(CO)3(PPh3)(DBSQ)] which thermally decomposes only in the presence of an excess of PPh3. The o-(semi)quinone complexes under study were electrogenerated inside a recently developed low temperature optically transparent thin-layer electrochemical (LT OTTLE) cell. The cell is ideally suited for UV–Vis and IR transmission spectroelectrochemical experiments at variable temperatures and allows the study of secondary reactions of the redox products. At T=223 K, the CO disproportionation reaction of the complexes containing the H2O ligand, decomposition of the tricarbonyl DBQ complexes, and even substitution of the axial CO ligand in [Mn(CO)3(PPh3)(DBSQ)] by PPh3 were fully inhibited. The UV–Vis spectra indicate that the observed thermal lability of the o-quinone complexes [Mn(CO)3(L)(DBQ)]+ (n=0, 1; L=H2O, PPh3) most likely originates from a considerably weaker π-acceptor character of the DBQ ligand in these species than imposed in the stable, delocalized complex [Mn(CO)3(PPh3)(DBQ)]+.

Keywords: Spectroelectrochemistry; Manganese carbonyls; Dioxolene complexes

1. Introduction

The chemistry of transition metal complexes with redox-active dioxolene ligands has expanded enormously during the last two decades and has produced a considerable number of structurally characterized compounds [1–3]. The suitability of the dioxolene complexes as model systems for many important biological electron transfer reactions has increased the interest in their redox behaviour. These complexes may exist in a variety of metal oxidation states and three oxidation states of the dioxolene ligand(s) (i.e. o-quinone (Q), o-semi-quinone (SQ = Q−) and catecholate (Cat = O2−)) linked together within a redox series. They often possess unique electronic and magnetic properties [1] which vary strongly with the oxidation state of dioxolene and directly reflect its bonding (i.e. donor/acceptor) properties. The bonding situation in most of the dioxolene complexes, their thermal, photo- and electrochemical reactivity and physicochemical properties may best be interpreted by using a qualitative 'localized-valence' model which has recently been introduced by Vlček, Jr. [4]; although, the number of charge-delocalized transition metal dioxolene complexes described up to now is also not negligible [1,4]. Apparently, the need to distinguish between these two cases requires the combined application of miscellaneous structural, spectroscopic and electrochemical methods. However, a reliable electronic description of the dioxolene bonding in the particular (in a majority of cases o-quinone) complexes of interest may become impossible at room temperature due to a pronounced thermal instability of these species.

As an example, the intriguing redox behaviour of the five-coordinated complex [Mn(CO)3(DBCat)]− (DBCat = 3,5-di-tert.butyl-catecholate anion) [5] has been studied by Hartl et al. [6–8] at room temperature
by a variety of (spectro)electrochemical methods. The anion can be reduced reversibly by 1e\(^-\) to give the metal-localized radical [Mn(CO)\(_3\)(DBCat)]\(^{2-}\), or oxidized in two successive ligand-localized 1e\(^-\) steps. The first oxidation to [Mn(CO)\(_3\)(DBSO)] is followed by a rapid uptake of a Lewis base L or CO giving rise to the formation of the thermally stable complexes [Mn(CO)\(_2\)(L)(DBSO)] or [Mn(CO)\(_4\)(DBSO)], respectively. The latter radical is only stable in a CO-saturated solution of a non-coordinating solvent.

More complicated is the oxidation of [Mn(CO)\(_3\)- (DBCat)]\(^-\) in Ar-saturated CH\(_2\)Cl\(_2\) [6]. This process induces a CO ligand disproportionation which affords [Mn(CO)\(_4\)(DBSO)]. At the same time, a small amount of an unstable foreign radical was detected by ESR spectroscopy at a similar g value which was tentatively assigned [6] to a second disproportionation product.

Related stable radicals [Mn(CO)\(_2\)(L)\(_x\)(DBSO)] (L=PPh\(_3\)) can be obtained by 1e\(^-\) oxidation of [Mn(CO)\(_3\)(DBCat)]\(^-\) in the presence of an excess of PPh\(_3\). This reaction competes with the formation of [Mn(CO)\(_3\)(PPh\(_3\))(DBSO)] and mainly precludes the UV-Vis characterization of the latter species [7].

The subsequent 1e\(^-\) oxidation of the radicals [Mn(CO)\(_{3-n}\) (L)\(_n\)(DBSO)] (n=0-2) is fully chemically reversible only for [Mn(CO)\(_2\)(L)(DBSO)] (L=PPh\(_3\), P(OR)\(_3\)) [2]. Contrary to this, the oxidation products [Mn(CO)\(_{3-n}\) (L)\(_n\)(DBQ)] \(^+\) (n=0, 1; L=THF, PPh\(_3\), pyridine) are generally chemically less stable at room temperature, and this has also prevented their reliable spectroscopic characterization so far [6,7].

As a main goal of this article, spectroelectrochemistry with a novel low-temperature optically transparent thin-layer electrochemical (LT OTTLE) cell has been employed as an indispensable technique to obtain IR and UV-Vis spectra of some of the unstable species listed above. The cations [Mn(CO)\(_2\)(L)(DBQ)]\(^+\) (L=H\(_2\)O, PPh\(_3\)) are the first spectroscopically characterized tricarbonyl \(\alpha\)-quinone complexes of Mn\(^{2+}\) reported in the literature. Their bonding properties are briefly discussed.

2. Experimental

2.1. Materials

Ferrocene (Fc; BDH) and PPh\(_3\) (Aldrich) were used as received. Bu\(_4\)N[Mn(CO)\(_3\)(DBCat)]·1/6C\(_6\)H\(_6\) was synthesized by a literature method [5]. [Cp\(_2\)Fe]PF\(_6\) (FcPF\(_6\)) was prepared by a similar procedure to that reported [9] for Fe[HgL], using a solution of NH\(_2\)PF\(_6\) instead of K\(_2[HgL]\) to precipitate a solution of ferricenium sulfate. The supporting electrolyte Bu\(_4\)NF(Ph) (Aldrich) was dried under vacuum at 80 °C for 12 h before use. Dichloromethane (CH\(_2\)Cl\(_2\)) and tetrahydrofuran (THF) were freshly distilled under an N\(_2\) atmosphere from P\(_2\)O\(_5\) and Na/benzophenone, respectively.

2.1.1. [Mn(CO)\(_2\)(PPh\(_3\))\(_2\)(DBQ)]PF\(_6\)

120 mg (0.2 mmol) of Bu\(_4\)N[Mn(CO)\(_3\)(DBCat)]·1/6C\(_6\)H\(_6\) and 131 mg (0.5 mmol) of PPh\(_3\) were dissolved under N\(_2\) in 20 ml of THF. The oxidation of the DBCat ligand was performed in situ with FcPF\(_6\) and followed with IR spectroscopy. The blue-violet oxidation product [Mn(CO)\(_3\)(THF)(DBSO)] underwent a fast successive substitution with two equivalents of PPh\(_3\) at 40 °C which gave rise to the formation of green [Mn(CO)\(_3\)(PPh\(_3\))(DBSO)]. The synthesis then continued with the oxidation of the latter radical by another portion of FcPF\(_6\) until deep blue-green [Mn(CO)\(_2\) (PPh\(_3\))\(_2\)(DBQ)]PF\(_6\) was completely formed. Hereafter, the solution was filtered from non-dissolved FcPF\(_6\) and reduced to 5 ml in volume by evaporation of the solvent under vacuum. Degasged hexane was then added to induce precipitation of the DBQ complex. The solid [Mn(CO)\(_2\)(PPh\(_3\))(DBQ)]PF\(_6\) was filtered out and washed several times with cold benzene to remove a small excess of PPh\(_3\). The yield was almost quantitative.

IR spectrum in nujol mull: two strong \(\nu(\text{C}=\text{O})\) bands at 2004 and 1944 cm\(^{-1}\), \(\nu(\text{C}=\text{O})\) of DBQ at 1599(\(w\)) cm\(^{-1}\). H NMR spectrum in CD\(_2\)Cl\(_2\) (ppm): \(\delta\) 1.13 (9H, CH\(_3\) of C\(_5\)-Bu\(_1\)), 1.23 (9H, CH\(_3\) of C\(_5\)-Bu\(_1\)), 6.07 (1H, d (\(J(\text{H},\text{H})=2\) Hz), H-C\(_4\)), 7.08 (1H, d (\(J(\text{H},\text{H})=2\) Hz), H-C\(_6\)), and a multiplet between 7.08 and 7.74 (20H), H-C\(_6\)). \(\delta\) 68.26 (two axial PPh\(_3\) ligands). C, H and P elemental analyses were consistent with the composition of [Mn(CO)\(_2\)(PPh\(_3\))(DBQ)]PF\(_6\).

2.1.2. [Mn(CO)\(_2\)(PPh\(_3\))\(_2\)(DBQ)]

This complex was generated in situ in a very pure form electrochemically by exhaustive 1e\(^-\) reduction of 10\(^{-2}\) M [Mn(CO)\(_2\)(PPh\(_3\))(DBQ)]PF\(_6\) in CH\(_2\)Cl\(_2\), or chemically by electron transfer reaction between 10\(^{-2}\) M [Mn(CO)\(_2\)(PPh\(_3\))(DBQ)]PF\(_6\) and 10\(^{-2}\) M Bu\(_4\)N[Mn(CO)\(_3\)(DBCat)] in THF/2×10\(^{-2}\) M PPh\(_3\). It has been found to decompose slowly upon irradiation with visible light [7].

IR spectrum (cm\(^{-1}\)) \(\nu(\text{C}=\text{O})\) at 1927(vs), 1850(s) (in THF). ESR and UV-Vis spectra: vide infra.

2.2. Spectroscopic measurements and instrumentation

FTIR spectra were measured on a Bio-Rad FTS-7 spectrometer (a thermostated DTGS detector, 16 scans, resolution of 2 cm\(^{-1}\)). Solvent bands were numerically subtracted. Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV-Vis spectrophotometer, equipped with a 3600 data station. Varian E4 and Bruker 300 X-band spectrometers with 100 kHz resolution were used for EPR and NMR measurements.

C, H, and P elemental analyses were consistent with the composition of [Mn(CO)\(_2\)(PPh\(_3\))(DBQ)]PF\(_6\).
modulation were used to measure ESR spectra. 2,2-Di-phenyl-1-picrylhydrazyl (DPPH, Aldrich) was employed as a standard \((g = 2.0037 \pm 0.0002)\) for the determination of \(g\) values. \(^1H\) and \(^31P\) NMR spectra were recorded on a Bruker AMX 300 spectrometer at 293 K.

Controlled-potential electrolyses within the LT OT-TLE cell \([10]\) were carried out using a model PA4 polarographic analyzer (EKOM, Czech republic) or a PAR model 173 potentiostat equipped with \(x-y\) recorders. For all spectroelectrochemical experiments, \(3 \times 10^{-3} \text{M } \text{Bu}_4\text{NPF}_6\) as supporting electrolyte and \(5 \times 10^{-3} \text{M } [\text{Mn(CO)}_3(\text{DBCat})^-]\) were used. Each spectroelectrochemical experiment began with recording the thin-layer cyclic voltammogram of \([\text{Mn(CO)}_3(\text{DBCat})^-]\) until the anodic peak of the one-electron oxidation of the complex was passed. At the end of the first oxidation step, indicated both spectroscopically and by zero anodic current, the potential of the working electrode was shifted more positively to monitor the second anodic step. All potentials are reported with respect to that of the standard ferrocene/ferrocenium (Fc/Fc\(^+\)) redox couple \([11]\).

3. Results

IR spectra of the oxidation products were investigated in the CO-stretching region. The \(\nu(\text{CO})\) frequencies and UV–Vis data are summarized in Table 1. The relative intensities of the \(\nu(\text{CO})\) bands for each carbonyl complex are given in the text in brackets.

### 3.1. Oxidation of \([\text{Mn(CO)}_3(\text{DBCat})^-]\) in \(\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}\)

The anion \([\text{Mn(CO)}_3(\text{DBCat})^-]\) was oxidized in \(\text{N}_2\)-saturated \(\text{CH}_2\text{Cl}_2\) at \(E_{1/2} = -0.48 \text{ V versus } \text{Fc/Fc}^+\) to the corresponding short-lived radical \([\text{Mn(CO)}_2(\text{DBSQ})^-]\) detectable only by cyclic voltammetry \((I_p, c/I_p, a \approx 0.5\) at room temperature and \(v = 100 \text{ mV } \text{s}^{-1}\)) \([6]\). When the oxidation was performed chemically by \(\text{FcPF}_6\) in very dry dichloromethane at \(T = 295 \text{ K}\), the only radical detected by ESR spectroscopy was \([\text{Mn(CO)}_4(\text{DBSQ})]\) (sextet of doublets, \(\alpha_{\text{Mn}} = 0.70 \text{ mT}, \alpha_{\text{H}} = 0.33 \text{ mT}, g = 2.0033\); Fig. 1(A)). The intensity of the ESR signal decayed slowly with time due to the thermal lability of the radical. However, when the oxidation of \([\text{Mn(CO)}_3(\text{DBCat})^-]\) by \(\text{FcPF}_6\) was carried out at \(T = 295 \text{ K}\) in \(\text{CH}_2\text{Cl}_2\), containing some water, a second radical product was observed by ESR spectroscopy (Fig. 1(B)). This radical also decomposed, but faster than \([\text{Mn(CO)}_4(\text{DBSQ})]\). Its structure became clear when \([\text{Mn(CO)}_3(\text{DBCat})^-]\) was oxidized with \(\text{Fc}^-\) at \(T = 230 \text{ K}\) in an Allendoerfer-type ESR spectroelectrochemical cell \([12]\). The \(\text{CH}_2\text{Cl}_2\) solution then contained only the second radical which did not further decompose. The ESR spectrum of the radical occurred at \(g = 2.0045\) as a sextet of doublets of triplets \((1:2:1)\) due to the hyperfine

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{max}}^\text{a} (\text{nm}))</th>
<th>(\nu(\text{CO})^\text{c})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mn(CO)}_3(\text{DBCat})^-])</td>
<td>430 (5600), 532 (8300) ((\text{broad})^{d})</td>
<td>2000, 1891</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{H}_2\text{O})(\text{DBSQ})^-])</td>
<td>520 (2700), 693 (1500) ((\text{sh})^{d})</td>
<td>2029, 1925</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{THF})(\text{DBSQ})^-])</td>
<td>524 (2370), 708 (1650) ((\text{broad})^{a})</td>
<td>2022.5, 1944.5, 1908</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBSQ})^-])</td>
<td>580 (sh), 665 (5400) ((\text{sh})^{d})</td>
<td>1935, 1859</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{THF})(\text{DBQ})^-])</td>
<td>654 (sh), 854 (3900) ((\text{broad})^{b})</td>
<td>2127, 2061, 2037, 2000</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBQ})^-])</td>
<td>792 (5600) ((\text{broad})^{d})</td>
<td>2055.5, 2013, 1981</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_2(\text{DBQ})^-])</td>
<td>688 (16000) ((\text{broad})^{d})</td>
<td>2050, 1980</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBQ})^-])</td>
<td>610 (6800) ((\text{broad})^{d})</td>
<td>2055.5, 2013, 1981</td>
</tr>
</tbody>
</table>

\(^{a}\) In nm.  
\(^{b}\) Molar absorption coefficient, \(M^{-1} \text{ cm}^{-1}\).  
\(^{c}\) In cm\(^{-1}\).  
\(^{d}\) In \(\text{CH}_2\text{Cl}_2\), 220–230 K.  
\(^{e}\) In \(\text{CH}_2\text{Cl}_2\), 293 K.  
\(^{f}\) In \(\text{CH}_2\text{Cl}_2\), 266 K.  
\(^{g}\) Ref. \([7]\).  
\(^{h}\) In \(\text{THF}, 293 \text{ K}\).  
\(^{i}\) In CO-saturated solution.
splitting of $^{55}$Mn ($I=5/2$), $^{1}$H at the C4 position of the DBSQ ligand [13] ($I=1/2$) and two equivalent $^{1}$H nuclei of coordinated H$_{2}$O, respectively: $a_{\text{Mn}}=0.71$ mT, $a_{\text{HDBSQ}}=0.56$ mT, $a_{\text{H}_{2}O}=0.28$ mT (Fig. 1(C)). These parameters clearly point to the formation of [Mn(CO)$_{3}$(H$_{2}$O)(DBSQ)]. The rather large value of $a_{\text{H}_{2}O}$ indicates a relatively high spin density on the hydrogen atoms. Such an interpretation points to a direct interaction between coordinated H$_{2}$O and the DBSQ radical ligand via formation of two equivalent hydrogen bonds O-H⋯O-C.

Application of the LT OTTLE cell

$T=293$ K. The ESR spectroelectrochemical results have been confirmed by IR spectra of the oxidized solution of [Mn(CO)$_{4}$(DBCat)]$^{-}$. In dry CH$_{2}$Cl$_{2}$, the spectra only showed the characteristic [6] $\nu$(CO) bands of [Mn(CO)$_{4}$(DBSO)] at 2105(w), 2029(s), 2004(m) and 1960(m) cm$^{-1}$.

$T=223$ K. Spectral changes accompanying the 1e$^{-}$ oxidation of [Mn(CO)$_{3}$(DBCat)]$^{-}$ in CH$_{2}$Cl$_{2}$/H$_{2}$O/0.3 M Bu$_{4}$NPF$_{6}$ within the LT OTTLE cell at $T=223$ K. (B) Disproportionation of the product [Mn(CO)$_{3}$(H$_{2}$O)(DBSO)] to [Mn(CO)$_{4}$(DBSO)] upon elevation of temperature from 223 to 273 K. (C) Oxidation of [Mn(CO)$_{3}$(H$_{2}$O)(DBSO)] to [Mn(CO)$_{4}$(H$_{2}$O)(DBSO)]$^{+}$ under the same conditions as given in (A).

The $\nu$(CO) bands of the parent complex at 2000(s) and 1891(s,broad) cm$^{-1}$ were replaced isosbesticly by bands at 2029(s) and 1925(s,broad) cm$^{-1}$. In accordance with the ESR results, these bands are assigned to [Mn(CO)$_{3}$(H$_{2}$O)(DBSO)]. Importantly, no [Mn(CO)$_{4}$(DBSO)] was detected in the solution at this temperature. However, when the temperature of the thin solution layer was raised from 223 to 280 K, whilst keeping the applied oxidation potential constant, [Mn(CO)$_{3}$(H$_{2}$O)(DBSO)] was smoothly converted into [Mn(CO)$_{3}$(DBSO)]$^{+}$ with retention of the isosbestic points (Fig. 2(B)). Apparently, the CO disproportionation reaction is dramatically slowed down or even completely suppressed at low temperatures which enables the coordination of the weakly bonded H$_{2}$O ligand. Unfortunately, the measured IR OTTLE spectra provided no evidence for this coordination, probably due to the low intensity of the $\nu$(O-H) bands. The only evidence thus comes from the LT ESR OTTLE experiments (vide supra). At $T=223$ K [Mn(CO)$_{3}$(DBCat)]$^{-}$, with a concentration as high as 10$^{-2}$ M, was completely converted into [Mn(CO)$_{3}$(H$_{2}$O) (DBSO)]. This observation is not surprising taking into account the fact that even quite dry CH$_{2}$Cl$_{2}$ may still be 10$^{-3}$ M in water [14]. In our case, the concentration of water was at least of an order of magnitude higher.

Since the 1e$^{-}$ oxidation of [Mn(CO)$_{3}$(DBCat)]$^{-}$ and the thermal reaction of [Mn(CO)$_{3}$(H$_{2}$O)(DBSO)] proceeded in N$_{2}$-saturated CH$_{2}$Cl$_{2}$ (vide supra), the formation of the tetracarbonyl product, [Mn(CO)$_{4}$(DBSO)]$^{-}$...
Fig. 3. UV-Vis spectral changes due to formation of [Mn(CO)₃(H₂O)(DBSQ)] (A) and [Mn(CO)₃(H₂O)(DBQ)]⁺ (B) measured during successive oxidation of [Mn(CO)₃(DBCat)]⁻ under identical conditions to those given in Fig. 2.

Of the two tricarbonyl complexes, out of both may decompose to give free CO and DBQ, which is concomitantly oxidized to free DBQ at the applied potential of the [Mn(CO)₃(DBCat)]⁻ oxidation. In fact, Sawyer and co-workers described [15] a similar decomposition of an Mn(DBSQ) complex generated by oxidation of [Mn(DBCat)]⁻. In that case, solvated Mn⁺ and free DBQ were formed as products. The above described mechanism of the [Mn(CO)₃(DBSQ)] disproportionation might also involve oxidation of Mn¹ to Mn²⁺ by free DBQ and formation of the tetrameric complex [Mn⁴⁺(DBSQ)₄] [16]. This product was indeed detected in the CH₂Cl₂ solution at room temperature after a thermal decomposition of [Mn(CO)₄(DBSQ)] had taken place.

The UV-Vis spectrum of [Mn(CO)₃(H₂O)(DBSQ)] exhibits, at T = 223 K, two absorption bands in the visible region, at λₘₐₓ = 520 (εₘₐₓ = 2700 M⁻¹ cm⁻¹) and 693 (εₘₐₓ = 1500 M⁻¹ cm⁻¹) nm (Fig. 3(A)). It is noteworthy that this spectrum strongly resembles [7] that of the more stable complex [Mn(CO)₃(THF)(DBSQ)] in THF at T = 295 K (λₘₐₓ = 524 (εₘₐₓ = 2370 M⁻¹ cm⁻¹) and 708 (εₘₐₓ = 1650 M⁻¹ cm⁻¹) nm). A similar close correspondence exists between the ν(CO) frequencies of the complexes [8,17]. This striking similarity in the positions and intensities of the absorption bands implies that the radicals [Mn(CO)₃(L)(DBSQ)] (L = H₂O, THF) may better be considered as an Mn(CO)₃(DBSQ) moiety with a loosely bound O-donor ligand the presence of which does not affect the absorption properties of the Mn(DBSQ) chromophore and the extent of the Mn to CO π-backbonding. On the other hand, both radicals differ very much in their ESR spectra, particularly in the value of aₘₑ (0.70 mT for L = H₂O, 0.37 mT for L = THF) and additional hyperfine splitting due to ¹H nuclei of the H₂O ligand (vide supra).

The radical [Mn(CO)₃(H₂O)(DBSQ)] was smoothly oxidized in the next 1e⁻ step to a novel cationic complex [Mn(CO)₃(H₂O)(DBQ)]⁺ (ν(CO) bands at 2050(s) and 1980(m, broad) cm⁻¹, see Fig. 2(C)) which could be observed at T = 223 K for more than one hour without any apparent decrease in concentration. The UV-Vis spectrum of [Mn(CO)₃(H₂O)(DBQ)]⁺ (Fig. 3(B)) shows an intense absorption band at λₘₐₓ = 792 nm (εₘₐₓ = 5600 M⁻¹ cm⁻¹). Its assignment will be discussed later. This cation also underwent a CO disproportionation at T = 273 K but the product [Mn(CO)₄(DBQ)]⁺ (ν(CO) at 2125(m), 2062(s), 2037(m) and 2000(m) cm⁻¹) readily decomposed.

3.2. Oxidation of [Mn(CO)₃(DBCat)]⁻ in CH₂Cl₂/PPh₃

The radical complex [Mn(CO)₃(PPh₃)(DBSQ)] has been characterized so far only by IR [17] and ESR [18] spectroscopy (in the latter case with the symmetric
3,6-DBSQ ligand). Its UV–Vis spectrum, which might provide valuable information about the bonding properties of the complexes \([\text{Mn(CO)}_3(L)(\text{DBSQ})]\), has not yet been recorded owing to difficulties with the synthesis of this radical species in its pure form. The usual preparative route utilizes the photochemical formation of \([\text{Mn(CO)}_4(\text{DBSQ})]\) from \([\text{Mn}_2(\text{CO})_{10}]\) and o-DBQ, followed by rapid coordination of PPh3. However, this procedure seems to be convenient only for collection of the ESR and IR spectra of \([\text{Mn(CO)}_4(\text{DBSQ})]\) due to the thermal and photochemical lability of the \([\text{Mn(CO)}_4(\text{DBSQ})]\) intermediate which is known \([16]\) to yield an ESR-silent green tetramer \([\text{Mn}_4(\text{DBSQ})_4]\). Moreover, \([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBSQ})]\) itself undergoes a facile thermal substitution of the axial CO ligand by another PPh3 molecule (vide infra) forming ultimately the stable product \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBSQ})]\). In contrast, the analogous complexes \([\text{Re(CO)}_3(\text{PR}_3)(\text{DBSQ})]\) are thermally stable under the same conditions and can only be converted into \([\text{Re(CO)}_2(\text{PR}_3)_2(\text{DBSQ})]\) (with 100% yield) by irradiation into their visible absorption band(s) \([19]\).

Alternatively, \([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBSQ})]\) may be generated in situ by oxidation of \([\text{Mn(CO)}_3(\text{DBCat})^{-}]\) with FcPF6 in THF and subsequent addition of an equivalent amount of PPh3 into the resulting solution of the relatively stable complex \([\text{Mn(CO)}_3(\text{THF})(\text{DBSQ})]\). However, this substitution of THF by PPh3 requires at least a small excess of PPh3 for its completion which further initiates the undesired formation of \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBSQ})]\). Solid evidence for this statement has been obtained from ESR spectroelectrochemistry at room temperature. In situ oxidation of \([\text{Mn(CO)}_3(\text{DBCat})^{-}]\) by ferrocenium was performed in CH2Cl2 in a vacuum-tight ESR tube, initially in the presence of a twofold excess of PPh3. The recorded ESR spectra revealed instantaneous generation of the radicals \([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBSQ})]\) \((g=2.0029, a_{\text{MN}}=1.00 \, \text{mT}, a_{\text{HH}}=0.32 \, \text{mT}, a_{\text{PH}}=3.35 \, \text{mT})\) and \([\text{Mn(CO)}_3(\text{PPh}_3)_2(\text{DBSQ})]\) \((g=2.0022, a_{\text{MN}}=1.79 \, \text{mT}, a_{\text{HH}}=0.32 \, \text{mT}, a_{\text{PH}}=3.94 \, \text{mT})\) in about equal steady state concentrations. When the experiment was repeated with exactly one equivalent of PPh3, the ESR spectrum showed the presence of \([\text{Mn(CO)}_3(\text{DBSQ})]\) which reacted further, but not completely, to give \([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBSQ})]\). Importantly, a small amount of \([\text{Mn(CO)}_3(\text{PPh}_3)_2(\text{DBSQ})]\) was then detected in the solution.

**Cyclic voltammetry at variable temperatures**

The only route which led to the facile generation of pure \([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBSQ})]\) was electrochemical oxidation of \(10^{-3} \, \text{M} \left[\text{Mn(CO)}_3(\text{DBCat})^{-}\right]\) in CH2Cl2/10^{-2} \, \text{M} \, \text{PPh}_3 \, \text{at} \, T=218 \, \text{K}. \) The cyclic voltammogram of this solution (Fig. 4(A)) exhibited only two anodic peaks at \(E_{p, a}=-0.940 \) and +0.075 V (versus Fc/Fc+).

The first, more negative one-electron oxidation was chemically reversible \((I_{p, c}/I_{p, a}=1 \text{ at } v=100 \, \text{mV s}^{-1})\) and electrochemically quasireversible \((\Delta E_p=180 \, \text{mV versus } 110 \, \text{mV of the Fc/Fc+ redox couple})\). It has been assigned by analogy with the oxidation of \([\text{Mn(CO)}_3(\text{DBCat})^{-}]\) in THF \([6]\) to the \([\left[\text{Mn(CO)}_3(\text{DBCat})^{-} \cdot \cdot \cdot \text{PPh}_3\right]^{-}/[\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBSQ})]\) couple. The successive one-electron oxidation of \([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBQ})]\) to \([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBQ})]^+ \text{ at } +0.075 \, \text{V was found to be both chemically and electrochemically } (\Delta E_p=110 \, \text{mV})\) reversible.

Upon warming up the solution to room temperature, the cyclic voltammogram became more complex (Fig. 4(B)) owing to the lability of \([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBQ})]\) \(\text{generated at } E_{p, a}=-0.975 \, \text{V (chemically partly reversible process A, } I_{p, c}/I_{p, a}<1; \Delta E_p=110 \, \text{mV versus } 70 \, \text{mV of Fc/Fc+}). \)

During the anodic scan, this complex partly reacted to \([\text{Mn(CO)}_3(\text{PPh}_3)_2(\text{DBSO})]\) which was further oxidized to \([\text{Mn(CO)}_3(\text{PPh}_3)_2(\text{DBQ})^+] \text{ at } E_{p, a}=-0.50 \, \text{V (process B, } \Delta E_p=80 \, \text{mV). The third anodic step in the cyclic voltammogram at } +0.075 \, \text{V (process C, } \Delta E_p=80 \, \text{mV) then corresponds to the } 1e^- \text{ oxidation of remaining } [\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBQ})]. \text{ The cathodic peak D, observed on the reverse scan at } E_{p, c}=-1.26 \, \text{V, obviously belongs to the } 1e^- \text{ reduction of
[Mn(CO)2(PPh3)2(DBQ)]. The accuracy of this assignment was proved by comparison with a cyclic voltammogram of an authentic sample of [Mn(CO)2(PPh3)2(DBQ)]⁺ (Fig. 4(C)) which afforded two one-electron reductions at $E_p = -0.42$ V ($\Delta E_p = 80$ mV, $I_p / I_p,_{\text{red}} = 1$) and $-1.26$ V ($I_p,_{\text{red}} / I_p,_{\text{ox}} < 0.5$). In the first (most positive) step, [Mn(CO)2(PPh3)2(DBQ)]⁺ was converted into [Mn(CO)2(PPh3)2(DBSQ)] which was further reduced to give the corresponding DBCat complex. The chemical irreversibility of the second reduction was ascribed to a fast follow-up conversion of [Mn(CO)2(PPh3)2(DBCat)]⁻ into [Mn(CO)3(DBCat)][PPh3]⁻. For the anodic peak of the final reduction product, [Mn(CO)3(DBCat)][PPh3]⁻, appeared on the reversed potential scan at $E_{p,\text{a}} = -0.975$ V. The reasons for the observed thermal lability of [Mn(CO)2(PPh3)2(DBCat)]⁻ will be discussed in a forthcoming article.

Application of the LT OTTLE cell

$T = 223$ K. In summary, the CV experiments outlined above have revealed that [Mn(CO)3(PPh3)(DBSQ)] is thermally stable at 218 K with respect to substitution of the axial [7,18] CO ligand by PPh3. This observation has been confirmed by IR OTTLE experiments performed at variable temperatures. When $5 \times 10^{-3}$ M [Mn(CO)3(DBCat)]⁻ was stepwise oxidized with 1e⁻ in the presence of a tenfold excess of PPh3 at $T = 223$ K, the CH2Cl2 solution contained only the radical product [Mn(CO)3(PPh3)(DBSQ)]. Its ν(CO) modes were only slightly shifted to lower frequencies in comparison with those at $T = 293$ K: 2022.5(s), 1944.5(m) and 1908(m) cm⁻¹. Importantly, neither substitution of CO by PPh3 took place nor was there any indication of a decomposition in the course of the electrolysis. Consequently, [Mn(CO)3(PPh3)(DBSQ)] could be converted in the second 1e⁻ oxidation step into the cation [Mn(CO)3(PPh3)(DBQ)]⁺ with ν(CO) vibrations at 2054(s), 2007(m) and 1976.5(m) cm⁻¹ (Fig. 5). The complete chemical reversibility of this reaction was also verified by the maintenance of strict isosbestic points in the successive IR spectra and full reappearance of the original spectrum of [Mn(CO)3(PPh3)(DBSQ)] by application of an appropriate back-reduction potential.

The electronic absorption spectrum of [Mn(CO)3(PPh3)(DBSQ)] was collected in CH2Cl2 at $T = 223$ K directly after the spectroelectrochemical 1e⁻ oxidation of [Mn(CO)3(DBCat)]⁻ had taken place. The end of the electrolysis was unambiguously determined by parallel IR OTTLE control. The spectrum of [Mn(CO)3(PPh3)(DBSQ)] exhibits the characteristic MLCT band at $\lambda_{\text{max}} = 665$ nm ($\epsilon_{\text{max}} = 5400$ M⁻¹ cm⁻¹), together with a shoulder at $\sim 580$ nm (Fig. 6). It is noteworthy that the corresponding MLCT band of the substituted complex, [Mn(CO)3(PPh3)2(DBSQ)], is strongly red-shifted with respect to [Mn(CO)3-

![Fig. 5. IR spectral changes in the ν(CO) region accompanying 1e⁻ oxidation of [Mn(CO)3(PPh3)(DBSQ)] in CH2Cl2/0.3 M Bu4NPF6 within the LT OTTLE cell at T=223 K.](image)

![Fig. 6. Electrochemical oxidation of [Mn(CO)3(PPh3)(DBSQ)] to [Mn(CO)3(PPh3)(DBQ)]⁺ within the LT OTTLE cell monitored by UV-Vis spectroscopy. The experimental conditions correspond to Fig. 5.](image)
a shoulder at ~361 nm. The assignment of the lowest energy band will be discussed in the next section.

\[ T = 293 \text{ K} \] at \[ T = 293 \text{ K} \], the \( 1e^- \) oxidation of \( 5 \times 10^{-3} \) M \([\text{Mn(CO)}_2(\text{DBCat})]^- \) in \( \text{CH}_2\text{Cl}_2/0.05 \text{ M PPh}_3 \) led directly oxidized within 40 s to \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]^{+} \) (\( \nu(\text{CO}) \) at 2003(s) and 1943(m) cm\(^{-1}\)). Finally, the remaining \([\text{Mn(CO)}_2(\text{PPh}_3)(\text{DBQ})]^{+} \) was oxidized. It is noteworthy that this \( 1e^- \) anodic step mainly gave rise again to \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]^{+} \). The primary oxidation product, \([\text{Mn(CO)}_2(\text{PPh}_3)(\text{DBQ})]^{+} \) (\( \nu(\text{CO}) \) at r.t.: \( 2055.5 \text{ (vs)} \), 2013(m) and 1981(m) cm\(^{-1}\)), was then found only at very low concentration.

In a potential-step experiment at \( T = 293 \text{ K} \), \( 5 \times 10^{-3} \) M \([\text{Mn(CO)}_2(\text{DBCat})]^- \) in \( \text{CH}_2\text{Cl}_2/\text{PPh}_3 \) was directly oxidized within 40 s to \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]^{+} \). During an additional 5 min, only a negligible amount of \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]^{+} \) was formed. Instead, \([\text{Mn(CO)}_2(\text{PPh}_3)(\text{DBQ})]^{+} \) persisted in the solution, having undergone only a slow decomposition of ~7% of the initial amount to an unidentified product. This would imply that \([\text{Mn(CO)}_2(\text{PPh}_3)(\text{DBQ})]^{+} \) is surprisingly more resistant towards the attack of \( \text{PPh}_3 \) than \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]^{+} \) under identical conditions. It is noted that the stability of \([\text{Mn(CO)}_2(\text{PPh}_3)(\text{DBQ})]^{+} \) strongly decreases in \( \text{THF} \). In this solvent the \( 1e^- \) oxidation of \([\text{Mn(CO)}_2(\text{PPh}_3)(\text{DBQ})]^{+} \) led at room temperature to a very fast decarbonylation which may result from substitution of the DBQ ligand by solvent molecules.

4. Discussion

Application of the LT OTTLE technique allowed us to record, for the first time, the UV-Vis and IR spectra of several tricarbonyl DBSQ and DBQ complexes of \( \text{Mn}^1 \) which possess a limited stability at room temperature towards decarbonylation and/or substitution of axial ligands. This is particularly true for the DBQ complexes which have so far been characterized spectroscopically [7] only in the case of the thermally stable \([\text{Mn(CO)}_2(L)_2(\text{DBQ})]^{+} \), where \( L = \text{PR}_3 \) or \( \text{P(OR)}_3 \).

The complexes \([\text{Mn(CO)}_2(L)_2(\text{DBQ})]^{+} \) have been recognized [4,7] to belong to delocalized Robin-Day class III mixed valence compounds [20]. It is noteworthy that this assignment is also valid for all as yet described stable \( o- \)-quinone complexes of \( d^6 \) metals [21]: \([\text{Re(CO)}_2(L)_2(\text{DBQ})]^{+} \), \([\text{Ru(bpy)}_2(\text{BO})]^{2+} \) (\( \text{BO} = \text{o-benzoquinone} \) and \([\text{Ru(bpy)}_2(\mu-O-Q)]^{2+} \) (\( O-Q = 3,3',4,4'-\text{teta-oxo-biphenyl} \)). These species possess very strong mixing between the metal \( d \) and dioxolene \( \pi^* \) frontier orbitals so that it is virtually impossible to distinguish between the resonance structures \( M^{+} = O \) and \( M^{(n+1)+} = \text{SO} \) [4]. The \( \pi^*_{\text{M-O}} \) HOMO and \( \pi^*_{\text{M-O}} \) LUMO of the complexes may be then looked upon as (nearly) completely delocalized on the metal–dioxolene unit. Hence, the \( \pi^*_{\text{M-O}} \to \pi^*_{\text{M-O}} \) electronic transition will have (almost) no charge transfer character as the electron in both the ground and excited states is equally localized on the metal and the \( O \) ligand. Furthermore, the corresponding absorption band is always very intense (\( \epsilon_{\text{max}} = 6000-40000 \text{ M}^{-1} \text{ cm}^{-1} \)) for all the above-mentioned stable delocalized \( o- \)-quinone complexes. At the same time, the \( \pi^*_{\text{M-O}} \to \pi^*_{\text{M-O}} \) transition has been found in all cases at considerably higher energy in comparison with the MLCT (\( d_u(M) \to \pi^* \text{(dioxolene)} \)) transition in the analogous \( o- \)-semiquinone complexes [21]: \( \Delta E_{\text{max}} \sim 5200-3000 \text{ cm}^{-1} \). This phenomenon was interpreted [7] to indicate a large energy gap between the \( \pi^*_{\text{M-O}} \) HOMO and \( \pi^*_{\text{M-O}} \) LUMO due to a much stronger \( \pi \)–interaction between the metal and the strong \( \pi \)-acceptor \( o- \)-quinone ligand than between the metal and the weak \( \pi \)-acceptor \( o- \)-semiquinone ligand. Alternatively, the relatively high excitation energy of the \( \pi^*_{\text{M-O}} \to \pi^*_{\text{M-O}} \) transition in the delocalized \( o- \)-quinone complexes may arise from a high reorganization energy ascribed to a distortion of the \( O \) ligand itself upon excitation. Direct evidence for this distortion has been obtained [7,19,22] from resonance Raman spectra of \([\text{Mn(CO)}_2(\text{P}(\text{OE})_3)_2(\text{DBQ})]^{+} \), \([\text{Re(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]^{+} \) and \([\text{Ru(bpy)}_2(\text{BO})]^{2+} \), respectively, which show large intensities for skeletal metal–\( O \) modes coupled to \( Q \)-ring deformation modes. Large resonance enhancement for this type of vibration is indeed a characteristic feature for transition metal complexes with strongly delocalized \( \pi \)-bonding between the metal and non-innocent ligands like \( \alpha \)-diamines [23,24] and quinone diimines [25,26].

The above results indicate that the thermal stability of the metal–\( Q \) complexes increases with stronger \( M \to Q \) \( \pi \)-backbonding. The studied Mn–DBQ complexes seem to fit in well with this trend. The most stable DBQ complex in the series, \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]^{+} \), exhibits the absorption band of the \( \pi^*_{\text{M-DBQ}} \to \pi^*_{\text{M-DBQ}} \) transition at \( \lambda_{\text{max}} = 610 \text{ nm} \), whereas the MLCT (\( d_u(M) \to \pi^* \text{(DBSQ)} \)) band of \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]^{+} \) occurs at \( \lambda_{\text{max}} = 854 \text{ nm} \) (in \( \text{THF} \)). The excitation energy for the DBQ species is therefore ~4680 cm\(^{-1} \) higher than for the DBSQ complex. This observation is again in contradiction with simple MO expectations that the \( \pi^* \) LUMO of DBQ will be at lower energy than the \( \pi^* \) SOMO of the DBSQ ligand [4]. It means that \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]^{+} \) can also be treated as a compound with strongly delocalized Mn–DBQ \( \pi \)-bonding due to the strong \( \pi \)-acceptor ability of the DBQ ligand. The resonance Raman spectrum
of [Mn(CO)3(PPh3)2(DBQ)]+ is also in line with this explanation.

For the related complex [Mn(CO)3(PPh3)(DBQ)]+, the \( \pi_{\text{Mn-DBQ}} \rightarrow \pi^*_{\text{Mn-DBQ}} \) transition has been found at slightly lower energy than the MLCT (\( d_\text{Mn}(\pi) \rightarrow \pi^*_{\text{DBSQ}} \)) transition in the reduced radical [Mn(CO)3(PH3)2(DBSQ)]: \( \lambda_{\text{max}} = 688 \) and 665 nm, respectively, i.e. \( \Delta E_{\text{max}} = -502 \) cm\(^{-1}\). This information provides evidence for a somewhat weaker stabilizing \( \pi \) interaction between Mn and DBQ in [Mn(CO)3(PPh3)(DBQ)]+ than in the thermally stable dicarbonyl derivative. This statement appears to be supported by the observed decomposition of the former compound at 293 K which is faster in coordinating solvents (vide supra). The UV–Vis spectrum of the least stable DBQ complex studied, [Mn(CO)3(H2O)(DBQ)]+ (see Fig. 3(B)), shows the presence of an intense absorption band at \( \lambda_{\text{max}} = 792 \) nm whereas the MLCT (\( d_{\text{Mn}}(\pi) \rightarrow \pi^*_{\text{DBSQ}} \)) absorption band of [Mn(CO)3(H2O)-DBQ] has been found at considerably higher energy: \( \lambda_{\text{max}} = 520 \) nm, i.e. \( \Delta E_{\text{max}} = -6604 \) cm\(^{-1}\) in this case! The relatively low excitation energy for [Mn(CO)3(H2O)(DBQ)]+ may again reflect the rather weak stabilizing Mn→DBQ \( \pi \)-backdonation in this case. This conclusion is fully in accord with the observed fast decomposition of the complex at room temperature and can probably also explain the short lifetime for [Mn(CO)3(DBQ)]+ (vide supra).

This explanation would also imply that the HOMO and the LUMO of the cation [Mn(CO)3(H2O)(DBQ)]+ will be more metal and DBQ localized, respectively. Hence, the lowest energy electronic transition is expected to have only weakly perturbed Mn→DBQ CT character and the complex should then be treated as a ‘localized valence’ compound [4]. The more stable complex [Mn(CO)3(PPh3)(DBQ)]+ may then be viewed as a weakly coupled mixed valence compound [4]. Unfortunately, attempts to prove the character of the lowest energy electronic transition of the latter species by resonance Raman spectroelectrochemistry at suitably low temperatures (vide supra) failed since no Raman bands belonging to the complex were recorded upon 620 nm excitation into the corresponding absorption band. The absence of the resonance Raman effect cannot be ascribed to the rather low (10\(^{-2}\) M) concentration of the electrogenerated product in the thin solution layer (\( l = 0.2 \) mm) as the resonance Raman spectrum of the parent complex [Mn(CO)3(DBCat)]3- [7] was easily recorded using the LT OTTLE cell under comparable conditions (temperature, laser power, concentration, absorbance at the excitation wavelength). This observation is also in sharp contrast with the resonance Raman spectra of the related derivative [Mn(CO)3(P(OEt)3)2(DBQ)]+ obtained straightforwardly [7] in the RT OTTLE cell [8] for a 10\(^{-2}\) M concentration of the complex. Apparently, additional low-temperature resonance Raman studies on the thermally labile o-quinone complexes need to be performed, to see whether the \( \pi \)-bonding in these compounds is indeed less delocalized than, for example, in [M(CO)2(PR3)2(DBQ)]+ (\( M = \text{Mn, Re} \)) [7,19], as indicated by their UV–Vis spectra.

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