UvA-DARE (Digital Academic Repository)

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

Hartl, F.

DOI

[10.1016/0020-1693\(94\)04395-C](https://doi.org/10.1016/0020-1693(94)04395-C)

Publication date

1995

Published in

Inorganica Chimica Acta

[Link to publication](#)

Citation for published version (APA):

Hartl, F. (1995). Spectroscopic Characterization of Some Unstable ortho-Semiquinone and ortho-Quinone Complexes of Mnl by Variable-Temperature Thin-Layer Spectroelectro-chemistry at Optically Transparent Electrodes. *Inorganica Chimica Acta*, 232, 99-108. [https://doi.org/10.1016/0020-1693\(94\)04395-C](https://doi.org/10.1016/0020-1693(94)04395-C)

General rights

It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations

If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: <https://uba.uva.nl/en/contact>, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (<https://dare.uva.nl>)

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 Chemisch Laboratorium, J.H. van't Hoff Research Instituut, Universiteit van Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, Netherlands

Received 22 January 1994; revised 19 October 1994

Abstract

Four carbonyl complexes of Mn^I 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 OTTE) 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)_{4–n}(L)_n(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)₂(PPh₃)₂(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 = Q^{2–})) 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 $[\text{Mn}(\text{CO})_3(\text{DBCat})]^{2-}$, or oxidized in two successive ligand-localized $1e^-$ steps. The first oxidation to $[\text{Mn}(\text{CO})_3(\text{DBSQ})]$ is followed by a rapid uptake of a Lewis base L or CO giving rise to the formation of the thermally stable complexes $[\text{Mn}(\text{CO})_3(\text{L})(\text{DBSQ})]$ or $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$, respectively. The latter radical is only stable in a CO-saturated solution of a non-coordinating solvent.

More complicated is the oxidation of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in Ar-saturated CH_2Cl_2 [6]. This process induces a CO ligand disproportionation which affords $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$. 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 $[\text{Mn}(\text{CO})_2(\text{L})_2(\text{DBSQ})]$ ($\text{L} = \text{PPh}_3$) can be obtained by $1e^-$ oxidation of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in the presence of an excess of PPh_3 . This reaction competes with the formation of $[\text{Mn}(\text{CO})_3(\text{PR}_3)(\text{DBSQ})]$ and mainly precludes the UV–Vis characterization of the latter species [7].

The subsequent $1e^-$ oxidation of the radicals $[\text{Mn}(\text{CO})_{4-n}(\text{L})_n(\text{DBSQ})]$ ($n = 0-2$) is fully chemically reversible only for $[\text{Mn}(\text{CO})_2(\text{L})_2(\text{DBSQ})]$ ($\text{L} = \text{PR}_3$, $\text{P}(\text{OR})_3$) [2]. Contrary to this, the oxidation products $[\text{Mn}(\text{CO})_{4-n}(\text{L})_n(\text{DBQ})]^+$ ($n = 0, 1$; $\text{L} = \text{THF}$, 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 $[\text{Mn}(\text{CO})_3(\text{L})(\text{DBQ})]^+$ ($\text{L} = \text{H}_2\text{O}$, PPh_3) are the first spectroscopically characterized tricarbonyl *o*-quinone complexes of Mn^{I} 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. $\text{Bu}_4\text{N}[\text{Mn}(\text{CO})_3(\text{DBCat})] \cdot 1/6\text{C}_6\text{H}_6$ was synthesized by a literature method [5]. $[\text{Cp}_2\text{Fe}]\text{PF}_6$ (FcPF_6) was prepared by a similar procedure to that reported [9] for $\text{Fc}[\text{HgI}_4]$, using a solution of NH_4PF_6 instead of $\text{K}_2[\text{HgI}_4]$ to precipitate a solution of ferricenium sulfate. The supporting electrolyte Bu_4NPF_6 (Aldrich) was dried under vacuum at 80°C for 12 h before use. Dichloromethane (CH_2Cl_2) and tetrahydrofuran (THF)

were freshly distilled under an N_2 atmosphere from P_2O_5 and Na/benzophenone, respectively.

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

120 mg (0.2 mmol) of $\text{Bu}_4\text{N}[\text{Mn}(\text{CO})_3(\text{DBCat})] \cdot 1/6\text{C}_6\text{H}_6$ 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 $[\text{Mn}(\text{CO})_3(\text{THF})(\text{DBSQ})]$ underwent a fast successive substitution with two equivalents of PPh_3 at 40°C which gave rise to the formation of green $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$. The synthesis then continued with the oxidation of the latter radical by another portion of FcPF_6 until deep blue–green $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]\text{PF}_6$ 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. Degassed hexane was then added to induce precipitation of the DBQ complex. The solid $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]\text{PF}_6$ was filtered out and washed several times with cold benzene to remove a small excess of PPh_3 . The yield was almost quantitative.

IR spectrum in nujol mull: two strong $\nu(\text{C}\equiv\text{O})$ bands at 2004 and 1944 cm^{-1} , $\nu(\text{C}=\text{O})$ of DBQ at $1589(\text{w})\text{ cm}^{-1}$. ^1H NMR spectrum in CD_2Cl_2 (ppm): δ 1.13 (9H, CH_3 of $\text{C}_3\text{-Bu}^t$), 1.23 (9H, CH_3 of $\text{C}_5\text{-Bu}^t$), 6.07 (1H, d ($J(\text{H},\text{H}) = 2\text{ Hz}$), H- C_4), 7.08 (1H, d ($J(\text{H},\text{H}) = 2\text{ Hz}$), H- C_6) and a multiplet between 7.08 and 7.74 (30H) due to two PPh_3 ligands. $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum in CD_2Cl_2 (ppm): δ 68.26 (two axial PPh_3 ligands). C, H and P elemental analyses were consistent with the composition of $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]\text{PF}_6$.

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

This complex was generated in situ in a very pure form electrochemically by exhaustive $1e^-$ reduction of 10^{-2} M $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]\text{PF}_6$ in CH_2Cl_2 , or chemically by electron transfer reaction between 10^{-2} M $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]\text{PF}_6$ and 10^{-2} M $\text{Bu}_4\text{N}[\text{Mn}(\text{CO})_3(\text{DBCat})]$ in $\text{THF}/2 \times 10^{-2}\text{ M}$ PPh_3 . It has been found to decompose slowly upon irradiation with visible light [7].

IR spectrum (cm^{-1}): $\nu(\text{C}\equiv\text{O})$ at $1927(\text{vs})$, $1850(\text{s})$ (in CH_2Cl_2) or $1935(\text{vs})$, $1859(\text{s})$ (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

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 ^{31}P 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, 3×10^{-1} M Bu_4NPF_6 as supporting electrolyte and 5×10^{-3} M $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ were used. Each spectroelectrochemical experiment began with recording the thin-layer cyclic voltammogram of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ 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 $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$

The anion $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ was oxidized in N_2 -saturated CH_2Cl_2 at $E_{1/2} = -0.48$ V versus Fc/Fc^+ to the corresponding short-lived radical $[\text{Mn}(\text{CO})_3(\text{DBSQ})]$ detectable only by cyclic voltammetry ($I_{p,c}/I_{p,a} \sim 0.5$ at room temperature and $v = 100$ mV s^{-1}) [6]. When the oxidation was performed chemically by FcPF_6 in very dry dichloromethane at $T = 295$ K, the only radical detected by ESR spectroscopy was $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ (sextet of doublets, $a_{\text{Mn}} = 0.70$ mT, $a_{\text{H}}^{\text{DBSQ}} = 0.33$ 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 $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ by FcPF_6 was carried out at $T = 295$ K in CH_2Cl_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 $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$. Its structure became clear when $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ was oxidized with $1e^-$ at $T = 230$ K in an Allendoerfer-type ESR spectroelectrochemical cell [12]. The CH_2Cl_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 1

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

Compound	λ_{max}^a (ϵ^b)	$\nu(\text{CO})^c$
$[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$	430 (6500), 532 (8300) ^d	2000, 1891(broad) ^d
$[\text{Mn}(\text{CO})_4(\text{DBSQ})]$	540 (2000), 720(sh) ^{e,i}	2109, 2030, 2002, 1959 ^e 2108, 2029, 2003, 1957 ^f
$[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$	520 (2700), 693 (1500) ^d	2029, 1925 (broad) ^d
$[\text{Mn}(\text{CO})_3(\text{THF})(\text{DBSQ})]^*$	524 (2370), 708 (1650) ^h	2030, 1934, 1923(sh) ^h
$[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$	580(sh), 665 (5400) ^d	2022.5, 1944.5, 1908 ^d 2024, 1946, 1910 ^e
$[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$	654(sh), 854 (3900) ^h	1935, 1859 ^h 1927, 1850 ^e
$[\text{Mn}(\text{CO})_4(\text{DBQ})]^+$		2127, 2061, 2037, 2000 ^f
$[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBQ})]^+$	792 (5600) ^d	2050, 1980 (broad) ^d
$[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$	688 (16000) ^d	2054, 2007, 1976.5 ^d 2055.5, 2013, 1981 ^e
$[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$	610 (6800) ^h	2003, 1943 ^e

^a In nm.

^b Molar absorption coefficient, $\text{M}^{-1} \text{cm}^{-1}$.

^c In cm^{-1} .

^d In CH_2Cl_2 , 220–230 K.

^e In CH_2Cl_2 , 293 K.

^f In CH_2Cl_2 , 266 K.

^g Ref. [7].

^h In THF, 293 K.

ⁱ In CO-saturated solution.

Fig. 1. (A) ESR spectrum of $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ generated by oxidation of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ with FcPF_6 in dry CH_2Cl_2 at $T=293$ K. (B) ESR spectrum of a mixture of radicals obtained in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}$. The bands marked with an asterisk (*) indicate the presence of $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ (see (C)). (C) ESR spectrum of pure $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ obtained by in situ electrochemical oxidation of 5×10^{-3} M $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in $\text{CH}_2\text{Cl}_2/\sim 10^{-2}$ M H_2O at $T=230$ K on a gold spiral working electrode within an Allendoerfer-type ESR spectroelectrochemical cell [12]. (D) Simulated ESR spectrum of $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ with the splitting constants taken from the text and a linewidth of 0.14 mT.

splitting of ^{55}Mn ($I=5/2$), ^1H at the C4 position of the DBSQ ligand [13] ($I=1/2$) and two equivalent ^1H nuclei of coordinated H_2O , respectively: $a_{\text{Mn}}=0.71$ mT, $a_{\text{H}}^{\text{DBSQ}}=0.56$ mT, $a_{\text{H}}^{\text{H}_2\text{O}}=0.28$ mT (Fig. 1(C)). These parameters clearly point to the formation of $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$. 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 H_2O 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

$T=293$ K. The ESR spectroelectrochemical results have been confirmed by IR spectra of the oxidized solution of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$. In dry CH_2Cl_2 , the spectra only showed the characteristic [6] $\nu(\text{CO})$ bands of $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ at 2105(w), 2029(s), 2004(m) and 1960(m) cm^{-1} .

$T=223$ K. Spectral changes accompanying the $1e^-$ oxidation of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in $\text{CH}_2\text{Cl}_2/\text{moisture}$ at the potential of the first anodic wave are shown in Figs. 2(A) and 3(A).

The $\nu(\text{CO})$ bands of the parent complex at 2000(s) and 1891(s,broad) cm^{-1} were replaced isospectically by bands at 2029(s) and 1925(s,broad) cm^{-1} . In accordance with the ESR results, these bands are assigned to $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$. Importantly, no $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ was detected in the solution at this temperature. However, when the temperature of the thin

Fig. 2. (A) IR spectral changes in the $\nu(\text{CO})$ region upon $1e^-$ oxidation of $\sim 5 \times 10^{-3}$ M $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in $\text{CH}_2\text{Cl}_2/\text{H}_2\text{O}/0.3$ M Bu_4NPF_6 within the LT OTTLE cell at $T=223$ K. (B) Disproportionation of the product $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ to $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ upon elevation of temperature from 223 to 273 K. (C) Oxidation of $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ to $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBQ})]^+$ under the same conditions as given in (A).

solution layer was raised from 223 to 280 K, whilst keeping the applied oxidation potential constant, $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ was smoothly converted into $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ 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 H_2O ligand. Unfortunately, the measured IR OTTLE spectra provided no evidence for this coordination, probably due to the low intensity of the $\nu(\text{O}-\text{H})$ bands. The only evidence thus comes from the LT ESR OTTLE experiments (vide supra). At $T=223$ K $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$, with a concentration as high as 10^{-2} M, was completely converted into $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$. This observation is not surprising taking into account the fact that even quite dry CH_2Cl_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 $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ and the thermal reaction of $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ proceeded in N_2 -saturated CH_2Cl_2 (vide supra), the formation of the tetracarbonyl product, $[\text{Mn}(\text{CO})_4-$

Fig. 3. UV-Vis spectral changes due to formation of $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ (A) and $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBQ})]^+$ (B) measured during successive oxidation of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ 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 $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ into $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ as isosbestic points were observed in the $\nu(\text{CO})$ 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 $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ was detected [6] by ESR spectroscopy during the in situ oxidation of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$. These data indicate that, in both cases, the pentacoordinated intermediate $[\text{Mn}(\text{CO})_3(\text{DBSQ})]$ disproportionates at room temperature to give $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ and, probably, $[\text{Mn}(\text{CO})_2(\text{DBSQ})]$ which concomitantly decomposes. This decomposition results in release of free CO that is readily trapped by other $[\text{Mn}(\text{CO})_3(\text{DBSQ})]$ molecules to give $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$. The cyclic voltammogram of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in N_2 -saturated CH_2Cl_2 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 Fc/Fc^+ . The first two, most positive reductions were ascribed [6] to the primary product $[\text{Mn}(\text{CO})_3(\text{DBSQ})]$ and the disproportionation product $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$, 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 DBSQ ligand which is concomitantly oxidized to free DBQ at the applied potential of the $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ oxidation. In fact, Sawyer and co-workers described [15] a similar decomposition of an $\text{Mn}(\text{DBSQ})$ complex generated by oxidation of $[\text{Mn}(\text{DBCat})_2]^-$. In that case, solvated Mn^{II} and free DBQ were formed as products. The above described mechanism of the $[\text{Mn}(\text{CO})_3(\text{DBSQ})]$ disproportionation might also involve oxidation of Mn^{I} to Mn^{II} by free DBQ and formation of the tetrameric complex $[\text{Mn}^{\text{II}}(\text{DBSQ})_2]_4$ [16]. This product was indeed detected in the CH_2Cl_2 solution at room temperature after a thermal decomposition of $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ had taken place.

The UV-Vis spectrum of $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ exhibits, at $T=223 \text{ K}$, two absorption bands in the visible region, at $\lambda_{\text{max}}=520$ ($\epsilon_{\text{max}}=2700 \text{ M}^{-1} \text{ cm}^{-1}$) and 693 ($\epsilon_{\text{max}}=1500 \text{ M}^{-1} \text{ cm}^{-1}$) nm (Fig. 3(A)). It is noteworthy that this spectrum strongly resembles [7] that of the more stable complex $[\text{Mn}(\text{CO})_3^-(\text{THF})(\text{DBSQ})]$ in THF at $T=295 \text{ K}$ ($\lambda_{\text{max}}=524$ ($\epsilon_{\text{max}}=2370 \text{ M}^{-1} \text{ cm}^{-1}$) and 708 ($\epsilon_{\text{max}}=1650 \text{ M}^{-1} \text{ cm}^{-1}$) nm). A similar close correspondence exists between the $\nu(\text{CO})$ frequencies of the complexes [8,17]. This striking similarity in the positions and intensities of the absorption bands implies that the radicals $[\text{Mn}(\text{CO})_3(\text{L})(\text{DBSQ})]$ ($\text{L}=\text{H}_2\text{O}$, THF) may better be considered as an $\text{Mn}(\text{CO})_3(\text{DBSQ})$ moiety with a loosely bound O-donor ligand the presence of which does not affect the absorption properties of the $\text{Mn}(\text{DBSQ})$ chromophore and the extent of the $\text{Mn} \rightarrow \text{CO}$ 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 $\text{L}=\text{H}_2\text{O}$, 0.37 mT for $\text{L}=\text{THF}$) and additional hyperfine splitting due to ^1H nuclei of the H_2O ligand (vide supra).

The radical $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ was smoothly oxidized in the next 1e^- step to a novel cationic complex $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBQ})]^+$ ($\nu(\text{CO})$ bands at $2050(\text{s})$ and $1980(\text{m, broad}) \text{ cm}^{-1}$, see Fig. 2(C)) which could be observed at $T=223 \text{ K}$ for more than one hour without any apparent decrease in concentration. The UV-Vis spectrum of $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBQ})]^+$ (Fig. 3(B)) shows an intense absorption band at $\lambda_{\text{max}}=792 \text{ nm}$ ($\epsilon_{\text{max}}=5600 \text{ M}^{-1} \text{ cm}^{-1}$). Its assignment will be discussed later. This cation also underwent a CO disproportionation at $T=273 \text{ K}$ but the product $[\text{Mn}(\text{CO})_4(\text{DBQ})]^+$ ($\nu(\text{CO})$ at $2125(\text{m})$, $2062(\text{s})$, $2037(\text{m})$ and $2000(\text{m}) \text{ cm}^{-1}$) readily decomposed.

3.2. Oxidation of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in $\text{CH}_2\text{Cl}_2/\text{PPh}_3$

The radical complex $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ 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 $[\text{Mn}(\text{CO})_3(\text{L})(\text{DBSQ})]$, 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 $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ from $[\text{Mn}_2(\text{CO})_{10}]$ and *o*-DBQ, followed by rapid coordination of PPh_3 . However, this procedure seems to be convenient only for collection of the ESR and IR spectra of $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ due to the thermal and photochemical lability of the $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ intermediate which is known [16] to yield an ESR-silent green tetramer $[\text{Mn}_4(\text{DBSQ})_8]$. Moreover, $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ itself undergoes a facile thermal substitution of the axial CO ligand by another PPh_3 molecule (vide infra) forming ultimately the stable product $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$. In contrast, the analogous complexes $[\text{Re}(\text{CO})_3(\text{PR}_3)(\text{DBSQ})]$ are thermally stable under the same conditions and can only be converted into $[\text{Re}(\text{CO})_2(\text{PR}_3)_2(\text{DBSQ})]$ (with 100% yield) by irradiation into their visible absorption band(s) [19].

Alternatively, $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ may be generated in situ by oxidation of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ with FcPF_6 in THF and subsequent addition of an equivalent amount of PPh_3 into the resulting solution of the relatively stable complex $[\text{Mn}(\text{CO})_3(\text{THF})(\text{DBSQ})]$. However, this substitution of THF by PPh_3 requires at least a small excess of PPh_3 for its completion which further initiates the undesired formation of $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$. Solid evidence for this statement has been obtained from ESR spectroelectrochemistry at room temperature. In situ oxidation of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ by ferrocenium was performed in CH_2Cl_2 in a vacuum-tight ESR tube, initially in the presence of a twofold excess of PPh_3 . The recorded ESR spectra revealed instantaneous generation of the radicals $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ ($g=2.0029$, $a_{\text{Mn}}=1.00$ mT, $a_{\text{H}}^{\text{DBSQ}}=0.32$ mT, $a_{\text{P}}=3.35$ mT) and $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$ ($g=2.0022$, $a_{\text{Mn}}=1.79$ mT, $a_{\text{H}}^{\text{DBSQ}}=0.32$ mT, $a_{\text{P}(1,2)}=3.94$ mT) in about equal steady state concentrations. When the experiment was repeated with exactly one equivalent of PPh_3 , the ESR spectrum showed the presence of $[\text{Mn}(\text{CO})_4(\text{DBSQ})]$ which reacted further, but not completely, to give $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$. Importantly, a small amount of $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$ was then detected in the solution.

Cyclic voltammetry at variable temperatures

The only route which led to the facile generation of pure $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ was electrochemical oxidation of 10^{-3} M $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in $\text{CH}_2\text{Cl}_2/10^{-2}$ M PPh_3 at $T=218$ K. The cyclic voltammogram of this solution (Fig. 4(A)) exhibited only two anodic peaks at $E_{\text{p,a}} = -0.940$ and $+0.075$ V (versus Fc/Fc^+).

Fig. 4. (A) and (B) Cyclic voltammogram of 10^{-3} M $\text{Bu}_4\text{N}[\text{Mn}(\text{CO})_3(\text{DBCat})]$. (C) Cyclic voltammogram of 10^{-3} M $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]\text{PF}_6$. Conditions: N_2 -saturated CH_2Cl_2 containing 0.1 M Bu_4NPF_6 and 10^{-2} M PPh_3 , Pt disk electrode 0.8 mm² surface, 100 mV s⁻¹ scan rate, $T=218$ K (A), $T=293$ K (B) and (C). The redox couples A–D are assigned in the text.

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

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

During the anodic scan, this complex partly reacted to $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$ which was further oxidized to $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$ at $E_{\text{p,a}} = -0.50$ V (process B, $\Delta E_{\text{p}}=80$ mV). The third anodic step in the cyclic voltammogram at $+0.075$ V (process C, $\Delta E_{\text{p}}=80$ mV) then corresponds to the $1e^-$ oxidation of remaining $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$. The cathodic peak D, observed on the reverse scan at $E_{\text{p,c}} = -1.26$ V, obviously belongs to the $1e^-$ reduction of

$[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$. The accuracy of this assignment was proved by comparison with a cyclic voltammogram of an authentic sample of $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$ (Fig. 4(C)) which afforded two one-electron reductions at $E_{p,c} = -0.42$ V ($\Delta E_p = 80$ mV, $I_{p,a}/I_{p,c} = 1$) and -1.26 V ($I_{p,a}/I_{p,c} < 0.5$). In the first (most positive) step, $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$ was converted into $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$ 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 $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBCat})]^-$ into $\{[\text{Mn}(\text{CO})_3(\text{DBCat})] \cdots \text{PPh}_3\}^-$. For, the anodic peak of the final reduction product, $\{[\text{Mn}(\text{CO})_3(\text{DBCat})] \cdots \text{PPh}_3\}^-$, appeared on the reversed potential scan at $E_{p,a} = -0.975$ V. The reasons for the observed thermal lability of $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBCat})]^-$ 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 $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ 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 5×10^{-3} M $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ was stepwise oxidized with $1e^-$ in the presence of a tenfold excess of PPh_3 at $T = 223$ K, the CH_2Cl_2 solution contained only the radical product $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$. Its $\nu(\text{CO})$ 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, $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ could be converted in the second $1e^-$ oxidation step into the cation $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$ with $\nu(\text{CO})$ 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 $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ by application of an appropriate back-reduction potential.

The electronic absorption spectrum of $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ was collected in CH_2Cl_2 at $T = 223$ K directly after the spectroelectrochemical $1e^-$ oxidation of $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ had taken place. The end of the electrolysis was unambiguously determined by parallel IR OTTLE control. The spectrum of $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ exhibits the characteristic MLCT band at $\lambda_{\text{max}} = 665$ nm ($\epsilon_{\text{max}} = 5400 \text{ M}^{-1} \text{ cm}^{-1}$), together with a shoulder at ~ 580 nm (Fig. 6). It is noteworthy that the corresponding MLCT band of the substituted complex, $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$, is strongly red-shifted with respect to $[\text{Mn}(\text{CO})_3-$

Fig. 5. IR spectral changes in the $\nu(\text{CO})$ region accompanying $1e^-$ oxidation of $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ in $\text{CH}_2\text{Cl}_2/0.3$ M Bu_4NPF_6 within the LT OTTLE cell at $T = 223$ K.

Fig. 6. Electrochemical oxidation of $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ to $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$ within the LT OTTLE cell monitored by UV-Vis spectroscopy. The experimental conditions correspond to Fig. 5.

$(\text{PPh}_3)(\text{DBSQ})]$: $\lambda_{\text{max}} = 854$ 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 $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ at 223 K towards attack by free PPh_3 .

Fig. 6 shows the UV-Vis spectral changes accompanying the gradual $1e^-$ oxidation of $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ to its cation $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$, again at $T = 223$ K. Also this UV-Vis OTTLE reaction was fully chemically reversible as $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ was completely recovered during the corresponding $1e^-$ back-reduction. The electronic absorption spectrum of $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$ exhibits a very intense band at $\lambda_{\text{max}} = 688$ nm ($\epsilon_{\text{max}} = 16\,000 \text{ M}^{-1} \text{ cm}^{-1}$), a smaller band at 466 nm ($\epsilon_{\text{max}} = 3400 \text{ M}^{-1} \text{ cm}^{-1}$) and

a shoulder at ~ 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 5×10^{-3} M $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in $\text{CH}_2\text{Cl}_2/5 \times 10^{-2}$ M PPh_3 led within 3 min to a $\sim 1:1$ mixture of two products, $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ ($\nu(\text{CO})$ at 2024(s), 1946(m) and 1910(m) cm^{-1}) and $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$ ($\nu(\text{CO})$ 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 $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$ to $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$ ($\nu(\text{CO})$ at 2003(s) and 1943(m) cm^{-1}). Finally, the remaining $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ was oxidized. It is noteworthy that this $1e^-$ anodic step mainly gave rise again to $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$. The primary oxidation product, $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$ ($\nu(\text{CO})$ 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, 5×10^{-3} M $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ in $\text{CH}_2\text{Cl}_2/0.05$ M PPh_3 was directly oxidized within 40 s to $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$. During an additional 5 min, only a negligible amount of $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$ was formed. Instead, $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$ 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 $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$ is surprisingly more resistant towards the attack of free PPh_3 than $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ under identical conditions. It is noted that the stability of $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$ strongly decreases in THF. In this solvent the $1e^-$ oxidation of $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$ 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 Mn^{I} 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 $[\text{Mn}(\text{CO})_2(\text{L})_2(\text{DBQ})]^+$, where $\text{L} = \text{PR}_3$ or $\text{P}(\text{OR})_3$.

The complexes $[\text{Mn}(\text{CO})_2(\text{L})_2(\text{DBQ})]^+$ 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^6 metals [21]: $[\text{Re}(\text{CO})_2(\text{L})_2(\text{DBQ})]^+$, $[\text{Ru}(\text{bpy})_2(\text{BQ})]^{2+}$ ($\text{BQ} = o$ -benzoquinone) and $[\text{Ru}(\text{bpy})_2]_2(\mu\text{-Q-Q})^{4+}$ ($\text{Q-Q} =$

3,3',4,4'-tetra-oxo-biphenyl). These species possess very strong mixing between the metal d_π and dioxolene π^* frontier orbitals so that it is virtually impossible to distinguish between the resonance structures $\text{M}^{n+}\text{-Q}$ and $\text{M}^{(n+1)+}\text{-SQ}$ [4]. The $\pi_{\text{M-Q}}$ HOMO and $\pi_{\text{M-Q}}^*$ LUMO of the complexes may be then looked upon as (nearly) completely delocalized on the metal–dioxolene unit. Hence, the $\pi_{\text{M-Q}} \rightarrow \pi_{\text{M-Q}}^*$ 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 ($\epsilon_{\text{max}} = 6000\text{--}40\,000 \text{ M}^{-1} \text{ cm}^{-1}$) for all the above-mentioned stable delocalized *o*-quinone complexes. At the same time, the $\pi_{\text{M-Q}} \rightarrow \pi_{\text{M-Q}}^*$ transition has been found in all cases at considerably *higher* energy in comparison with the MLCT ($d_\pi(\text{M}) \rightarrow \pi^*(\text{dioxolene})$) transition in the analogous *o*-semiquinone complexes [21]: $\Delta E_{\text{max}} \sim 5200\text{--}3000 \text{ cm}^{-1}$. This phenomenon was interpreted [7] to indicate a large energy gap between the $\pi_{\text{M-Q}}$ HOMO and $\pi_{\text{M-Q}}^*$ LUMO due to a much stronger π -interaction between the metal and the strong π -acceptor *o*-quinone ligand than between the metal and the weak π -acceptor *o*-semiquinone ligand. Alternatively, the relatively high excitation energy of the $\pi_{\text{M-Q}} \rightarrow \pi_{\text{M-Q}}^*$ 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 $[\text{Mn}(\text{CO})_2\text{-}\{(\text{P}(\text{OEt})_3)_2(\text{DBQ})\}]^+$, $[\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$ and $[\text{Ru}(\text{bpy})_2(\text{BQ})]^{2+}$, 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 π -bonding between the metal and non-innocent ligands like α -diimines [23,24] and quinone diimines [25,26].

The above results indicate that the thermal stability of the metal–Q complexes increases with stronger $\text{M} \rightarrow \text{Q}$ π -backbonding. The studied Mn^{I} -DBQ complexes seem to fit in well with this trend. The most stable DBQ complex in the series, $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$, exhibits the absorption band of the $\pi_{\text{Mn-DBQ}} \rightarrow \pi_{\text{Mn-DBQ}}^*$ transition at $\lambda_{\text{max}} = 610$ nm, whereas the MLCT ($d_\pi(\text{Mn}) \rightarrow \pi^*(\text{DBSQ})$) band of $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBSQ})]$ 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 π^* LUMO of DBQ will be at lower energy than the π^* SOMO of the DBSQ ligand [4]. It means that $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$ can also be treated as a compound with strongly delocalized Mn-DBQ π -bonding due to the strong π -acceptor ability of the DBQ ligand. The resonance Raman spectrum

of $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$ is also in line with this explanation¹.

For the related complex $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$, the $\pi_{\text{Mn-DBQ}} \rightarrow \pi^*_{\text{Mn-DBQ}}$ transition has been found at slightly lower energy than the MLCT ($d_{\pi}(\text{Mn}) \rightarrow \pi^*(\text{DBSQ})$) transition in the reduced radical $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBSQ})]$: $\lambda_{\text{max}} = 688$ and 665 nm, respectively, i.e. $\Delta E_{\text{max}} = -502$ cm^{-1} . This information provides evidence for a somewhat weaker stabilizing π interaction between Mn^{I} and DBQ in $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$ 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, $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBQ})]^+$ (see Fig. 3(B)), shows the presence of an intense absorption band at $\lambda_{\text{max}} = 792$ nm whereas the MLCT ($d_{\pi}(\text{Mn}) \rightarrow \pi^*(\text{DBSQ})$) absorption band of $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBSQ})]$ 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 $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBQ})]^+$ may again reflect the rather weak stabilizing $\text{Mn} \rightarrow \text{DBQ}$ π -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 $[\text{Mn}(\text{CO})_4(\text{DBQ})]^+$ (vide supra).

This explanation would also imply that the HOMO and the LUMO of the cation $[\text{Mn}(\text{CO})_3(\text{H}_2\text{O})(\text{DBQ})]^+$ will be more metal and DBQ localized, respectively. Hence, the lowest energy electronic transition is expected to have only weakly perturbed $\text{Mn} \rightarrow \text{DBQ}$ CT character and the complex should then be treated as a 'localized valence' compound [4]. The more stable complex $[\text{Mn}(\text{CO})_3(\text{PPh}_3)(\text{DBQ})]^+$ 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 $[\text{Mn}(\text{CO})_3(\text{DBCat})]^-$ [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 $[\text{Mn}(\text{CO})_2\{\text{P}(\text{OEt})_3\}_2(\text{DBQ})]^+$ 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 π -bonding in these compounds is indeed less delocalized than, for example, in $[\text{M}(\text{CO})_2(\text{PR}_3)_2(\text{DBQ})]^+$ ($\text{M} = \text{Mn}, \text{Re}$) [7,19], as indicated by their UV-Vis spectra.

Acknowledgements

The author is very grateful to Dr J.G.M. van der Linden (University of Nijmegen) for his help with recording the ESR spectroelectrochemical data at low temperatures. Professor D.J. Stufkens (University of Amsterdam) and Dr A. Vlček, Jr. (J. Heyrovsky Institute of Physical Chemistry, Prague) are thanked for their careful reading of the manuscript.

References

- [1] C.G. Pierpont and C.W. Lange, *Prog. Inorg. Chem.*, **41** (1994) 331.
- [2] C.G. Pierpont and R.M. Buchanan, *Coord. Chem. Rev.*, **38** (1981) 45.
- [3] W.P. Griffith, *Transition Met. Chem.*, **18** (1993) 250.
- [4] A. Vlček, Jr., *Comments Inorg. Chem.*, **16** (1994) 207.
- [5] F. Hartl, A. Vlček, Jr., L.A. deLearie and C.G. Pierpont, *Inorg. Chem.*, **29** (1990) 1073.
- [6] F. Hartl and A. Vlček, Jr., *Inorg. Chem.*, **30** (1991) 3048.
- [7] F. Hartl, D.J. Stufkens and A. Vlček, Jr., *Inorg. Chem.*, **31** (1992) 1687.
- [8] M. Krejčík, M. Daněk and F. Hartl, *J. Electroanal. Chem.*, **317** (1991) 179.
- [9] I. Pavlík and J. Klička, *Coll. Czech. Chem. Commun.*, **30** (1965) 664.
- [10] F. Hartl, H. Luyten, H.A. Nieuwenhuis and G.C. Schoemaker, *Appl. Spectrosc.*, **48** (1994) 1522.
- [11] G. Gritzner and J. Kuta, *Pure Appl. Chem.*, **56** (1984) 461.
- [12] R.D. Allendoerfer, G.A. Martinchek and S. Bruckenstein, *Anal. Chem.*, **47** (1975) 890.
- [13] C.C. Felix and R.C. Seally, *J. Am. Chem. Soc.*, **104** (1982) 1555.
- [14] A.J. Fry and W.E. Britton, in W.R. Heinemann (ed.), *Laboratory Techniques in Electroanalytical Chemistry*, Marcel Dekker, New York, 1984, p. 376.

¹ Resonance Raman (rR) spectra of the PF_6^- salt of $[\text{Mn}(\text{CO})_2(\text{PPh}_3)_2(\text{DBQ})]^+$ have been measured in CH_2Cl_2 at 293 K. Excitation with the 544 and 614 nm laser lines into the lowest energy band of the $\pi_{\text{Mn-DBQ}} \rightarrow \pi^*_{\text{Mn-DBQ}}$ transition at $\lambda_{\text{max}} = 610$ nm resulted in a very strong rR effect for the band at 570 cm^{-1} which is assigned to the $\text{Mn}-\text{O}$ stretching mode of the $\text{Mn}(\text{DBQ})^+$ chelate ring [7]. The rR spectra also show weaker, but still significant enhancement for the bands at 598, 529 and 459 cm^{-1} which have been attributed to ring deformation modes of the quinone ligand [7,22]. The Raman peaks at 1404, 1359, 1310, 746 and 640 cm^{-1} due to internal vibrations of the DBQ ligand possess similar intensities, particularly the band at 1359 cm^{-1} which was resonantly more enhanced than in the case of the bis($\text{P}(\text{OEt})_3$) derivative [7]. Finally, a band of low intensity was present in the rR spectra at 243 cm^{-1} .

- [15] (a) S.E. Jones, D.-H. Chin and D.T. Sawyer, *Inorg. Chem.*, **20** (1981) 4257; (b) D.-H. Chin, D.T. Sawyer, W.P. Schaeffer and Ch.J. Simmons, *Inorg. Chem.*, **22** (1983) 752.
- [16] M.W. Lynch, D.N. Hendrickson, B.J. Fitzgerald and C.G. Pierpont, *J. Am. Chem. Soc.*, **106** (1984) 2041.
- [17] T. van der Graaf, D.J. Stufkens, J. Víchová and A. Vlček, Jr., *J. Organomet. Chem.*, **401** (1990) 305.
- [18] B.L. Tumanskii, K. Sarbasov, S.P. Solodovnikov, N.N. Bubnov, A.I. Prokof'ev and M.I. Kabachnik, *Dokl. Akad. Nauk USSR*, **259** (1981) 611.
- [19] F. Hartl and A. Vlček, Jr., *Inorg. Chem.*, **31** (1992) 2869.
- [20] M.B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, **10** (1967) 247.
- [21] (a) M. Haga, E.S. Dodsworth and A.B.P. Lever, *Inorg. Chem.*, **25** (1986) 447; (b) H. Masui, A.B.P. Lever and P.R. Auburn, *Inorg. Chem.*, **30** (1991) 2402; (c) L.F. Joulíé, E. Schatz, M.D. Ward, F. Weber and J. Yellowlees, *J. Chem. Soc., Dalton Trans.*, (1994) 799.
- [22] D.J. Stufkens, T.L. Snoeck and A.B.P. Lever, *Inorg. Chem.*, **27** (1988) 953.
- [23] P.C. Servaas, H.K. van Dijk, T.L. Snoeck, D.J. Stufkens and A. Oskam, *Inorg. Chem.*, **24** (1985) 4494.
- [24] D.J. Stufkens, *Coord. Chem. Rev.*, **104** (1990) 39.
- [25] A.B.P. Lever, H. Masui, R.A. Metcalfe, D.J. Stufkens, E.S. Dodsworth and P.R. Auburn, *Coord. Chem. Rev.*, **125** (1993) 317.
- [26] F. Hartl, T.L. Snoeck, D.J. Stufkens and A.B.P. Lever, *Inorg. Chem.*, submitted for publication.