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Hartl, F.

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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

F. Hartl
Anorganisch Chemisches Laboratorium, J.H. van't Hoff Research Instituut, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, Netherlands

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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 ortho-semiquinone 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 ortho-quinone complexes [Mn(CO)3(L)(DBQ)]+ (n=0, 1; L=H2O, PPh3) most likely originates from a considerably weaker r-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-semiquinone (SQ = Q-) and catecholate (Cat = o-)) 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 \([\text{Mn(CO)}_3(\text{DBCAt})]^2-\), or oxidized in two successive ligand-localized 1e\(^-\) steps. The first oxidation to \([\text{Mn(CO)}_3(\text{DBSQ})]\) is followed by a rapid uptake of a Lewis base \(L\) or \(CO\) giving rise to the formation of the thermally stable complexes \([\text{Mn(CO)}_3(L)(\text{DBSQ})]\) or \([\text{Mn(CO)}_4(\text{DBSQ})]\), respectively. The latter radical is only stable in a CO-saturated solution of a non-coordinating solvent.

More complicated is the oxidation of \([\text{Mn(CO)}_3-(\text{DBCAt})]^2-\) in Ar-saturated \(\text{CH}_2\text{Cl}_2\) [6]. This process induces a CO ligand disproportionation which affords \([\text{Mn(CO)}_4(\text{DBSQ})]\). 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 \([\text{Mn(CO)}_2(\text{L})(\text{DBSQ})]\) \((L=\text{PPh}_3)\) can be obtained by 1e\(^-\) oxidation of \([\text{Mn(CO)}_3(\text{DBCAt})]^2-\) in the presence of an excess of \(\text{PPh}_3\). This reaction competes with the formation of \([\text{Mn(CO)}_3(\text{PR}_3)(\text{DBSQ})]\) and mainly precludes the UV-Vis characterization of the latter species [7].

The subsequent 1e\(^-\) oxidation of the radicals \([\text{Mn(CO)}_3(L)(\text{DBQ})]^2-\) \((n=0-2)\) is fully chemically reversible only for \([\text{Mn(CO)}_3(L)(\text{DBSQ})]\) \((L=\text{PR}_3,\text{P}(<\text{OR}>_3))\) [2]. Contrary to this, the oxidation products \([\text{Mn(CO)}_3(L)(\text{DBSQ})]^2-\) \((n=0,1; L=\text{THF},\text{PPh}_3,\text{pyridine})\) 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 \([\text{Mn(CO)}_3(L)(\text{DBQ})]^2+\) \((L=\text{H}_2\text{O},\text{PPh}_3)\) are the first spectroscopically characterized tricarbonyl \(\alpha\)-quinone complexes of \(\text{Mn}^3\) reported in the literature. Their bonding properties are briefly discussed.

2. Experimental

2.1. Materials

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

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

120 mg (0.2 mmol) of \(\text{Bu}_4\text{N}[\text{Mn(CO)}_3(\text{DBCAt})]\) \(1/6\text{C}_6\text{H}_6\) and 131 mg (0.5 mmol) of \(\text{PPh}_3\) were dissolved under \(\text{N}_2\) in 20 ml of THF. The oxidation of the DBCat ligand was performed in situ with \(\text{FcPF}_6\) and followed with IR spectroscopy. The blue-violet oxidation product \([\text{Mn(CO)}_3(\text{THF})(\text{DBSQ})]\) underwent a fast successive substitution with two equivalents of \(\text{PPh}_3\) at 40 °C which gave rise to the formation of green \([\text{Mn(CO)}_3(\text{PPh}_3)_2(\text{DBSQ})]\). The synthesis then continued with the oxidation of the latter radical by another portion of \(\text{FePF}_6\) until deep blue-green \([\text{Mn(CO)}_2-(\text{PPh}_3)_2(\text{DBQ})]\) \(\text{PF}_6\) was completely formed. Hereafter, the solution was filtered from non-dissolved \(\text{FcPF}_6\) and reduced to 5 ml in volume by evaporation of the solvent under vacuum. Degassed hexane was then added to induce precipitation of the DBQ complex. The solid \([\text{Mn(CO)}_3(\text{PPh}_3)_2(\text{DBQ})]\) \(\text{PF}_6\) was filtered out and washed several times with cold benzene to remove a small excess of \(\text{PPh}_3\). 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 \(\text{DBQ}\) at 1589(w) cm\(^{-1}\). H NMR spectrum in \(\text{CD}_2\text{Cl}_2\) (ppm): \(\delta\) 1.13 (9H, \text{CH}_3\ of \text{C}_6\text{H}_5-\text{Bu}), 1.23 (9H, \text{CH}_3\ of \text{C}_6\text{H}_5-\text{Bu}), 6.07 (1H, \text{d} \((J(\text{H},\text{H})=2\text{ Hz})\), \text{H-C}_4), 7.08 (1H, \text{d} \((J(\text{H},\text{H})=2\text{ Hz})\), \text{H-C}_6) and a multiplet between 7.08 and 7.74 (20H), \(\delta\) 68.26 (two axial \(\text{PPh}_3\) ligands). C, H and P elemental analyses were consistent with the composition of \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]\) \(\text{PF}_6\).

2.1.2. \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBSQ})]\)

This complex was generated in situ in a very pure form electrochemically by exhaustive 1e\(^-\) reduction of \(10^{-2}\) M \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBSQ})]\) \(\text{PF}_6\) in \(\text{CH}_2\text{Cl}_2\), or chemically by electron transfer reaction between \(10^{-2}\) M \([\text{Mn(CO)}_2(\text{PPh}_3)_2(\text{DBQ})]\) \(\text{PF}_6\) and \(10^{-2}\) M \(\text{Bu}_4\text{N}[\text{Mn(CO)}_3(\text{DBCAt})]\) in THF/2\(\times\)10\(^{-2}\) M \(\text{PPh}_3\). 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 \(\text{CH}_2\text{Cl}_2\) or 1935(vs), 1859(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 of 2 cm\(^{-1}\). Solvent bands were numerically subtracted.
modulation were used to measure ESR spectra. 2,2-
Di-phenyl-1-picrylhydrazyl (DPPH, Aldrich) was em-
ployed as a standard \( g = 2.0037 \pm 0.0002 \) for the
determination of \( g \) values. \(^1\)H and \(^3\)P NMR spectra
were recorded on a Bruker AM 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 \( x-y \) re-
corders. For all spectroelectrochemical experiments,
\( 3 \times 10^{-1} \) M \( \text{Bu}_4\text{NPF}_6 \) as supporting electrolyte and
\( 5 \times 10^{-3} \) M \([\text{Mn(CO)}_3(\text{DBCat})]^- \) were used. Each spec-
troelectrochemical 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 \( E_{1/2} = -0.48 \) V versus \( \text{Fc/Fc}^+ \) to
the corresponding short-lived radical \([\text{Mn(CO)}_3-
(\text{DBSQ})]^- \) detectable only by cyclic voltammetry \( (I_p,c/\)
\( I_p,a \approx 0.5 \) at room temperature and \( \nu = 100 \text{ mV s}^{-1} \)
\[6\]. When the oxidation was performed chemically by
\( \text{FcPF}_6 \) in very dry dichloromethane at \( T = 295 \) K, the
only radical detected by ESR spectroscopy was
\([\text{Mn(CO)}_4(\text{DBSQ})]^- \) (sextet of doublets, \( a_{\text{Mn}} = 0.70 \) mT,
\( a_{\text{H(DBS)}} = 0.33 \text{ mT}, g = 2.0033; \text{Fig. 1(A)}. \)
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 \( T = 295 \) K in \( \text{CH}_2\text{Cl}_2 \), containing
some water, a second radical product was observed at
low concentration 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 \( \text{le-} \) at \( T = 230 \)
K in an Allendoerfer-type ESR spectroelectrochemical

Table 1
Absorption maxima in the visible region and CO stretching frequencies of \([\text{Mn(CO)}_3(\text{DBCat})]^- \) and products of its oxidation studied by the
UV–Vis/IR OTTLE method at 220–293 K

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \lambda_{\text{max}}^a (\text{e}^b) )</th>
<th>( \nu(\text{CO})^c )</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mn(CO)}_3(\text{DBCat})]^- )</td>
<td>430 (6500), 532 (8300) ( ^d )</td>
<td>2000, 1891 (broad) ( ^d )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{DBSQ})]^- )</td>
<td>540 (2000), 720 (sh) ( ^e )</td>
<td>2109, 2030, 2002, 1959 ( ^e )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_5(\text{H}_2\text{O})(\text{DBSQ})]^- )</td>
<td>520 (2700), 693 (1500) ( ^d )</td>
<td>2108, 2029, 2003, 1957 ( ^f )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{THF})(\text{DBSQ})]^- )</td>
<td>524 (2370), 708 (1650) ( ^g )</td>
<td>2029, 1925 (broad) ( ^g )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBSQ})]^- )</td>
<td>580 (sh), 665 (5400) ( ^d )</td>
<td>2030, 1934, 1922 (sh) ( ^h )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{PPh}_3)_2(\text{DBSQ})]^- )</td>
<td>654 (sh), 854 (3900) ( ^h )</td>
<td>2022.5, 1944.5, 1908 ( ^d )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_4(\text{DBQ})]^+ )</td>
<td>792 (5600) ( ^d )</td>
<td>2024, 1946, 1910 ( ^* )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{H}_2\text{O})(\text{DBQ})]^+ )</td>
<td>688 (16000) ( ^d )</td>
<td>1935, 1859 ( ^h )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{PPh}_3)(\text{DBQ})]^+ )</td>
<td>610 (6800) ( ^h )</td>
<td>1927, 1850 ( ^h )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{PPh}_3)_2(\text{DBQ})]^+ )</td>
<td>727, 2061, 2037, 2000 ( ^f )</td>
<td>2127, 2061, 2037, 2000 ( ^f )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_5(\text{PPh}_3)_2(\text{DBQ})]^+ )</td>
<td>2050, 1980 (broad) ( ^d )</td>
<td>2054, 2007, 1976.5 ( ^d )</td>
</tr>
<tr>
<td>([\text{Mn(CO)}_3(\text{PPh}_3)_2(\text{DBQ})]^+ )</td>
<td>2055.5, 2013, 1981 ( ^* )</td>
<td>2003, 1943 ( ^* )</td>
</tr>
</tbody>
</table>

\(^a\) In nm.
\(^b\) Molar absorption coefficient, M\(^{-1}\) cm\(^{-1}\).
\(^c\) In cm\(^{-1}\).
\(^d\) In CH\(_2\)Cl\(_2\), 220–230 K.
\(^e\) In CH\(_2\)Cl\(_2\), 293 K.
\(^f\) In CH\(_2\)Cl\(_2\), 265 K.
\(^g\) Ref. \[7\].
\(^h\) In THF, 293 K.
\(^*\) In CO-saturated solution.
splitting of $^{55}\text{Mn} (I=5/2)$, $^1\text{H}$ at the C4 position of the DBSQ ligand [13] ($I=1/2$) and two equivalent $^1\text{H}$ nuclei of coordinated $\text{H}_2\text{O}$, respectively: $a_{\text{Mn}}=0.71\text{ mT}$, $a_{\text{H}}^{\text{DBSQ}}=0.56\text{ mT}$, $a_{\text{H}}^{\text{H}_2\text{O}}=0.28\text{ mT}$ (Fig. 1(C)). These parameters clearly point to the formation of $[\text{Mn(CO)}_3(\text{H}_2\text{O})(\text{DBSQ})]$. The rather large value of $a_{\text{H}}^{\text{H}_2\text{O}}$ indicates a relatively high spin density on the hydrogen atoms. Such an interpretation points to a direct interaction between coordinated $\text{H}_2\text{O}$ and the DBSQ radical ligand via formation of two equivalent hydrogen bonds $\text{O}-\text{H}\cdots\text{O}-\text{C}$.

Application of the LT OTTLE cell

$T=293\text{ K}$. The ESR spectroelectrochemical results have been confirmed by IR spectra of the oxidized solution of $[\text{Mn(CO)}_3(\text{DBCat})]^-$ in dry $\text{CH}_2\text{Cl}_2$. The spectra only showed the characteristic [6] $\nu(\text{CO})$ bands of $[\text{Mn(CO)}_4(\text{DBSQ})]$ at $2105(\text{w})$, $2029(\text{s})$, $2004(\text{m})$ and $1960(\text{m})\text{ cm}^{-1}$.

$T=223\text{ K}$. Spectral changes accompanying the $1e^-$ oxidation of $\sim 5\times 10^{-3}\text{ M }[\text{Mn(CO)}_3(\text{DBCat})]^-$ in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}/0.3\text{ M Bu}_4\text{NPF}_6$ within the LT OTTLE cell at $T=223\text{ K}$. (B) Disproportionation of the product $[\text{Mn(CO)}_4(\text{H}_2\text{O})(\text{DBSQ})]$ to $[\text{Mn(CO)}_3(\text{DBSQ})]$ upon elevation of temperature from 223 to 273 K. (C) Oxidation of $[\text{Mn(CO)}_3(\text{H}_2\text{O})(\text{DBSQ})]$ to $[\text{Mn(CO)}_3(\text{H}_2\text{O})(\text{DBSQ})]^+$ under the same conditions as given in (A).

The $\nu(\text{CO})$ bands of the parent complex at $2000(\text{s})$ and $1891(\text{s,broad})\text{ cm}^{-1}$ were replaced isosbestic by bands at $2029(\text{s})$ and $1925(\text{s,broad})\text{ cm}^{-1}$. In accordance with the ESR results, these bands are assigned to $[\text{Mn(CO)}_3(\text{H}_2\text{O})(\text{DBSQ})]$. Importantly, no $[\text{Mn(CO)}_3(\text{DBSQ})]$ 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, $[\text{Mn(CO)}_3(\text{H}_2\text{O})(\text{DBSQ})]$ was smoothly converted into $[\text{Mn(CO)}_3(\text{DBSQ})]$ 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 $\text{H}_2\text{O}$ ligand. Unfortunately, the measured IR OTTLE spectra provided no evidence for this coordination, probably due to the low intensity of the $\nu(\text{O-H})$ bands. The only evidence thus comes from the LT ESR OTTLE experiments (vide supra). At $T=223\text{ K }[\text{Mn(CO)}_3(\text{DBCat})]^-$, with a concentration as high as $10^{-2}\text{ M}$, was completely converted into $[\text{Mn(CO)}_3(\text{H}_2\text{O})(\text{DBSQ})]$. This observation is not surprising taking into account the fact that even quite dry $\text{CH}_2\text{Cl}_2$ may still be $10^{-3}\text{ M}$ in water [14]. In our case, the concentration of water was at least of an order of magnitude higher.

Since the $1e^-$ oxidation of $[\text{Mn(CO)}_3(\text{DBCat})]^-$ and the thermal reaction of $[\text{Mn(CO)}_3(\text{H}_2\text{O})(\text{DBSQ})]$ proceeded in $\text{N}_2$-saturated $\text{CH}_2\text{Cl}_2$ (vide supra), the formation of the tetracarbonyl product, $[\text{Mn(CO)}_4($}
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.

(DBSQ)], out of both tricarbonyl complexes implies that other, CO-releasing reactions should occur as well. Apparently, no other carbonyl complex was formed in a detectable amount in the course of the conversion of [Mn(CO)₃(H₂O)(DBSQ)] into [Mn(CO)₄(DBSQ)] as isosbestic points were observed in the ν(CO) region of the measured IR spectra (see Fig. 2(B)). Also, no mononuclear intermediate containing the DBSQ radical ligand other than a small amount of [Mn(CO)₃(H₂O)(DBSQ)] was detected [6] by ESR spectroscopy during the in situ oxidation of [Mn(CO)₃(DBCat)]⁻. These data indicate that, in both cases, the pentacoordinated intermediate [Mn(CO)₃(DBSQ)] disproportionates at room temperature to give [Mn(CO)₄(DBSQ)] and, probably, [Mn(CO)₂(DBSQ)] which concomitantly decomposes. This decomposition results in release of free CO that is readily trapped by other [Mn(CO)₃(DBSQ)] molecules to give [Mn(CO)₄(DBSQ)]. The cyclic voltammogram of [Mn(CO)₃(DBCat)]⁻ in N₂-saturated CH₂Cl₂ showed [6] on the reverse scan at 100 mV s⁻¹, after passing the electrochemically reversible 1e⁻ anodic process, three cathodic peaks at +0.24, −0.80 and −1.07 V versus Fe/Fe³⁺. The first two, most positive reductions were ascribed [6] to the primary product [Mn(CO)₃(DBSQ)] and the disproportionation product [Mn(CO)₄(DBSQ)], respectively. The most negative cathodic peak may reasonably be assigned to the reduction of free DBQ [7]. Evidently, the disproportionation reaction is accompanied not only by a CO release but also by dissociation of the DBQ ligand 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(DBQ) complex generated by oxidation of [Mn(DBCat)]⁻. In that case, solvated Mn¹ 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 λ_max = 520 (ε_max = 2700 M⁻¹ cm⁻¹) and 693 (ε_max = 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 (λ_max = 524 (ε_max = 2370 M⁻¹ cm⁻¹) and 708 (ε_max = 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= n₂O, 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→CO π-back-bonding. On the other hand, both radicals differ very much in their ESR spectra, particularly in the value of a_Mn (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 1950(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 λ_max = 792 nm (ε_max = 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 [Mn(CO)₃(L)(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 [Mn(CO)₄(DBSQ)] from [Mn₂(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 [Mn(CO)₅(PPh₃)(DBSQ)] due to the thermal and photochemical lability of the [Mn(CO)₄(DBSQ)] intermediate which is known [16] to yield an ESR-silent green tetramer [Mn₄(DBSQ)]₄. Moreover, [Mn(CO)₃(PPh₃)(DBSQ)] itself undergoes a facile thermal substitution of the axial CO ligand by another PPh₃ molecule (vide infra) forming ultimately the stable product [Mn(CO)₂(PPh₃)₂(DBSQ)]. In contrast, the analogous complexes [Re(CO)₃(PR₃)(DBSQ)] are thermally stable under the same conditions and can only be converted into [Re(CO)₂(PR₃)₂(DBSQ)] (with 100% yield) by irradiation into their visible absorption band(s) [19].

Alternatively, [Mn(CO)₃(PPh₃)(DBSQ)] may be generated in situ by oxidation of [Mn(CO)₃(DBCat)]⁻ with FeP₂F₆ in THF and subsequent addition of an equivalent amount of PPh₃ into the resulting solution of the relatively stable complex [Mn(CO)₅(THF)(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 [Mn(CO)₃(PPh₃)(DBSQ)]. Solid evidence for this statement has been obtained from ESR spectroelectrochemistry at room temperature. In situ oxidation of [Mn(CO)₃(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 [Mn(CO)₃(PPh₃)(DBSQ)] (g = 2.0029, aₘn = 1.00 mT, aₜ=DBSQ = 0.32 mT, aₚ = 3.35 mT) and [Mn(CO)₃(PPh₃)(DBQ)] (g = 2.0022, aₘn = 1.79 mT, aₜ=DBSQ = 0.32 mT, aₚ = 3.94 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 [Mn(CO)₃(DBSQ)] which reacted further, but not completely, to give [Mn(CO)₃(PPh₃)(DBSQ)]. Importantly, a small amount of [Mn(CO)₃(PPh₃)(DBSQ)] was then detected in the solution.

**Cyclic voltammetry at variable temperatures**

The only route which led to the facile generation of pure [Mn(CO)₃(PPh₃)(DBSQ)] was electrochemical oxidation of 10⁻³ M [Mn(CO)₃(DBCat)]⁻ in CH₂Cl₂/10⁻² M PPh₃ at T = 218 K. The cyclic voltammogram of this solution (Fig. 4(A)) exhibited only two anodic peaks at Eₚ,a = -0.940 and +0.075 V (versus Fe/Fc⁺).

The first, more negative one-electron oxidation was chemically reversible (Iₚ,c/Iₚ,a = 1 at v = 100 mV s⁻¹) and electrochemically quasi-reversible (ΔEₚ = 180 mV versus 110 mV of the Fe/Fc⁺ redox couple). It has been assigned by analogy with the oxidation of [Mn(CO)₃(DBCat)]⁻ in THF [6] to the ([Mn(CO)₃(DBCat)]⁻ - PPh₃)/[Mn(CO)₃(PPh₃)(DBSQ)] couple.

Upon warming up the solution to room temperature, the cyclic voltammogram became more complex (Fig. 4(B)) owing to the lability of [Mn(CO)₃(PPh₃)(DBSQ)] which reacted further, but not completely, to give [Mn(CO)₃(PPh₃)(DBSQ)]. Importantly, a small amount of [Mn(CO)₃(PPh₃)(DBSQ)] was then detected in the solution.

![Cyclic voltammogram](image-url)
[Mn(CO)$_2$(PPh$_3$)$_2$(DBSQ)]. The accuracy of this assignment was proved by comparison with a cyclic voltammogram of an authentic sample of [Mn(CO)$_2$-(PPh$_3$)$_2$(DBQ)]$^+$ (Fig. 4(C)) which afforded two one-electron reductions at $E_{p,c} = -0.42$ V ($\Delta E_{p,c} = 80$ mV, $I_{p,c}/I_{p,a} = 1$) and $-1.26$ V ($I_{p,c}/I_{p,a} < 0.5$). In the first (most positive) step, [Mn(CO)$_2$(PPh$_3$)$_2$(DBQ)]$^+$ was converted into [Mn(CO)$_2$(PPh$_3$)$_2$(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)$_2$(PPh$_3$)$_2$(DBCat)]$^-$ into [{Mn(CO)$_3$(DBCat)}] ... PPh$_3}$-. For, the anodic peak of the final reduction product, [{Mn(CO)$_3$(DBCat)}] ... PPh$_3}$-, appeared on the reversed potential scan at $E_{p,a} = -0.975$ V. The reasons for the observed thermal lability of [Mn(CO)$_2$(PPh$_3$)$_2$(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)$_3$(PPh$_3$)(DBSQ)] is thermally stable at 218 K with respect to substitution of the axial [7,18] CO ligand by PPh$_3$. 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 PPh$_3$ at $T = 223$ K, the CH$_2$Cl$_2$ solution contained only the radical product [Mn(CO)$_3$(PPh$_3$)(DBSQ)]. Its $\nu$(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 PPh$_3$ took place nor was there any indication of a decomposition in the course of the electrolysis. Consequently, [Mn(CO)$_3$(PPh$_3$)(DBSQ)] could be converted in the second 1e$^-$ oxidation step into the cation [Mn(CO)$_3$(PPh$_3$)(DBQ)]$^+$ with $\nu$(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)$_3$(PPh$_3$)(DBSQ)] by application of an appropriate back-reduction potential.

The electronic absorption spectrum of [Mn(CO)$_3$(PPh$_3$)(DBSQ)] was collected in CH$_2$Cl$_2$ 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)$_3$(PPh$_3$)(DBSQ)] exhibits the characteristic MLCT band at $\lambda_{max} = 665$ nm ($\epsilon_{max} = 5400$ 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)$_3$(PPh$_3$)$_2$(DBSQ)], is strongly red-shifted with respect to [Mn(CO)$_3$-(PPh$_3$)(DBSQ)]: $\lambda_{max} = 854$ nm in THF. This band is apparently not present in the UV–Vis spectrum of Fig. 6. This observation again confirms the inherent stability of [Mn(CO)$_3$(PPh$_3$)(DBSQ)] at 223 K towards attack by free PPh$_3$.

Fig. 6 shows the UV–Vis spectral changes accompanying the gradual 1e$^-$ oxidation of [Mn(CO)$_3$(PPh$_3$)(DBSQ)] to its cation [Mn(CO)$_3$(PPh$_3$)(DBQ)]$^+$ within the LT OTTLE cell monitored by UV–Vis spectroscopy. The experimental conditions correspond to Fig. 5.
a shoulder at $\sim 361$ nm. The assignment of the lowest energy band will be discussed in the next section.

$T = 293$ K. At $T = 293$ K, the $1e^-$ oxidation of $5 \times 10^{-3}$ M $[\text{Mn(CO)}_2\text{(DBCat)}^-]$ in CH$_2$Cl$_2$/0.05 M PPh$_3$ led to an initially mixture of two products, $[\text{Mn(CO)}_2\text{(PPh)}_3\text{(DBSQ)}]$ ($\nu$(CO) at 2024(s), 1946(m) and 1910(m) cm$^{-1}$) and $[\text{Mn(CO)}_2\text{(PPh)}_3\text{(DBQ)}]$ ($\nu$(CO) at 1927(s) and 1850(s) cm$^{-1}$). The concentration of the latter radical gradually increased with time. Further positive sweep of the electrode potential led first to the oxidation of $[\text{Mn(CO)}_2\text{(PPh)}_3\text{(DBSQ)}]$ to $[\text{Mn(CO)}_2\text{(PPh)}_3\text{(DBQ)}]^+$ ($\nu$(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 $[\text{Mn(CO)}_2\text{(PPh)}_3\text{(DBSQ)}]$. The primary oxidation product, $[\text{Mn(CO)}_3\text{(PPh)}_3\text{(DBQ)}]^+$ ($\nu$(CO) at r.t.: 2055.5(vs), 2013(m) and 1981(m) cm$^{-1}$), was then found only at very low concentration.

In a potential-step experiment at $T = 293$ K, $5 \times 10^{-3}$ M $[\text{Mn(CO)}_3\text{(DBCat)}^-]$ in CH$_2$Cl$_2$/0.05 M PPh$_3$ was directly oxidized within 40 s to $[\text{Mn(CO)}_3\text{(PPh)}_3\text{(DBQ)}]^+$. During an additional 5 min, only a negligible amount of $[\text{Mn(CO)}_2\text{(PPh)}_3\text{(DBQ)}]$ was formed. Instead, $[\text{Mn(CO)}_3\text{(PPh)}_3\text{(DBQ)}]^+$ persisted in the solution, having undergone only a slow decomposition of $\sim 7\%$ of the initial amount to an unidentified product. This would imply that $[\text{Mn(CO)}_3\text{(PPh)}_3\text{(DBQ)}]^+$ is surprisingly more resistant towards the attack of free PPh$_3$ than $[\text{Mn(CO)}_3\text{(PPh)}_3\text{(DBQ)}]$ under identical conditions. It is noted that the stability of $[\text{Mn(CO)}_3\text{(PPh)}_3\text{(DBQ)}]^+$ strongly decreases in 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 decarboxylation 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 Mn$^I$ which possess a limited stability at room temperature towards decarboxylation 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 $[\text{Mn(CO)}_3\text{(L)}_2\text{(DBQ)}]^+$, where $L = \text{PR}_3$ or $\text{P(OR)}_3$.

The complexes $[\text{Mn(CO)}_3\text{(L)}_2\text{(DBQ)}]^+$ 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$^8$ metals [21]: $[\text{Re(CO)}_2\text{(L)}_2\text{(DBQ)}]^+$, $[\text{Ru(bpy)}_2\text{(BO)}]^2+$, $[\text{Ru(bpy)}_2\text{(BO)}]^2+$ and $[\text{Ru(bpy)}_2\text{(\mu-Q-O)}]^2+$, $\text{Q-O-Q} = 3,3',4,4'$-tetra-oxo-biphenyl). These species possess very strong mixing between the metal d$e$ and dioxolene $\pi^*$ frontier orbitals so that it is virtually impossible to distinguish between the resonance structures $\text{M}^+\pi^*\text{Q}$ and $\text{M}^+\pi^*\text{Q}$ LUMO of the complexes may be then looked upon as (nearly) completely delocalized on the metal–dioxolene unit. Hence, the $\pi_{\text{M}^-\text{Q}} \rightarrow \pi^*\text{M}^-\text{Q}$ 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 Q ligand. Furthermore, the corresponding absorption band is always very intense ($\epsilon_{\text{max}} = 6000-4000$ M$^{-1}$ cm$^{-1}$) for all the above-mentioned stable delocalized o-quinone complexes. At the same time, the $\pi_{\text{M}^-\text{Q}} \rightarrow \pi^*\text{M}^-\text{Q}$ transition has been found in all cases at considerably higher energy in comparison with the MLCT ($\text{d}_\pi\text{(M)} \rightarrow \pi^*\text{(dioxolene)})$ transition in the analogous o-semiquinone complexes [21]: $\Delta\varepsilon_{\text{max}} \sim 5200-3000$ cm$^{-1}$. This phenomenon was interpreted [7] to indicate a large energy gap between the $\pi_{\text{M}^-\text{Q}}$ HOMO and $\pi^*\text{M}^-\text{Q}$ 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 relative high excitation energy of the $\pi_{\text{M}^-\text{Q}} \rightarrow \pi^*\text{M}^-\text{Q}$ transition in the delocalized o-quinone complexes may arise from a high reorganization energy ascribed to a distortion of the Q ligand itself upon excitation. Direct evidence for this distortion has been obtained [7,19,22] from resonance Raman spectra of $[\text{Mn(CO)}_2\text{(P(OEt)}_3\text{(DBQ)}]^+$, $[\text{Re(CO)}_2\text{(PPh)}_3\text{(DBQ)}]^+$ and $[\text{Ru(bpy)}_2\text{(BO)}]^2+$, respectively, which show large intensities for skeletal metal–Q 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 $\alpha$-diimines [23,24] and quinone diimines [25,26].

The above results indicate that the thermal stability of the metal–Q complexes increases with stronger $\text{M} \rightarrow \text{Q}$ $\pi$-backbonding. The studied Mn$^I$-DBQ complexes seem to fit in well with this trend. The most stable DBQ complex in the series, $[\text{Mn(CO)}_3\text{(PPh)}_3\text{(DBQ)}]^+$, exhibits the absorption band of the $\pi_{\text{M}^-\text{-DBQ}} \rightarrow \pi^*\text{M}^-\text{-DBQ}$ transition at $\lambda_{\text{max}} = 610$ nm, whereas the MLCT ($\text{d}_\pi\text{(Mn)} \rightarrow \pi^*\text{(DBSQ)}$) band of $[\text{Mn(CO)}_3\text{(PPh)}_3\text{(DBQ)}]$ occurs at $\lambda_{\text{max}} = 854$ nm (in 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 $\pi^*\text{LUMO of DBQ will be at lower energy than the \pi^*\text{SOMO of the DBQS ligand}}$ [4]. It means that $[\text{Mn(CO)}_3\text{(PPh)}_3\text{(DBQ)}]^+$ 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)3(DBQ)] is also in line with this explanation.1

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 (\( d_{\text{Mn}}(\text{Mn}) \rightarrow \pi^*(\text{DBQ}) \)) transition in the reduced radical [Mn(CO)3(PPh3)(DBQ)]: \( \lambda_{\text{max}} = 688 \) and 665 nm, respectively, i.e. \( \Delta E_{\text{max}} = -502 \text{ cm}^{-1} \). 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 \( \lambda_{\text{max}} = 792 \text{ nm} \) whereas the MLCT (\( d_{\text{Mn}}(\text{Mn}) \rightarrow \pi^*(\text{DBQ}) \)) absorption band of [Mn(CO)3(H2O)-(DBQ))] has been found at considerably higher energy: \( \lambda_{\text{max}} = 520 \text{ nm} \), i.e. \( \Delta E_{\text{max}} = -6604 \text{ cm}^{-1} \) 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 \( \pi \) 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 \( 10^{-2} \text{ M} \) concentration of the electrogenerated product in the thin solution layer (\( l = 0.2 \text{ mm} \)) as the resonance Raman spectrum of the parent complex [Mn(CO)3(DBCat)] + [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)3(DBQ)] + obtained straightforwardly [7] in the RT OTTLE cell [8] for a \( 10^{-2} \text{ M} \) concentration of the complex. Apparently, additional low-temperature resonance Raman studies on the thermally labile \( \pi \)-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)3(DBQ)] + (M=Mn, Re) [7,19], as indicated by their UV–Vis spectra.

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