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The mechanisms of the photochemical reactions of $M_2(CO)_{10}$ (M = Mn, Re) with *ortho-* and *para*-quinones: a combined EPR and FTIR study

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Abstract

A study has been made of the photolysis of $M_2(CO)_{10}$ (M = Mn, Re) in the presence of *ortho-* and *para*-quinones in coordinating (THF, 2-MeTHF, 10^{-1} *M* pyridine in toluene) and in inert (toluene, CH_2Cl_2, 2-chlorobutane) solvents. For comparison, the same reactions have been studied for $M_2(CO)_8(bpy')$ (bpy' = 4,4'-dimethyl-2,2'-bipyridine). Both EPR and FTIR techniques have been used to monitor the photochemical reactions under various conditions. A comprehensive picture of the overall reaction mechanism has been established. Both primary photoproducts, $M(CO)_5$ and $M_2(CO)_9$, were found to react with quinones. Oxidative addition to $M(CO)_5$ produces unstable M(I) complexes that contain either a *p*-semiquinone (*p*-SQ) or monodentate *o*-semiquinone (*o*-SQ) ligand. The former species are stabilized by polar solvents. $M(CO)_5$(*p*-SQ), $M(CO)_5$(*o*-SQ), $Mn(CO)_3L_2$(*p*-SQ) (L = THF, py) and $Re(CO)_{5-n}(THF)_n$(*p*-SQ) have been identified as photoproducts by EPR and IR spectroscopy. The *o*-semiquinone complexes undergo a thermal or photochemical intramolecular substitution of CO by the second *o*-semiquinone oxygen atom, producing complexes that contain a chelating *o*-semiquinone radical anionic ligand *O,O-o*-SQ. The *cis*-CO ligand of these complexes is loosely bound and can therefore easily be substituted, thermally as well as photochemically, by a Lewis base (L) to give $M(CO)_3L$ (*O,O-o*-SQ) complexes as final products. Both quinone isomers also coordinate to the primary photoproducts $M_2(CO)_9$. The resulting $M_2(CO)_9$(quinone) species are unstable and react with CO to regenerate the parent compounds $M_2(CO)_{10}$. In the case of the *o*-quinones, they undergo thermal intramolecular electron transfer reaction resulting in M–M bond splitting, leading again to $M(CO)_3L$(*O,O-o*-SQ) species. Apparently, EPR-active radical products can also be formed by an entirely non-radical process, since the quinones first coordinate to $M_2(CO)_9$ before the electron transfer takes place. This result shows that the occurrence of "spin-trapping" cannot unambiguously be deduced from the observation of EPR-active products only. The photochemical reactions with $M_2(CO)_8(bpy')$ produce for both quinone isomers the novel complexes $M(CO)_3(bpy')(SQ)$, which have been characterized by IR and EPR spectroscopy.

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Introduction

The photochemistry of organometallic compounds containing single unbridged M–M bond continues to attract much attention [1–7]. The simple dimeric carbonyls $M_2(CO)_{10}$ (M = Mn, Re) are representative examples which exhibit all the typical photoreaction pathways of this broad class of compounds [1]. Both $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ have been shown [1–7 and references therein] to undergo two primary photoprocesses, viz. (i) homolytic dissociation of the M–M bond to give $M(CO)_5$ radicals and (ii) release of CO with formation of the coordinatively unsaturated $M_2(CO)_9$. Until recently, most of the photoreactions observed, i.e., disproportionation, electron transfer, atom transfer and CO-substitution [1–5], were assumed to arise from the highly reactive $M(CO)_5$ radicals. The possible role of the other photoproduct $M_2(CO)_9$ has been practically neglected, except for the monosubstitution by Lewis bases that produces $M_2(CO)_9B$ (B = amines, phosphines, nitriles, tetrahydrofuran etc.).

In many instances the formation of radical adducts of the type $M^I(CO)_5(L^{\cdot-})$ or $M^I(CO)_4(LL^{\cdot-})$ upon photolysis of $M_2(CO)_{10}$ in the presence of the oxidized form of L (L = organic nitroso-compounds [8–11], *p*-quinones [12–14], *o*-quinones [12–21] and α-diimines [22]) have often been observed by EPR spectroscopy. Most of these reactions were interpreted as oxidative additions of species L to the photogenerated $M(CO)_5$ radicals leading to one-electron oxidation of the metal and reduction of L with concomitant M–L bond formation. These reactions were often called "spin-trapping" and the appearance of EPR-active products $M(CO)_{5-n}L_n$ ($n = 1$, 2) was regarded as indirect evidence for the photoformation of $M(CO)_5$ radicals from the corresponding dimeric carbonyls $M_2(CO)_{10}$. However, no thorough mechanistic investigation of these reactions has been carried out so far, except for one study [12] limited to EPR observations of the formation of radical products during the photolysis of $Mn_2(CO)_{10}$ with *o*- and *p*-quinones under various experimental conditions.

Although EPR spectroscopy proved to be a very suitable method for studying radical formation in photochemical reactions, it may exaggerate the relative importance of the radical pathways owing to its high sensitivity. Also, when the spin-trapping technique is applied to metal-carbonyl photochemistry, EPR spectroscopy usually does not reveal the composition of the coordination sphere, namely the number of carbonyl ligands. In order to understand the mechanism of "spin-trapping" reactions involving quinones as "traps" and to characterize unequivocally their various intermediates and products, we have undertaken a combined FTIR and EPR study of the photochemistry of $M_2(CO)_{10}$ (M = Mn, Re) in the presence of the *ortho*- and *para*-quinones, *o*- and *p*-DBQ *, respectively (see Fig. 1). In order to obtain a better insight into the mechanisms of the photoreactions, both coordinating and inert solvents were employed and the reactions studied at different temperatures.

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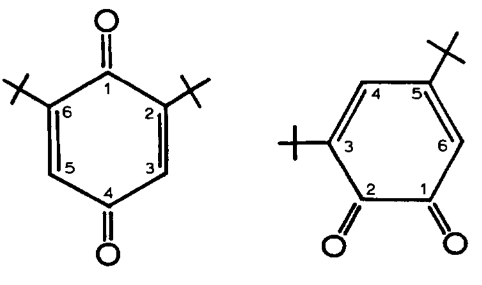
* The following abbreviations are used: *p*-DBQ = 2,6-di-tert-butyl-1,4-benzoquinone, *o*-DBQ = 3,5-tert-butyl-1,2-benzoquinone. DBSQ stands for the corresponding radical anions, DBSQ = DBQ^{-}. The prefixes *O*- and *O,O*-are used to denote the coordination of *o*-DBQ via one or two oxygen atoms, respectively.

The products of these reactions, especially the *o*-semiquinone complexes of Re(I), are themselves very interesting because of their radical character and great intrinsic stability. They exhibit interesting spectroscopic, structural and chemical properties [15,24–26], and are also intermediates in the synthesis of other Re(I)-semiquinone [27], Re(VI)-catecholate [28,29] and Mn(II)-semiquinone complexes [30].

Experimental

Both *o*- and *p*-DBQ were obtained from Aldrich. The *p*-DBQ was vacuum-sublimed and *o*-DBQ was recrystallized from heptane. $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (Fluka, Strem) were vacuum-sublimed and used as obtained, respectively. 4,4′-Dimethyl-2,2′-bipyridine (bpy′, Aldrich) was used as received. The complexes $M_2(CO)_8(bpy')$ ($M = Mn$, Re) were synthesized by published procedures [31,32]. All solvents including pyridine were of spectroscopic grade. THF was purified by distillation from sodium/benzophenone under an inert atmosphere. Toluene was distilled from sodium and 2-chlorobutane from anhydrous $CaCl_2$. All samples were fershly prepared by Schlenk-techniques under pure argon. Irradiation by daylight was excluded.

Irradiation was carried out on samples in IR or EPR-cells which had been placed in the sample holders of the spectrometers. An Osram HBO 200 W mercury lamp was used in the EPR experiments. The 366 nm and 313 nm mercury lines were selected for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, respectively, in order to irradiate into the $\sigma_b \rightarrow \sigma^*$ transitions of these complexes. The light intensity was diminished by a slit during most EPR experiments in order to generate only a low concentration of M-semiquinone radicals, otherwise concentration-broadening took place and spectral resolution was significantly decreased. During the IR experiments, irradiation was carried out with the 351 and 364 nm lines (power 10 mW) of a Spectra Physics 2025 argon-ion laser. Preliminary experiments were performed to establish the influence of the light source on the photoreactions. For this purpose the solutions containing the quinone and $M_2(CO)_{10}$ were irradiated in two separate experiments by the 351/364 nm lines of the argon-ion laser and the appropriate line of the mercury lamp, respectively. Since the same products were formed, laser light was used in all subsequent IR experiments because of its much higher intensity. Usually, $4\text{–}5 \times 10^{-3}$ *M* $M_2(CO)_{10}$ with a 2 to 10-fold excess of quinone was used. In most of



p–DBQ o–DBQ

Fig. 1. Structures of the *ortho*- and *para*-quinones used.

Table 1

CO stretching frequencies of the most relevant manganese and rhenium compounds.

Compound	*T* (K)	solvent	ν(CO) (cm^{-1}) [a]							
Mn$_2$(CO)$_{10}$	183	toluene	2046 s	2022 w	2009 s	1982 m				
Re$_2$(CO)$_{10}$	RT	toluene	2070 m	2011 s	1970 m					
Mn$_2$(CO)$_9$	90	2-Cl-But	2082 vw	2054 w	2021 m	1995 s	1984 s	1965 m	1938 m	1759 vw
Mn$_2$(CO)$_9$(*o*-DBQ)	220	2-Cl-But	2082 w	2029 m	1997 s	1981 s				
Mn$_2$(CO)$_9$(*p*-DBQ)	220	toluene	2086 w	2023 m	1992 s	1982 s	1976 sh			
Mn$_2$(CO)$_9$(*p*-DBQ)	220	pentane	2087 w	2027 m	1996 s	1983 s	1976 m			
Re$_2$(CO)$_9$(*p*-DBQ)	295	toluene	2099 w	2012 m	1994 s	1983 s	1965 m			
Mn$_2$(CO)$_9$(*p*-BQ) [b]	220	toluene	2086 m	2018 m	1987 s		1978 s	1959 m		
Mn$_2$(CO)$_9$(acetone)	220	toluene	2090 w	2020 m	1991 s		1978 s	1962 w		
Mn$_2$(CO)$_9$(THF)	RT	THF	2089 w	2016 m	1987 s		1976 s	1958 m		
Mn$_2$(CO)$_9$(2-MeTHF)	RT	2-MeTHF	2088 w	2016 m	1988 s		1977 s	1957 w		
Mn$_2$(CO)$_9$(PPh$_3$)	RT	THF	2090 w	2020 m	1991 s		1970 s	1934 m		
Mn(CO)$_5$(*p*-DBSQ)	183	toluene	2144 w	2055 vs	2001 m					
Re(CO)$_5$(*p*-DBSQ)	183	toluene	2154 w	2042 s	[c]					
Mn(CO)$_5$(*p*-BSQ) [b]	183	toluene	2141 w	2050 vs	[c]					
Mn(CO)$_5$(Me$_4$-*p*-BSQ) [b]	183	toluene	2138 w	2047 vs	[c]					
Mn(CO)$_5$Cl	RT	toluene	2139 w	2054 vs	1999 m					
Re(CO)$_5$Cl	RT	toluene	2143 w	2050 vs	1990 m					
Mn(CO)$_5$(*O*-*o*-DBSQ)	183	toluene	2138 w	2053 vs	1988 s					
Mn(CO)$_5$(4-Me-*O*-*o*-BSQ)	183	toluene	2141 w	2051 s	1998 m					
Mn(CO)$_5$(*O*-PSQ) [d]	183	CH$_2$Cl$_2$	2146 w	2054 s	1986 m					
Mn(CO)$_5$(*O*-ASQ) [e]	183	CH$_2$Cl$_2$	2146 w	2054 s	[c]					
Mn(CO)$_4$(*O*,*O*-*o*-DBSQ)	RT	toluene	2105 w	2029 s	2004 m	1960 m				
Re(CO)$_4$(*O*,*O*-*o*-DBSQ)	RT	toluene	2109 m	2010 s	1986 s	1943 s				
Mn(CO)$_4$- (4-Me-*O*,*O*-*o*-BSQ)	RT	toluene	2107 m	2030 s	2007 m	1962 s				

$Mn(CO)_4(O,O\text{-PSQ})$ [d]	183	CH_2Cl_2	2111 w	2030 s	2003 s	1957 m
$Mn(CO)_4(O,O\text{-ASQ})$ [e]	183	CH_2Cl_2	2100 m	2038 s	2004 s	1986 s
$Mn(CO)_4(PPh_3)Cl$ [f]	RT	THF	2091 m	2027 s	2010 s	1960 s
$Mn(CO)_3(THF)$-(O,O-o-DBSQ)	RT	THF	2030 s	1934 m	1923 sh	
$Re(CO)_3(THF)$-(O,O-o-DBSQ)	RT	THF	2020 s	1910 m	1902 m	
$Mn(CO)_3(CH_3CN)$-(O,O-o-DBSQ)	RT	toluene	2034 s	1948 m	1928 m	
$Mn(CO)_3(PPh_3)$-(O,O-o-DBSQ)	RT	toluene	2026 s	1931 m	1915 m	
$Mn(CO)_3(THF)_2$-(p-DBSQ)	RT	THF	2019 m	1905 s		
$Mn(CO)_3(acetone)_3^+$ [g]	RT	acetone	2021 vs	1931 vs		
$Mn(CO)_3(py)_3^+$ [g]	RT	CH_3CN	2041 vs	1947 vs		
$Mn(CO)_3(CH_3CN)_3^+$ [g]	RT	CH_3CN	2063 vs	1974 vs		
$Mn(CO)_3(bpy')$-(O-o-DBSQ)	RT	toluene	2023 s	1932 m	1911 m	
$Re(CO)_3(bpy')$-(O-o-DBSQ)	RT	toluene	2027 s	1927 m	1908 m	
$Mn(CO)_3(bpy')$-(p-DBSQ)	RT	THF	2024 s	1927 m	1916 m	
$Re(CO)_3(bpy')$-(p-DBSQ)	RT	toluene	2037 s	1918 m	1907 m	
$Mn(CO)_3(bpy)Br$ [h]	203	toluene	2027 s	1948 m	1913 m	
$Re(CO)_3(bpy)Br$ [h]	203	toluene	2022 s	1923 m	1897 m	

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[a] vs = very strong, s = strong, m = medium, w = weak, sh = shoulder. [b] B(S)Q = benzo(semi)quinone. [c] Obscured by bands from other photoproducts. [d] PSQ = 9,10-phenanthrenesemiquinone. [e] ASQ = acenaphthenesemiquinone. [f] From ref. 50. [g] From ref. 51. [h] From ref. 45.

the EPR experiments, the quinones were in 2-fold excess. The light was almost exclusively absorbed by $M_2(CO)_{10}$ except when the $Re_2(CO)_{10}$/*o*-DBQ mixture was irradiated with the laser light. However, irradiation into the *o*-DBQ-absorption band did not influence the overall photochemistry in this case, except for a parallel decrease of the *o*-DBQ concentration due to its own photodecomposition.

The IR spectra were measured on a Nicolet 7199B FT-IR interferometer with a liquid nitrogen-cooled MCT detector (32 scans, resolution 1.0 cm^{-1}). EPR spectra were obtained with Varian E-4 and Bruker ER 200D-MR X-band spectrometers with 100 kHz modulation. 2,2-Di-phenyl-1-picrylhydrazyl, (DPPH, Aldrich) was used as a standard ($g = 2.0037 \pm 0.0002$) for the determination of *g*-values.

Low temperature IR and ESR measurements were performed using an Oxford Instruments DN 1704/54 liquid nitrogen cryostat and the Bruker VT1000 temperature accessory, respectively. Electronic absorption spectra were recorded on a Perkin Elmer Lambda 5 spectrophotometer, equipped with a Perkin Elmer 3600 Data Station.

Results and discussion

Temperature and solvent dependent photolysis of $M_2(CO)_{10}$

The photoreactions of $M_2(CO)_{10}$ (M = Mn, Re) with quinones took place alongside the photoreactions between these carbonyls and the solvents. The latter reactions are rather complicated, especially for coordinating solvents [1–5, 33–35], and the possibility of a reaction between the quinone and some intermediate or product of a $M_2(CO)_{10}$–solvent photoreaction should therefore always be considered. Because of this, the photochemical behaviour of $M_2(CO)_{10}$ solutions in the absence of quinones will be discussed first.

Both carbonyls have been shown to form two primary photoproducts, $M(CO)_5$ radicals and $M_2(CO)_9$. Upon excitation with the 355 nm line of a Nd:YAG laser [6,7] the M–M bond splitting and CO dissociation appeared to have approximately the same quantum yield for Mn whereas in the case of Re the CO loss was about 10 times more important than the Re–Re splitting. Both $M(CO)_5$ radicals dimerize, the rate being nearly four times higher for Re than for Mn [6,7]. They also react rapidly with CCl_4, the rate constant for this reaction being 64 times larger for Re than for Mn [3,7]. The other photoproduct, $M_2(CO)_9$, which was shown [36] to contain a bridging CO in the case of Mn, was generated as the only photoproduct in alkane glasses at low temperatures [36]. In this work, a 2-chlorobutane glass at 90 K was used and $Mn_2(CO)_9$ and free CO were identified by their IR bands (Table 1). For both metals, $M_2(CO)_9$ recombines with CO when the glass is melted, the rate of this reaction being 10 times lower for Re than for Mn at room temperature [7]. Both $M(CO)_5$ and $M_2(CO)_9$ photoproducts may, in principle, react with quinones, although the reaction with $M_2(CO)_9$ is expected to be more important for Re than for Mn. In coordinating solvents, $M_2(CO)_9$ readily takes up a solvent molecule (S) to give $M_2(CO)_9S$ [1]. $Mn(CO)_5$ radicals behave as strong reductants in the presence of Lewis bases [1,2,36] due to the formation of 19-electron species of the type $Mn(CO)_5S$ and, especially, $Mn(CO)_3S_3$ [2,4,5,33,35]. It is however, unlikely that the latter species are formed via CO substitution of $Mn(CO)_5$ by the solvent molecules used in this study (THF, CH_3CN and 10^{-1} *M* pyridine in toluene). CH_3CN has definitely been shown not to substitute CO in $Mn(CO)_5$ [36] and photolysis of $Mn_2(CO)_{10}$ in pyridine produced only $Mn_2(CO)_9(py)$ and no $Mn_2(CO)_8(py)_2$ [34]. This is clear evidence against substitution of CO in $Mn(CO)_5$ by py since it is generally accepted that the complexes $Mn_2(CO)_8L_2$ are formed by dimerization of substituted $Mn(CO)_4L$ radicals [1]. On the other hand $Mn_2(CO)_9(py)$ is primarily formed by the reaction of $Mn_2(CO)_9$ with py. We studied the photolysis of $Mn_2(CO)_{10}$ in THF and 2-Me THF (S), and observed only $Mn_2(CO)_9S$ (Table 1), with no evidence for $Mn_2(CO)_8S_2$. This again rules out the substitution of CO in $Mn(CO)_5$ by THF or 2-MeTHF. Yet, in all these solvents (THF, CH_3CN, py) a photodisproportionation of $Mn_2(CO)_{10}$ into $Mn(CO)_3S_3^+$ (and to Mn^{2+} at a later stage) and $Mn(CO)_5^-$ occurred [33], which involves 19-electron $Mn(CO)_3S_3$ species as the key intermediates [4,5,33,35]. In view of the above observations, these intermediates are most probably not formed from the $Mn(CO)_5$ radicals, but instead by photosplitting of the Mn–Mn bond in $Mn_2(CO)_9S$. The $Mn(CO)_4S$ radicals thus formed may undergo a thermal substitution of the fourth CO by a solvent molecule. Addition of one more S molecule will produce the strongly reducing 19 electron complex $Mn(CO)_3S_3$ [2].

We have found peculiar photochemical behaviour of $Mn_2(CO)_{10}$ in 2-MeTHF upon variation of the temperature. In a 2-MeTHF glass at 77 K [36] or 88 K, $Mn_2(CO)_9$(2-MeTHF) was formed, whereas the dominating photoproduct in 2-MeTHF fluid solutions between 133 and 173 K was $Mn_2(CO)_5{}^-$, which was characterized by IR bands at 1890 and 1865 cm^{-1}. At 220 K, however, $Mn_2(CO)_9$(2-MeTHF) dominated again (Table 1) with only traces of $Mn(CO)_5^-$ being formed at the same time. The same photoproducts $Mn_2(CO)_9S$ (S = 2-MeTHF, THF) were obtained at room temperature and $Mn(CO)_5^-$ was formed only upon prolonged intense irradiation, especially by polychromatic light. These observations may be explained by considering the stability of the $Mn(CO)_5$–(2-MeTHF) bond. Up to 173 K the 19-electron $Mn(CO)_5$(2-MeTHF) species will be stable and will reduce both $Mn_2(CO)_{10}$ and $Mn_2(CO)_9$(2-MeTHF), ultimately forming $Mn(CO)_5^-$. As the temperature increases, this 19-electron species becomes less stable and $Mn_2(CO)_9$(2-MeTHF) predominantes. At room temperature, no $Mn(CO)_5$(2-MeTHF) will be formed out of the $Mn(CO)_5$ radicals and the photodisproportionation can only occur via secondary photolysis of $Mn_2(CO)_9$(2-MeTHF).

The photochemistry of $Re_2(CO)_{10}$ in coordinating solvents has not been studied in detail.

Photoreactions of $M_2(CO)_{10}$ with para*-quinones*

Non-coordinating solvents. Toluene, CH_2Cl_2 and 2-chlorobutane were used as solvents since they were found not to react photochemically with $Mn_2(CO)_{10}$ under the conditions used. In the case of $Re_2(CO)_{10}$ only toluene was used.

When the temperature of a 2-chlorobutane glass in which $Mn_2(CO)_9$ has been photogenerated at 90 K was raised in the dark above its melting point (ca. 130 K), $Mn_2(CO)_{10}$ was regenerated (small amounts of side-products due to unidentified impurities were also formed even in the most thoroughly purified solvents). When *p*-DBQ was present in the glass in a 100-fold excess over $Mn_2(CO)_{10}$, no formation of $Mn_2(CO)_9$ took place at 90 K but increasing the temperature to 210 K gave rise to the formation of another species in addition to $Mn_2(CO)_{10}$ as the main product and the impurities mentioned above. The new species is suggested to be $Mn_2(CO)_9$(*p*-DBQ) since its IR CO stretching frequencies closely resemble those of other $Mn_2(CO)_9L$ (L = acetone, THF) complexes (Table 1).

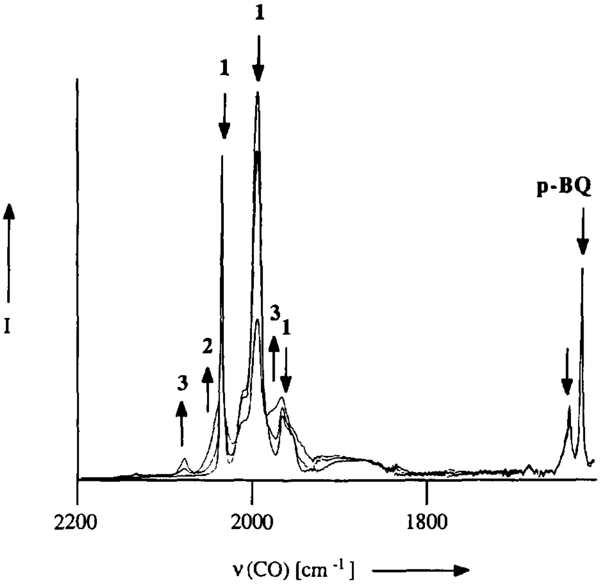

Fig. 2. IR spectral changes upon photolysis of a $Mn_2(CO)_{10}$/*p*-BQ (1 : 5) solution in toluene at 220 K with 351/364 nm (20 mW) light. (Bands are labelled as follows: 1 = $Mn_2(CO)_{10}$, 2 = $Mn(CO)_5$(*p*-BSQ), 3 = $Mn_2(CO)_9$(*p*-BQ).)

The same product was also formed in liquid non-coordinating solvents. At 220 K, it appeared to be the dominating photoproduct formed by photolysis of $Mn_2(CO)_{10}$ and *p*-DBQ in toluene, CH_2Cl_2 and 2-chlorobutane. Figure 2 shows the IR spectral changes during this reaction in toluene for the unsubstituted *p*-benzoquinone (*p*-BQ). The yield of $Mn_2(CO)_9$(*p*-DBQ) in CH_2Cl_2 at 220 K was unaffected by CCl_4 added in 10 to 150-fold excess over $Mn_2(CO)_{10}$. This clearly rules out any involvement of $Mn(CO)_5$ in its formation. $Mn_2(CO)_9$(*p*-DBQ) is obviously formed by a simple coordination of a quinone oxygen to the primary photoproduct $Mn_2(CO)_9$.

Above 220 K, $Mn_2(CO)_9$(*p*-DBQ) reacted thermally with photoproduced CO to give $Mn_2(CO)_{10}$. On the other hand, when a solution of $Mn_2(CO)_9$(*p*-DBQ) formed at 220 K was cooled down to 180 K in the dark, the photoproduct was thermally stable and decayed only slowly upon further photolysis.

The Re analogue, $Re_2(CO)_9$(*p*-DBQ), was formed upon photolysis of $Re_2(CO)_{10}$ and *p*-DBQ in toluene, and its IR spectrum resembled that of its Mn counterpart (see Table 1). This product could still be observed at 295 K, although at this temperature it slowly reunited with CO to form $Re_2(CO)_{10}$. It was, however, rather stable at 253 K, and this enabled us to measure its absorption spectrum in the visible region. An absorption band was observed at 720 nm that probably belongs to (a) Re(d_π) → quinone (π^*) MLCT transition(s), in analogy to a similar low-energy absorption band observed recently for the *p*-quinone complex $Cr(CO)_5$(*p*-DBQ) [38]. In addition to $Re_2(CO)_9$(*p*-DBQ), another species (IR band at 1936 cm^{-1}) was photoproduced both at 253 and 295 K, but its IR-spectrum did not allow a full characterization.

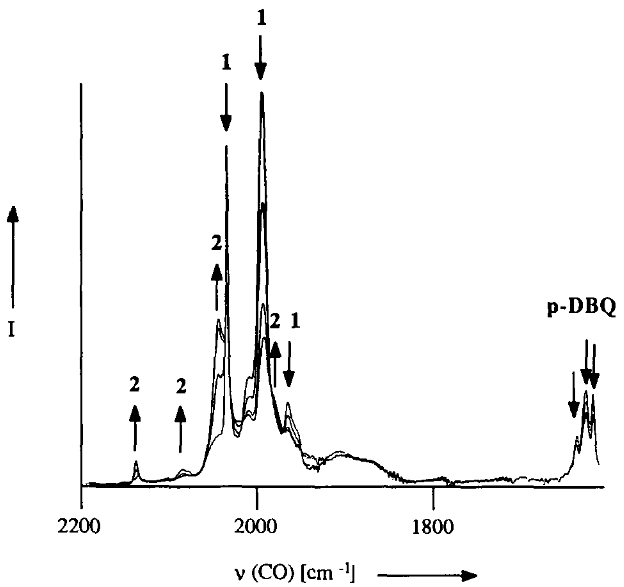

Fig. 3. IR spectral changes upon photolysis of a $Mn_2(CO)_{10}/p$-DBQ (1 : 5) solution in toluene at 183 K with 351/364 nm (20 mW) light. (Bands are labelled as follows: $1 = Mn_2(CO)_{10}$, $2 = Mn(CO)_5(p$-DBSQ).)

Obviously, p-DBQ behaves as a Lewis base towards the coordinatively unsaturated $M_2(CO)_9$ primary photoproduct and adds without electron transfer:

$$M_2(CO)_{10} \xrightarrow{h\nu} M_2(CO)_9 + CO \tag{1}$$

$$M_2(CO)_9 + p\text{-DBQ} \rightarrow M_2(CO)_9(p\text{-DBQ}) \tag{2}$$

(M = Mn, Re)

When, however, a solution of $M_2(CO)_{10}$ and p-DBQ in a non-coordinating solvent was irradiated below 220 K (see Figs. 3 and 4), much less $M_2(CO)_9(p$-DBQ) was formed, especially for Mn. At these temperatures a completely different product dominated for both carbonyls, its IR spectrum strongly resembling that of $M(CO)_5Cl$ (Table 1). At the same time, the irradiated solutions exhibited EPR spectra (Fig. 4, Table 2) with hyperfine splitting due to the metal nuclei (^{187,185}Re, $I = 5/2$; ^{55}Mn, $I = 5/2$). For Mn a narrow EPR signal was observed. The very small manganese splitting constant together with a g-value close to that of a free p-DBSQ (data Table 2) points to a Mn(I) complex with a p-DBSQ radical-anionic ligand loosely bound via its oxygen atom. In the case of $Re_2(CO)_{10}$ a broader ($\Delta H = 16.5$ G at 193 K), poorly resolved, signal was observed. Its shape is typical for an unresolved splitting due to $I = 5/2$ nuclei further complicated by line-width changes with magnetic field due to second-order effects. The g-factor is again very close to that of free p-DBSQ. Upon warming the solution in the dark, the width of the signal significantly decreased and between 295 and 308 K the signal collapsed into an unresolved narrow singlet ($\Delta H = 0.55$ G). Upon cooling again to 193 K in the dark, the signal resumed its original shape which means that the effect of the temperature on the EPR spectrum is not caused by a chemical transformation into a different radical. An identical but much weaker and narrow EPR signal was observed after photolysis

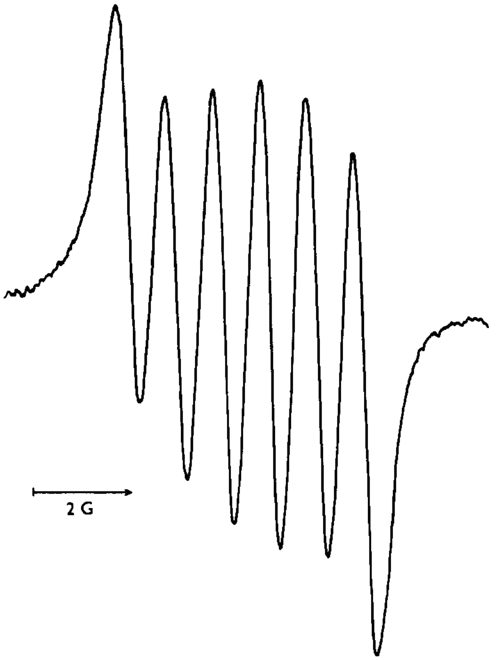

Fig. 4. EPR spectrum of $Mn(CO)_5(p\text{-DBSQ})$ generated by 366 nm-irradiation of 3.9×10^{-3} *M* $Mn_2(CO)_{10}$ and 3.7×10^{-3} *M* *p*-DBQ in toluene at 208 K.

of a toluene solution of $Re_2(CO)_{10}$ and *p*-DBQ at room temperature, but this signal rapidly decayed thermally (*vide infra*). Upon prolonged irradiation, another radical showed up, whose EPR-signal was a little broader and had exactly the same *g*-value but its overlap with the much stronger original signal precluded its analysis.

On the basis of the above IR and EPR data, the main photoproducts formed at 173–180 K are formulated as $M(CO)_5(p\text{-DBSQ})$ complexes with Mn and Re in the oxidation state I. These complexes could still be detected by IR as minor products at 220 K. The Re complex was even observable by EPR up to 295 K because of its greater thermal stability. At 223 and 203 K the formation of $Mn(CO)_5(p\text{-DBSQ})$ in CH_2Cl_2 was completely quenched already by a 10-fold excess of CCl_4, whereas the concomitant formation of $Mn_2(CO)_9(p\text{-DBQ})$ was unaffected even by a much larger excess of CCl_4 as evidenced by IR spectroscopy. This result clearly shows that $Mn(CO)_5(p\text{-DBSQ})$ is formed from the radicals, and rules out the possibility that $Mn_2(CO)_9(p\text{-DBQ})$ is formed by a secondary reaction involving $Mn(CO)_5(p\text{-DBSQ})$. According to the EPR spectrum, the formation of $Re(CO)_5(p\text{-DBSQ})$ in toluene at room temperature was only partially quenched by 10^{-1} *M* CCl_4 (20-fold excess), but completely scavenged by 1 *M* CCl_4.

From this it follows that the $Mn(CO)_5(p\text{-DBSQ})$ complexes are formed by one-electron oxidative addition of *p*-DBQ to the primary photoproducts $M(CO)_5$:

$$M_2(CO)_{10} \xrightarrow{h\nu} 2\ M(CO)_5 \tag{3}$$

$$M(CO)_5 + p\text{-DBQ} \rightarrow M^I(CO)_5(p\text{-DBSQ}) \tag{4}$$

(M = Mn, Re)

Table 2

EPR parameters [a] of the radical products of $M_2(CO)_{10}$/quinone photoreactions and related compounds

Compound	T(K)	Medium	g-factor	[a]M	[a]H	[a]N	Notes
p-DBSQ	295	THF	2.0051	–	2.0	–	[b], ref. 12
o-DBSQ	295	THF	2.0051	–	3.2	–	[b], ref. 12
$Mn(CO)_5(p\text{-DBSQ})$	208	toluene	2.006	0.94	–	–	[c]
	203	THF	–	1.56	0.53	–	[c]
	295	THF	2.0051	0.41	0.40	–	[c], ref. 12
$Mn(CO)_3(THF)_2(p\text{-DBSQ})$	295	THF	2.0048	1.5	0.8	–	[c], ref. 12
$Mn(CO)_3(py)_2(p\text{-DBSQ})$	295	10^{-1} M py/tol.	2.0051	–	–	–	[c], ref. 12
	295	10^{-1} M py/CH_2Cl_2	–	0.59	–	0.54	[c]
$Mn(CO)_3(bpy')(p\text{-DBSQ})$	295	toluene	2.0050	0.96	–	0.48	[c]
	295	THF	–	0.56	–	0.50	[c]
$Re(CO)_5(p\text{-DBSQ})$	295	toluene	2.0051	–	–	–	[c,d,e]
	295	THF	2.0052	1.5	–	–	[c,f]
"$Re(CO)_{5-n}(THF)_n(p\text{-DBSQ})$"	295	THF	2.0055	–	–	–	[c,e]
$Mn(CO)_5(O\text{-}o\text{-DBSQ})$	180	toluene	2.0045	2.3	[i]	–	[c]
$Mn(CO)_4(O,O\text{-}o\text{-DBSQ})$	295	toluene	2.0036	7.0	3.5	–	[c], ref. 12,20
$Mn(CO)_3(THF)(O,O\text{-}o\text{-DBSQ})$	295	THF	2.0044	3.7	3.5	–	[c,g]
$Mn(CO)_3(py)(O,O\text{-}o\text{-DBSQ})$	295	10^{-1} M py/tol.	2.0041	6.1	3.2	2.0	ref. 12
$Re(CO)_5(O\text{-}o\text{-DBSQ})$	193	toluene	2.005	5.5	–	–	[c,f]
$Re(CO)_4(O,O,o\text{-DBSQ})$	295	toluene	2.0022	28.2	3.46	–	[c]
	295	THF	2.0019	28.0	3.6	–	[c]
$Re(CO)_3(THF)(O,O\text{-}o\text{-DBSQ})$	295	THF	2.0043	7.5	–	–	[c,h]

[a] Splitting constants a in Gauss. a_H corresponds to hydrogen atoms at C3 and C5 positions of p-DBSQ and to a hydrogen atom at the C4 position of o-DBSQ [49]. [b] Electrochemically generated in the presence of 10^{-1} M Bu_4NPF_6. [c] This work. [d] $g = 2.006$, $a_{Re} = 1.9$ G at 193 K. [e] Narrow single-line signal. [f] Poorly resolved, distorted by second-order effect, a_{Re} roughly estimated. [g] Splitting due to hydrogen atoms of the C5-bound ^{t}Bu-group: $a_H = 0.26$ G. [h] Signal distorted by second-order effects, a_{Re} estimated (± 0.5 G). [i] Spectrum broadened by viscosity effects, $a_H \cong a_{Mn}$.

For Re, another parallel process not involving $Re(CO)_5$ apparently takes place, as shown by the quenching experiments. A photochemical intramolecular electron transfer of $Re_2(CO)_9(p\text{-DBQ})$ producing $Re^I(CO)_5(p\text{-DBSQ})$ and other, presumably polynuclear, Re complexes, seems to be a plausible explanation (recall the formation of a photoproduct at 253–295 K characterized by a 1936 cm^{-1} band that corresponds neither to $Re_2(CO)_9(p\text{-DBQ})$ nor to $Re(CO)_5(p\text{-DBSQ})$).

The thermal stability of the $M(CO)_5(p\text{-DBSQ})$ complexes strongly depends upon the metal. $Mn(CO)_5(p\text{-DBSQ})$ decomposed even 198 K to give $Mn_2(CO)_{10}$ as evidenced by the IR spectrum. For the intensity of its EPR signal a perfectly linear correlation was found between $1/I$ and time which points to a second-order process $k_{exp} = 1.85 \times 10^{-4}$ M^{-1} s^{-1} at 205 K whose rate strongly increased with temperature ($E_A \cong 40$ kJ mol^{-1}). The kinetic data point to a disproportionation (reaction 5) that must involve some interaction between the

$$2\,Mn(CO)_5(p\text{-DBSQ}) \rightarrow Mn_2(CO)_{10} + 2\,p\text{-DBQ} \qquad (5)$$

two $Mn(CO)_5(p\text{-DBSQ})$ molecules. An analogous decay mechanism has been found for nitroxide Aryl–N(O·)–$Re(CO)_5$ spin adducts [11]. The high rate of this reaction at $T > 220$ K together with the rapid recombination of $Mn_2(CO)_9(p\text{-DBQ})$ with CO explains why no carbonyl-containing photoproducts were observed upon irradiation of $Mn_2(CO)_{10}/p\text{-DBQ}$ solutions in non-coordinating solvents at room temperature. The species assumed to contain p-DBSQ bound to Mn via its C atom described by Foster and Wan [13] was never observed in our experiments. This may be due to the fact that Foster and Wan irradiated their solution with the 337 nm line of a high-power (1 MW) N_2-laser. $Re(CO)_5(p\text{-DBSQ})$ on the other hand appeared to be much more stable. At room temperature it decomposed thermally by first-order kinetics (ln(EPR intensity) vs. time afforded a linear correlation) with a rate-determining reductive elimination of p-DBQ (reactions 6 and 7) just as in the case of the anilino Aryl–N · –O–$Re(CO)_5$ adducts [11].

$$Re(CO)_5(p\text{-DBSQ}) \leftrightharpoons Re(CO)_5 + p\text{-DBQ} \tag{6}$$

$$2\ Re(CO)_5 \rightarrow Re_2(CO)_{10} \tag{7}$$

Both photoproducts $M(CO)_5(p\text{-DBSQ})$ and $M_2(CO)_9(p\text{-DBQ})$ were formed by photolysis of toluene solutions at 183 K, the former product always strongly dominating at this temperature. In order to establish quantitatively the relative efficiences of the formation of $M_2(CO)_9(p\text{-DBQ})$ at 183 K for Re and Mn, the intensities of well-developed bands of $M_2(CO)_9(p\text{-DBQ})$ (2086 cm^{-1} (Mn) and 2100 cm^{-1} (Re)) were measured with respect to those of $M_2(CO)_{10}$ (2009 cm^{-1} (Mn) and 2008 cm^{-1} (Re)) during the photoreaction. For both decacarbonyls the starting concentrations and the intensities of their 2009, 2008 cm^{-1} bands were the same. When 50% of $M_2(CO)_{10}$ had reacted, the resulting absorption ratios of these $\nu(CO)$ bands were 0.04 for Mn and 0.15 for Re. This implies that at 183 K $M_2(CO)_9(p\text{-DBQ})$ is formed almost four times more efficiently for Re than for Mn, provided that the extinction coefficients of the $\nu(CO)$ bands do not depend on the metal. The equal starting $M_2(CO)_{10}$ absorptions show that this assumption holds for these decacarbonyls (see also ref. 39). Although the correctness of this assumption could not be proven for the $M_2(CO)_9(p\text{-DBQ})$ complexes owing to their thermal instability, its validity has been demonstrated for the corresponding IR bands of $(CO)_5MM'(CO)_4(PPh_3)$ (M, M' = Mn, Re) [40]. The higher efficiency for the formation of $Re_2(CO)_9(p\text{-DBQ})$ may best be explained in terms of the different properties of the $M_2(CO)_9$ primary photoproducts. $Re_2(CO)_9$ reunites with CO ten times more slowly than $Mn_2(CO)_9$, and is also formed nearly then times more efficiently that $Mn_2(CO)_9$ during the primary photoreaction of $M_2(CO)_{10}$ [7], *vide supra*.

Between 173 and 180 K the radical adducts $M(CO)_5(p\text{-DBSQ})$ dominate, whereas the $M_2(CO)_9(p\text{-DBQ})$ complexes are only minor products. At 220 K on the other hand, $M_2(CO)_9(p\text{-DBQ})$ is the main product whereas only traces of the radical adduct are found. This effect has to be due to a difference in the efficiency of $M_2(CO)_9(p\text{-DBQ})$ formation at these temperatures since both $M_2(CO)_9(p\text{-DBQ})$ complexes are thermally stable at 183 K and photochemically less labile than $M(CO)_5(p\text{-DBSQ})$. Moreover, the latter products do not participate in the formation of $M_2(CO)_9(p\text{-DBQ})$ as was shown by the quenching experiment discussed above. A possible explanation involves different activation energies for the reactions of CO and p-DBQ with $M_2(CO)_9$. If the activation energy of the CO addition is lower, $M_2(CO)_9$ will recombine faster with CO than with p-DBQ at 173–180 K, whereas the p-DBQ addition might be more competitive at 220 K. The very fast recombination of $Mn_2(CO)_9$ with CO became evident when a glass containing these molecules was raised in temperature above its melting point (e.g. 2-MeTHF, 130 K);

$Mn_2(CO)_{10}$ was formed instantly, and no $Mn_2(CO)_9$ was ever observed in fluid solutions. The yield of $Mn_2(CO)_9$(*p*-DBQ) increased only by 10% when the molar excess of *p*-DBQ was increased from 2-fold to 1000-fold over $Mn_2(CO)_{10}$ in toluene solutions at 183 K. Replacement of *p*-DBQ by an unsubstituted *p*-benzoquinone (*p*-BQ) doubled the yield of $Mn_2(CO)_9$(*p*-BQ). This is in accordance with statistics arising from the steric factors since *p*-BQ has two oxygen donor atoms available and *p*-DBQ only one owing to the steric hindrance by the tert-butyl groups. Steric hindrance is probably the main reason for the higher activation energy for the quinone-addition to $Mn_2(CO)_9$ compared to that for CO-addition. The recombination of $Mn_2(CO)_9$ with CO is obviously so fast at 183 K that the reaction with *p*-quinones is not competitive even when a large excess of quinone is used. The increased solvent viscosity at this temperature may also contribute to this effect. For all the *p*-quinones used (*p*-DBQ, *p*-BQ, 2,3,5,6-tetra-methyl-1,4-benzoquinone), the $Mn(CO)_5$(*p*-semiquinone) complex is the main product observed (Table 1) in toluene at 183 K regardless the first reduction potentials, −0.67, −0.32, −0.69 V, respectively, vs. SCE in DMF [41]. This shows that the ability of the quinone to add oxidatively to $Mn(CO)_5$ or to coordinate to $Mn_2(CO)_9$ is not determined by electronic factors. In order to compare the reactivity of different Mn radicals and to investigate the EPR spectra of substituted Mn-carbonyl-*p*-semiquinone complexes, the photoreaction between $(CO)_5MnMn(CO)_3(bpy')$ and *p*-DBQ was investigated in toluene at room temperature with irradiation with 546 nm light. This compound is known [1,2,31,42] to undergo a Mn–Mn bond homolysis upon irradiation by visible light, producing ultimately $Mn_2(CO)_{10}$ and $Mn_2(CO)_6(bpy')_2$. In the presence of *p*-DBQ a radical was formed that was characterized by a 15-line EPR spectrum that showed a splitting caused by one manganese and two symmetrically equivalent nitrogen nuclei ^{14}N ($I = 1$), see Table 2, Fig. 5. The *g*-value was again very close to that of free *p*-DBSQ. From this EPR spectrum the radical was

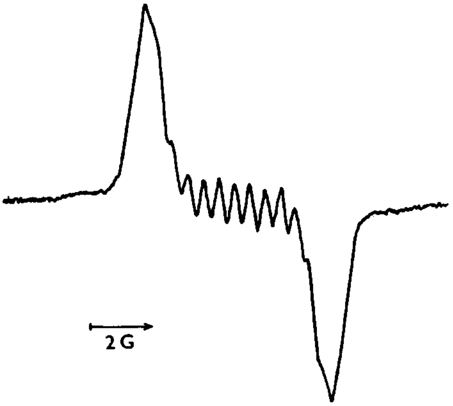

Fig. 5. EPR spectrum of $Mn(CO)_3(bpy')$(*p*-DBSQ) generated by 546 nm-irradiation of 10^{-2} *M* $Mn_2(CO)_8(bpy')$ and 2×10^{-2} M *p*-DBQ in toluene at 295 K.

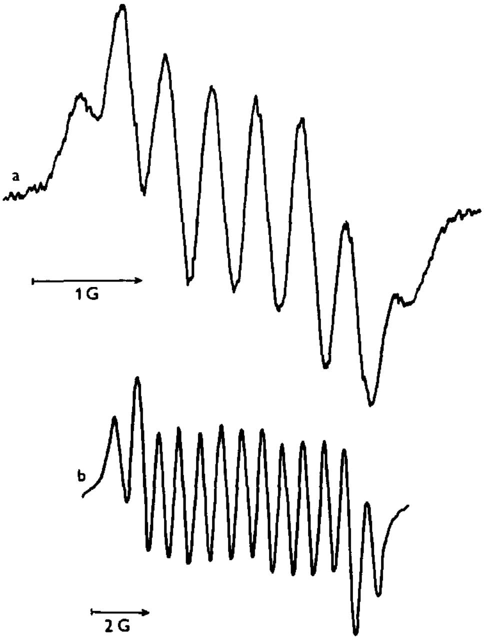

Fig. 6. EPR spectra of **a**: $Mn(CO)_5(p\text{-DBSQ})$ generated by 366 nm-low intensity irradiation of 5×10^{-3} *M* $Mn_2(CO)_{10}$ and 10^{-2} *M* *p*-DBQ in THF at 295 K. **b**: $Mn(CO)_3(THF)_2(p\text{-DBSQ})$ obtained by prolonged intense 366 nm-irradiation of 10^{-2} *M* $Mn_2(CO)_{10}$ and 2×10^{-2} *M* *p*-DBQ in THF at 295 K, measured after interruption of the irradiation.

identified as *fac*-$Mn(CO)_3(bpy')(p\text{-DBSQ})$, formed by an oxidative addition reaction:

$$Mn_2(CO)_8(bpy') \xrightarrow{h\nu} Mn(CO)_5 + Mn(CO)_3(bpy') \qquad (8)$$

$$Mn(CO)_3(bpy') + p\text{-DBQ} \rightarrow Mn(CO)_3(bpy')(p\text{-DBSQ}) \qquad (9)$$

This assignment was confirmed by the IR spectrum of the product, which exhibited the bands of a fac-$Mn(CO)_3^+$ structural unit (see Table 1). The product is thermally stable but it decomposed slowly upon prolonged irradiation with 546 nm without formation of any other EPR-active species. *p*-DBQ adducts of $Mn(CO)_5$ were not detected due to their thermal instability at 298 K (*vide supra*).

Coordinating solvents. In coordinating solvents, the $M_2(CO)_{10}/p$-DBQ photoreactions become more complex. The mechanism of the photoreaction in THF has already been studied by one of us [12] mainly by monitoring the intensity changes of two EPR signals that appear successively under continuous irradiation. It was concluded that two sequential photoprocesses take place. By using less concentrated solutions and low-intensity light (to generate radicals in low concentration in order to avoid concentration line-broadening) it was now possible to resolve the EPR signal that appeared immediately at the beginning of the photoreaction of $Mn_2(CO)_{10}$ and *p*-DBQ in THF at room temperature, Fig. 6. This EPR spectrum shows a splitting due to one Mn atom and two symmetrical hydrogen atoms ^1H ($I = 1/2$) (Table 2), which proves that the photoproduct contains the *p*-DBSQ radical anion directly bound to a Mn central atom via its oxygen atom [43,44]. Its

EPR spectrum could only be studied under continuous irradiation since it decomposed thermally very rapidly without formation of any EPR active species. In order to determine the number of CO ligands present in this radical, the photoreaction of $Mn_2(CO)_{10}$ with *p*-DBQ in THF and in 2-MeTHF was monitored by IR and EPR spectroscopy at lower temperatures. In 2-MeTHF the only photoproduct observed with IR at 173 K appeared to be $Mn(CO)_5$(*p*-DBSQ), its IR spectrum being identical to that observed in toluene (Table 1). At 220 K, $Mn_2(CO)_9$(2-MeTHF) was the main product and only traces of $Mn(CO)_5$(*p*-DBSQ) were detected by IR spectroscopy. However, the fast thermal decomposition of $Mn(CO)_5$(*p*-DBSQ) precluded observation of any of its IR bands at room temperature. Irradiation of $Mn_2(CO)_{10}$ and *p*-DBQ in THF at 183–223 K with low intensity 366 nm light caused the appearance of a well developed EPR sextet of triplets due to one ^{55}Mn and two equivalent ^{1}H nuclei. The a_{Mn} splitting constant decreased markedly with increasing temperature: 1.68 G (183 K), 1.56 G (203 K), 1.32 G (223 K), 0.99 G (253 K), whereas a_H decreased much less: 0.61 G (183 K), 0.53 G (223 K). In this way the whole signal gradually changed its shape into that observed at room temperature at the beginning of the irradiation (Fig. 6a, $a_{Mn} = 0.41$ G, $a_H = 0.40$ G), this transformation being caused by changes of the splitting constants and not by a chemical change of the radical. Obviously, this signal belongs to the $Mn(CO)_5$(*p*-DBSQ) complex. This conclusion was supported by the lack of any IR evidence for the substitution of CO in $Mn(CO)_5$(*p*-DBSQ) by THF in the temperature range 183–220 K. The greater thermal stability of this complex in THF than in toluene is probably attributable to the much better solvation by the polar THF molecules.

Upon further photolysis at room temperature, the intensity of the EPR signal of $Mn(CO)_5$(*p*-DBSQ) decayed and another signal with the same splitting pattern but with larger a_{Mn} and a_H constants appeared [12] after an induction period, (Fig. 6). The *g*-factors of both signals are nearly the same, and fall well within the range typical for *p*-DBSQ radicals (Table 2). In accordance with previous observations [12], the second spectrum is assigned to the $Mn(CO)_3(THF)_2$(*p*-DBSQ) radical. The formation of both radicals was quenched even by low concentrations (2×10^{-2} *M*) of CCl_4. Traces of other radicals were observed at the beginning of the irradiation with CCl_4, but these were clearly different from both $Mn(CO)_5$(*p*-DBSQ) and $Mn(CO)_3(THF)_2$(*p*-DBSQ).

At room temperature, the only photoproduct observed in the IR of the reaction between $Mn_2(CO)_{10}$ and *p*-DBQ in THF was $Mn_2(CO)_9$(THF). It was present from the very beginning and its concentration built up in the course of the irradiation. Upon prolonged irradiation by either the 366 nm line of the mercury lamp or the 351 and 364 nm lines of the argon-ion laser (10 mW), the concentration of $Mn_2(CO)_9$(THF) decreased and new bands showed up at 2019 (m) and 1905 cm^{-1} (s) after a distinct induction period. These bands, which are typical of a complex containing an $Mn(CO)_3{}^+$ structural unit (Table 1), obviously belong to the same compound that was observed in THF by EPR at later stages of the photoreaction. The assignment of this EPR signal to $Mn(CO)_3(THF)_2$(*p*-DBSQ) has thus been confirmed independently by IR spectroscopy. The intensities of both the EPR and IR signals showed however, that this species was formed in rather low yield.

The above experimental evidence points to the following mechanism for the reaction in THF at room temperature:

(i) $Mn(CO)_5$ and $Mn_2(CO)_9$(THF) are both formed as primary photoproducts.

(ii) p-DBQ adds oxidatively to $Mn(CO)_5$ via reaction 4 and the resulting $Mn(CO)_5(p\text{-DBSQ})$ decays by reaction 5.
(iii) In addition, $Mn_2(CO)_9(THF)$ may undergo the secondary photochemical reaction 10, proposed by Meyer and Caspar [2]:

$$Mn_2(CO)_9(THF) \xrightarrow{h\nu} Mn(CO)_5 + Mn(CO)_4(THF) \tag{10}$$

The $Mn(CO)_5$ radicals formed then take up a p-DBQ molecule, thus contributing to the further formation of $Mn(CO)_5(p\text{-DBSQ})$ (step ii)).
(iv) After an induction period, the concentration of $Mn(CO)_5(p\text{-DBSQ})$ and hence its light absorption is high enough to start the photoreaction 11:

$$Mn(CO)_5(p\text{-DBSQ}) \xrightarrow[THF]{h\nu} Mn(CO)_3(THF)_2(p\text{-DBSQ}) + 2CO \tag{11}$$

$Mn(CO)_3(THF)_2(p\text{-DBSQ})$ is then formed as a final photoproduct. Its concentration will, however, be small since reaction 5 is very competitive. p-DBQ may, in principle, also add oxidatively to $Mn(CO)_4(THF)$ formed in reaction 10, producing ultimately $Mn(CO)_3(THF)_2(p\text{-DBSQ})$. Although this is consistent with experimental results, definite proof is still lacking. Preliminary investigations of the thermal reaction of $Mn_2(CO)_9(THF)$ with p-DBQ, *vide infra*, do not favour this reaction between $Mn(CO)_4THF$ and p-DBQ. The photolysis of $Mn_2(CO)_8(bpy')$ by the 546 nm Hg line was also studied in THF at room temperature. A thermally stable radical was formed, which had the same IR CO-stretching frequencies as $Mn(CO)_3(bpy')(p\text{-DBSQ})$ produced in toluene (*vide supra*, Table 1), showing that no substitution of CO by THF had occurred. The EPR spectrum exhibited splittings due to one manganese atom and two symmetrically equivalent nitrogen atoms. The value of a_{Mn} was about half that in toluene.

The photoreaction between $Mn_2(CO)_{10}$ and p-DBSQ was also monitored by EPR spectroscopy for solutions in toluene and in CH_2Cl_2 containing 10^{-1} M pyridine. A strong EPR signal was present from the very beginning of the irradiation [12]. We have now resolved this signal by using CH_2Cl_2 instead of toluene and by avoiding concentration-broadening. It exhibited splittings due to one manganese atom and two symmetrically equivalent nitrogen atoms (Fig. 7), very similar to that of $Mn(CO)_3(bpy')(p\text{-DBSQ})$ in THF. This signal was thus attributed to *fac*-$Mn(CO)_3(py)_2(p\text{-DBSQ})$. Its formation was completely quenched by 10^{-1} M CCl_4. Thus, $Mn(CO)_3(py)_2(p\text{-DBSQ})$ will be formed by oxidative addition of p-DBQ to the primary photoproduct $Mn(CO)_5$ and to the $Mn(CO)_5$ and $Mn(CO)_4(py)$ radicals formed by secondary photolysis of $Mn_2(CO)_9(py)$ [2,34]. Substitution of CO ligands in $Mn(CO)_5(p\text{-DBSQ})$ by py was much faster than by THF and it seemed to occur thermally as well.

Upon prolonged irradiation, another EPR signal showed up [12] which had exactly the same g-value and looked like a "satellite" to the signal of $Mn(CO)_3(py)_2(p\text{-DBSQ})$. Its width (7.5 G) ruled out the previous [12] attribution of this EPR signal to the free p-DBSQ radical-anion [12]. It was instead tentatively assigned to $Mn(CO)_2(py)_3(p\text{-DBSQ})$ but further analysis was prevented by the strong overlap with the much more intense signal of $Mn(CO)_3(py)_2(p\text{-DBSQ})$. The value of a_{Mn} was roughly estimated from the signal- and line-widths to be 1.3 G. Both compounds thermally decomposed, the dicarbonyl decayed faster. The same radicals were formed in CH_2Cl_2 as well as toluene in the presence of 10^{-1} M py.

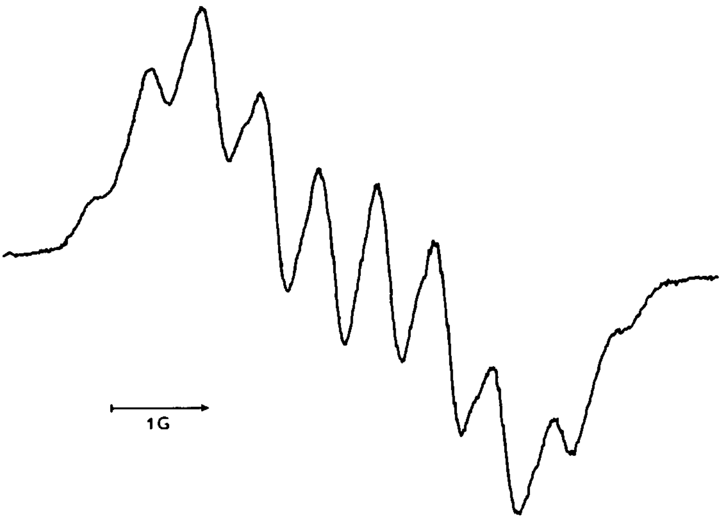

Fig. 7. EPR spectrum of $Mn(CO)_3(py)_2(p\text{-DBSQ})$ obtained by 366 nm-photolysis of 5×10^{-3} *M* $Mn_2(CO)_{10}$, 10^{-2} *M* *p*-DBQ and 10^{-1} M pyridine in CH_2Cl_2 at 295 K.

The EPR signal of $Mn(CO)_3(py)_2(p\text{-DBSQ})$ was better developed in CH_2Cl_2 whereas the "satellite" was better resolved in toluene.

Finally, it should be noted that a very weak EPR signal belonging to $Mn(CO)_5(p\text{-DBSQ})$ was observed when *p*-DBQ was added in the dark to a previously irradiated solution of $Mn_2(CO)_{10}$ in THF. No $Mn(CO)_3(THF)_2(p\text{-DBSQ})$ was formed at all. Upon addition of *p*-DBQ in the dark to a pre-irradiated solution of $Mn_2(CO)_{10}$ in 10^{-1} *M* py/toluene a slowly increasing EPR signal due to $Mn(CO)_3(py)_2(p\text{-DBSQ})$ was observed. (Traces of $Mn(CO)_2(py)_3(p\text{-DBSQ})$ were also present immediately after addition of *p*-DBQ.) The thermal formation of $Mn(CO)_3(py)_2(p\text{-DBSQ})$ was slowed down but not completely quenched when 10^{-1} *M* CCl_4 was added to the solution just before the addition of *p*-DBQ. These radical complexes are most probably formed by reaction of the photoproduct $Mn_2(CO)_9L$ (L = THF, py) with *p*-DBQ. It is noteworthy that free *p*-DBSQ has never been observed, which argues against a simple outer-sphere electron transfer. The transience of the formation of $Mn(CO)_3(py)_2(p\text{-DBSQ})$ and its inefficient quenching by CCl_4 shows that these thermal reactions do not contribute significantly to the photochemistry described above. This conclusion is also supported by the observation that the intensities of the EPR signals of the thermally produced *p*-DBSQ complexes are lower than those observed after direct photolysis of $Mn_2(CO)_{10}$ and *p*-DBQ.

The photochemistry of $Re_2(CO)_{10}$ with *p*-DBQ in THF has also been followed by EPR. From the beginning of the irradiation there was a signal centred at $g = 2.0052$ (Fig. 8). It exhibited poorly resolved splittings due to a Re nucleus and resembled the signal of $Re(CO)_5(p\text{-DBSQ})$ in low-temperature toluene solution. The value of a_{Re} was roughly estimated as 1.5 G. Subsequently another, much narrower, signal, with $g = 2.0055$, began to develop. When the irradiation was interrupted, the former signal decreased and the latter increased thermally. On the basis of the *g*-values and the small a_{Re}, both signals were tentatively assigned to $Re(CO)_{5-n}(THF)_n(p\text{-DBSQ})$

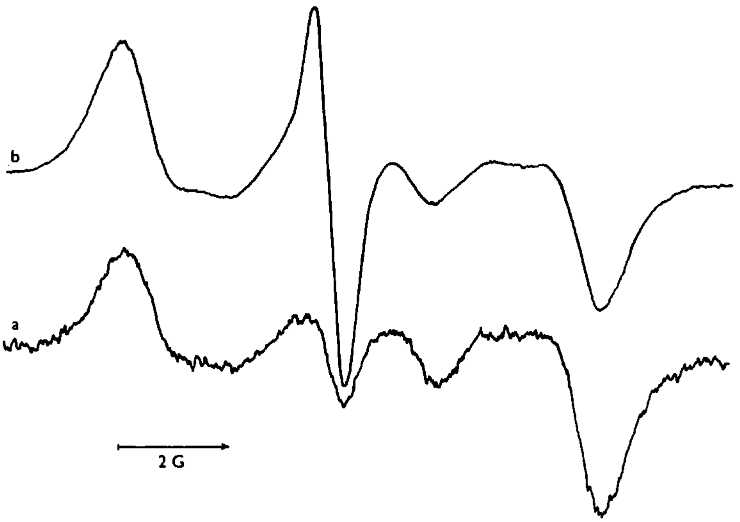

Fig. 8. EPR spectra of products obtained by 313 nm-photolysis of 5×10^{-3} *M* $Re_2(CO)_{10}$ and 10^{-2} *M* *p*-BDQ in THF at 295 K. **a**: spectrum obtained at the beginning of the irradiation, assigned to $Re(CO)_5$(*p*-DBSQ). **b**: after further irradiation and standing in the dark for 2 minutes. The new signal in the centre is formed thermally. Spectrum **b** was recorded with a sensitivity 2.5-times lower than that of spectrum **a**.

radicals that only differ in the number of CO-ligands. The former broader spectrum most probably belongs to $Re(CO)_5$(*p*-DBSQ). Their formation was only partially quenched by 10^{-1} *M* CCl_4, but completely by 1 *M* CCl_4. As in the case of the solutions in toluene, $Re_2(CO)_9$(*p*-DBQ) seemed to be involved in the reaction mechanism.

Photoreactions of $M_2(CO)_{10}$ with ortho-*quinones*

The photoreactions of $M_2(CO)_{10}$ (M = Mn, Re) with *o*-quinones studied so far have mostly been interpreted as oxidative additions of quinones to photogenerated $M(CO)_5$ radicals [12,14–18,20,21]. The M(I)-semiquinone complexes of the type $M(CO)_3(L)$(*O,O-o*-SQ) (M = Mn, Re; L = CO, Lewis base; *O,O-o*-SQ = *o*-semiquinone radical–anionic ligand bound to the metal via both oxygen donor atoms) were the only final products observed. However, we have observed by EPR spectroscopy that the formation of these complexes both in toluene and THF is unaffected by 10^{-1} *M* CCl_4 and only partially quenched by 1 *M* CCl_4 (200-fold excess over $M_2(CO)_{10}$). This rather surprising result led us to a more detailed investigation of the role of the $M_2(CO)_9$ photoproduct in the reaction mechanism.

$Mn_2(CO)_9$ was generated photochemically in a 2-chlorobutane glass containing a 100-fold excess of *o*-DBQ. When the temperature was raised in the dark to 220 K most of the photoproduct recombined with CO to produce $Mn_2(CO)_{10}$. At the same time, however, a weak IR band showed up at 2082 cm^{-1} together with some other bands (Table 1) indicating that $Mn_2(CO)_9$(*O-o*-DBQ) (*O-o*-DBQ stands for the *o*-DBQ ligand coordinated by one oxygen atom only) had been formed since the main IR band of the corresponding $Mn_2(CO)_9$(*p*-DBQ) complex was observed at 2086 cm^{-1}, *vide supra*. This reaction shows that *o*-DBQ coordinates to $Mn_2(CO)_9$ as a simple Lewis base, exactly as *p*-DBQ does. $Mn_2(CO)_9$(*O-o*-DBQ) was, however, not stable at the temperature at which it was formed (220 K) and reacted thermally to give $Mn(CO)_4(O,O\text{-}o\text{-}DBSQ)$, which was characterized by IR spectroscopy (*vide infra*, Table 1). When the 2-chlorobutane glass contained only a 10-fold excess of *o*-DBQ, no $Mn_2(CO)_9(O\text{-}o\text{-}DBQ)$ was detected and $Mn_2(CO)_{10}$ was obtained as the main product upon melting of the glass. On the other hand, traces of $Mn(CO)_5(O\text{-}o\text{-}DBSQ)$ and $Mn(CO)_4(O,O\text{-}o\text{-}DBSQ)$ were detected when the temperature was raised to 170 or 220 K, respectively.

Similar behaviour was observed in THF. The $Mn_2(CO)_9(THF)$ complex was generated by photolysis of $Mn_2(CO)_{10}$ in THF in a Schlenk tube at room temperature. This solution was cooled to 233 K and *o*-DBQ then added. No thermal reaction took place at 233 K. When the temperature was raised to 283 K, $Mn(CO)_3(THF)(O,O\text{-}o\text{-}DBSQ)$ was produced and characterized by IR spectroscopy (Table 1), *vide infra*.

The above evidence points to the following mechanism for the formation of $Mn(CO)_3L(O,O\text{-}o\text{-}DBSQ)$ (L = CO, THF) via the primary photoproduct $Mn_2(CO)_9$:

$$Mn_2(CO)_9 + o\text{-}DBQ \rightarrow Mn_2(CO)_9(O\text{-}o\text{-}DBQ) \tag{14}$$

$$Mn_2(CO)_9 + THF \rightarrow Mn_2(CO)_9(THF) \tag{15}$$

$$Mn_2(CO)_9(THF) + o\text{-}DBQ \leftrightharpoons Mn_2(CO)_9(O\text{-}o\text{-}DBQ) + THF \tag{16}$$

$$Mn_2(CO)_9(O\text{-}o\text{-}DBQ) \rightarrow Mn(CO)_5 + Mn^I(CO)_4(O,O\text{-}o\text{-}DBSQ) \tag{17}$$

The last reaction represents a thermal intramolecular Mn → *o*-DBQ one-electron transfer that results in Mn–Mn bond splitting. The reactions of $Re_2(CO)_9$ were not studied in such detail. The same mechanism (eqs. 14–17) seems, however, to apply here since the radical products were only partially quenched with 1 *M* CCl_4 as observed by EPR.

Irradiation of $Mn_2(CO)_{10}$ and *o*-DBQ in CH_2Cl_2, toluene or 2-MeTHF at 180 K afforded species whose IR spectra resembled those of $M(CO)_5X$ (X = *p*-DBSQ, Cl), see Table 1. The EPR spectrum (Fig. 9) recorded at 188 K for the Mn complex exhibited a splitting due to one Mn atom and one hydrogen atom. The *g*-value was very similar to that for free *o*-DBSQ and the value of a_{Mn} was smaller than that for $Mn(CO)_4(O,O\text{-}o\text{-}DBSQ)$, Table 2. The corresponding Re product exhibited a broad, poorly resolved, signal with unresolved coupling due to one Re nucleus. The products formed at 180 K were thus, on IR and EPR grounds, characterized as $M^I(CO)_5(O\text{-}o\text{-}DBSQ)$ species. Since $Mn_2(CO)_9$ was shown not to react with quinones at 180 K, *vide supra*, this product must be formed by oxidative addition of *o*-DBQ to photogenerated $M(CO)_5$ radicals, just as for *p*-DBQ, eq. 4.

Both the Mn and Re radicals $M(CO)_5(O\text{-}o\text{-}DBSQ)$ are thermally stable at 180 K. When the temperature was raised to 230 K, the Mn complex afforded mainly $Mn_2(CO)_{10}$, which was detected by IR spectroscopy. The EPR spectrum showed, however, the typical signal of $Mn(CO)_4(O,O\text{-}o\text{-}DBSQ)$ [12,20], which appeared even during warming the solution from 180 to 195 K. Obviously, $Mn(CO)_5(O\text{-}o\text{-}DBSQ)$ disproportionates thermally into $Mn_2(CO)_{10}$ in a reaction analogous to that in eq. 5. At the same time, an intramolecular substitution of a CO ligand by the second semiquinone oxygen atom takes place, producing a chelated *O,O*-*o*-DBSQ ligand, as in the case of reaction 18.

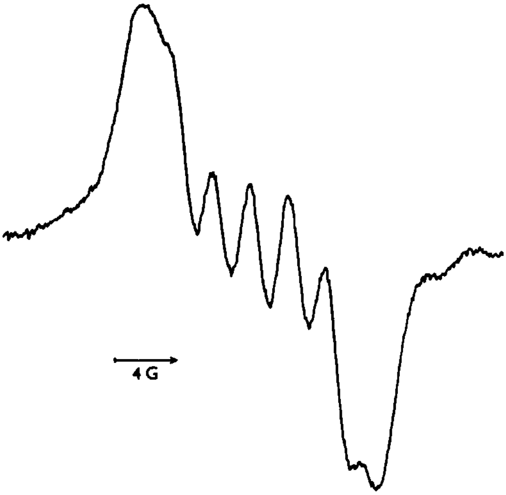

Fig. 9. EPR spectrum of $Mn(CO)_5(O\text{-}o\text{-}DBSQ)$ generated by 366 nm photolysis of 3.8×10^{-3} *M* $Mn_2(CO)_{10}$ and 10^{-2} *M* *o*-DBQ in toluene at 188 K.

The thermal stability of $Re(CO)_5(O\text{-}o\text{-}DBSQ)$ could not be studied by EPR spectroscopy since the line-width of the $Re(CO)_4(O,O\text{-}o\text{-}DBSQ)$ signal broadened at low temperatures and the signals due to both species coincided.

However, the intramolecular substitution leading to the formation of $M(CO)_4(O,O\text{-}o\text{-}DBSQ)$ occurred very rapidly photochemically even at 183 K:

$$M(CO)_5(O\text{-}o\text{-}DBSQ) \xrightarrow{h\nu} M(CO)_4(O,O\text{-}o\text{-}DBSQ) + CO \qquad (18)$$

This process was monitored by IR and EPR spectroscopy under laser or Hg-lamp irradiation. The $M(CO)_4(O,O\text{-}o\text{-}DBSQ)$ products were identified from their well known [12,15,20] EPR spectra. Their IR spectra showed four $\nu(CO)$ bands (Fig. 10), as expected for a tetracarbonyl complex of C_{2v} symmetry. The IR frequencies pointed to the oxidation state +1 for the metal. The photochemical reaction was faster for Re than for Mn. The tetracarbonyl complexes were formed via reaction 18 in both inert and coordinating (2-MeTHF) solvents.

The rate of reaction 18 was compared for different *o*-quinones by comparing the concentration ratio of $Mn(CO)_5(O\text{-}o\text{-}SQ)$ and $Mn(CO)_4(O,O\text{-}o\text{-}SQ)$ present after a given period of irradiation by a 10 mW Ar^+ laser (351 + 364 nm) in toluene at 183 K. All *o*-quinones afforded the *O*-*o*-SQ species as primary photoproducts which were thermally stable at 183 K but yielded $Mn_2(CO)_{10}$ upon warming to 220 K as followed by IR. However, the photoconversion at 183 K into $Mn(CO)_4(O,O\text{-}o\text{-}SQ)$ was faster for 9,10-phenanthrenequinone (PQ) and acenaphthenequinone (AQ) than for *o*-DBQ, 3,4,5,6-tetrachloro-1,2-benzoquinone and 3,4,5,6-tetramethyl-1,2-benzoquinone (in the case of AQ and PQ CH_2Cl_2 was used as a solvent for solubility reasons). Seric strain in the $Mn(CO)_5(O\text{-}o\text{-}SQ)$ complexes containing bulky quinones probably hampers their photoconversion into the *O*,*O*-*o*-SQ products. The corresponding thermal conversion of $Co(CN)_5(O\text{-}o\text{-}SQ)^{3-}$ into $Co(CN)_4(O,O\text{-}o\text{-}SQ)^{3-}$ was also found to be much faster for 9,10-phenanthrenesemiquinone and 1,2-naphthosemiquinone than for *o*-DBSQ [44].

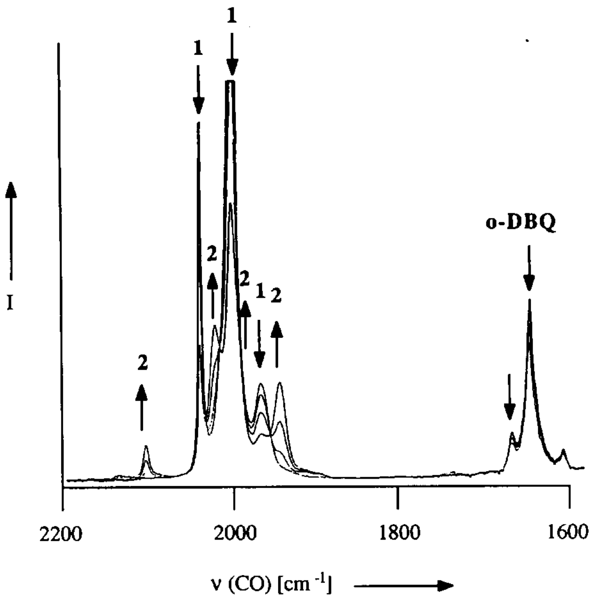

Fig. 10. IR spectral changes upon photolysis of a $Mn_2(CO)_{10}$/*o*-DBQ (1 : 5) solution in CH_2Cl_2 at RT with 351/364 nm (20 mW) light. (Bands are labelled as follows: 1 = $Mn_2(CO)_{10}$, 2 = $Mn(CO)_4$(*O*,*O*-*o*-DBSQ).

The experiments outlined indicate that $M(CO)_4$(*O*,*O*-*o*-DBSQ) is formed both via $M_2(CO)_9$, (eq. 14–17), and by oxidative addition of *o*-DBQ to $M(CO)_5$. Additional indirect evidence is the partial quenching by 1 *M* CCl_4. In order to confirm this reaction pathway, we also monitored by IR spectroscopy the photoreactions of $M_2(CO)_8$(bpy′) with *o*-DBQ under 514.5 (Re) and 546 nm (Mn) irradiation in toluene at room temperature. $M(CO)_5$ radicals were then produced by visible light, and in the absence of quinones they dimerized to give $M_2(CO)_{10}$. $M_2(CO)_{10}$ is, however, photoinert under 514.5 or 546 nm irradiation since it does not absorb at these wavelengths. Because of this, $M_2(CO)_9$ cannot contribute to the observed photochemistry. For both Mn and Re, the visible-light photolysis with *o*-DBQ afforded $M(CO)_4$(*O*,*O*-*o*-DBSQ), the photoproduction of $M_2(CO)_{10}$ being suppressed. The formation of $M(CO)_4$(*O*,*O*-*o*-DBSQ) via $M(CO)_5$ as the primary photoproduct was thus confirmed. In addition to $M(CO)_4$(*O*,*O*-*o*-DBSQ), other products were formed having CO-stretching modes at 2027, 1927 and 1908 cm^{-1} (Re) and 2023, 1932 and 1911 cm^{-1} (Mn), respectively, which resemble those of $M(CO)_3$(bpy)Br. These IR bands are tentatively assigned to $M(CO)_3$(bpy′)(*O*-*o*-DBSQ) but no detailed study has been carried out so far.

The $M(CO)_4$(*O*,*O*-*o*-SQ) complexes are known to undergo thermal substitution of one or two *cis*-CO ligand(s) by a large number of Lewis bases [12,17,18,20,21,23–26]. Our IR study showed that the substitution of a *cis*-CO ligand in $Mn(CO)_4$(*O*,*O*-*o*-DBSQ) by THF at 220 K does not occur thermally but that it can take place photochemically. The typical bands of the $Mn(CO)_3^+$ structural unit were formed upon irradiation of the THF solutions at 220 K (Table 1). However, the $Re(CO)_4$(*O*,*O*-*o*-DBSQ) species was formed out of $Re_2(CO)_{10}$ and *o*-DBQ even in THF at room temperature when the photoreaction took place in a flat EPR-cell

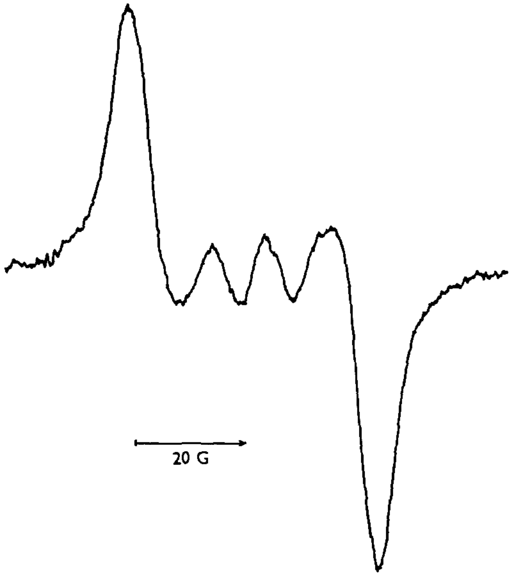

Fig. 11. EPR spectrum of $Re(CO)_3(THF)$(*O*,*O*-*o*-DBSQ) produced by prolonged (136 min) 313 nm photolysis of 5×10^{-4} $Re_2(CO)_{10}$ and 10^{-3} *M* *o*-DBQ in THF in a Schlenk tube at 295 K.

from which CO could not escape. The EPR spectrum previously attributed to $Re(CO)_3(THF)$(*O*,*O*-*o*-DBSQ) [20] belongs, in fact, to the tetracarbonyl species. The real $Re(CO)_3(THF)$(*O*,*O*-*o*-DBSQ) complex was formed in THF at 295 K after irradiation for a long time with 313 nm in a flat EPR cell or, much more efficiently, by photolysis in a Schlenk tube. The unusual appearance of its EPR spectrum (Fig. 11) was caused by the broadening of the $m = 3/2$ lines and unequal splitting between the lines [15,23]. Overlaps caused the virtual disappearance of two lines from the spectrum. EPR parameters are given in Table 2. In inert solvents $Mn(CO)_4$(*O*,*O*-*o*-DBSQ) slowly reacted thermally to give the EPR-inactive, CO-free compound $Mn_4(DBSQ)_8$ [30]. The $Mn(CO)_4$(*O*,*O*-*o*-DBSQ) was, however, stabilized in CO-saturated solutions.

The reaction mechanism

The IR and EPR studies outlined above allow identification of the role of both primary photoproducts of $M_2(CO)_{10}$ in the formation of manganese and rhenium semiquinone complexes. It is obvious that both *ortho*- and *para*-isomers of quinones react identically with both primary photoproducts. They coordinate as a Lewis base to $M_2(CO)_9$ and add oxidatively in one-electron process to $M(CO)_5$. The latter reaction can be regarded as a true radical (or spin) trapping. The analogous behaviour of *o*- and *p*-quinones seems to be rather general since it was previously established for an oxidative addition to $Co(CN)_5^{3-}$ [43,44] and for outer-sphere electron transfer [41]. The metal–semiquinone bond is, however, rather weak for the ligand coordinated via one oxygen atom only (*p*-SQ or *O*-*o*-SQ).

The *cis*-CO ligands in $M(CO)_5$(*p*-SQ) and $M(CO)_5$(*O*-*o*-SQ) are loosely bound and may easily be substituted either by other Lewis bases (THF, py) in the case of the *p*-SQ complexes or by the second oxygen atom of the *o*-semiquinone ligand in the case of the *O*-*o*-SQ complexes. The ability of *O*-*o*-SQ ligands to form a chelate ring (*O*,*O*-*o*-SQ type of coordination) is an important stabilizing factor which drives the one-electron oxidative addition to low-valent transition metals towards the formation of stable *O*,*O*-*o*-SQ complexes [36,44,46]. The chelated *O*,*O*-*o*-SQ ligand is formed by an intramolecular substitution of CO that can occur either as a thermal or photochemical process.

Surprisingly, the $M(CO)_3L$(*O*,*O*-*o*-DBSQ)-complexes were also formed from $M_2(CO)_9$(*O*-*o*-DBQ) by an intramolecular electron transfer leading to M–M bond homolysis. This process is somewhat analogous to the Cr(0) → *O*-*o*-DBQ electron transfer taking place in $Cr(CO)_5$(*O*-*o*-DBQ), which produces an *O*,*O*-coordinated *o*-DBSQ ligand and results in a strong labilization of the Cr–CO bonds [38]. It is evident that the $M(CO)_3L$(*O*,*O*-*o*-DBSQ) radical species are also formed via the $M_2(CO)_9$ intermediate, i.e., by an entirely non-radical pathway. This shows that the use of *o*-quinone "spin traps" as a diagnostic tool for radical formation in organometallic photochemistry may be misleading if based on the detection of *O*,*O*-*o*-SQ-containing radical products only.

The above results show that the combination of IR and EPR techniques is very useful for the study of photochemical reactions of metal carbonyls. Whereas EPR enables recognition of radical pathways and characterization of EPR-active parts of the radical products, IR spectroscopy can be used to complete their structural determination and to establish the role and importance of parallel non-radical pathways.

The bonding properties of the semiquinone complexes

The radical anionic semiquinone ligands are expected to introduce interesting structural, spectroscopic, photochemical and electrochemical properties into transition-metal complexes due to the unpaired electron residing in the π^*-orbital of the semiquinone ring. Spectroscopic and photochemical studies of these complexes are thus currently under way in our laboratories. From the results discussed in the preceding sections, the following conclusions concerning the metal–semiquinone bond may be drawn:

The IR spectra in the ν(CO)-region of $M(CO)_5$(*p*-DBSQ) and $M(CO)_5$(*O*-*o*-DBSQ) species are rather similar to those of $M(CO)_5Cl$. This shows, that the semiquinone ligands bound by one oxygen atom behave as π-donors. This is in accord with the description of the bonding in the analogous $Co(CN)_5(SQ)^{3-}$ complexes [43,44]. The oxygen donor atom of the monodentate semiquinone ligand (*o*- or *p*-) is considered to have a phenolate-like structure, i.e. bearing a negative charge. The M–O bond seems to be rather weak since the "phenolate" oxygen behaves as a "hard" donor atom. This is shown also by the EPR data. The *g*-factors are very close to those of uncoordinated semiquinone anion radicals. The doublet ground state of the semiquinone seems to be virtually unperturbed by the admixture of any excited states arising from the metal (see e.g. ref. 47 for the discussion of g-factors in metal complexes with radical ligands). The a_M-values are unusually small, reflecting negligible interaction between the semiquinone π^*-singly occupied orbital (SOMO) and the metal d_π-orbitals. The small a_H values observed for the hydrogens at the C3 and C5 positions of the *p*-DBSQ ligand shows that the unpaired electron is localized on that part of the *p*-DBSQ, that is remote to the C1-bound oxygen donor atom, most likely on the C4-bound oxygen atom. This picture of bonding and localization of the unpaired electron is analogous to that applied to the isoelectronic (and probably isostructural) $Co(CN)_5(p\text{-}SQ)^{3-}$ and $Co(CN)_5(O\text{-}o\text{-}SQ)^{3-}$ complexes [43,44]. The large decrease of a_{Mn} and especially of a_{Re} with increasing temperature is most probably due to a hindered rotation of the *p*-DBSQ ligand around the C–O and M–O bonds [52,53]. The chemical properties of the complexes containing a monodentate *o*- or *p*-SQ ligand are also in agreement with this bonding model. The semiquinone ligands are bound rather weakly. The Mn and Re complexes decompose via inter- and intramolecular electron transfer, respectively (eqs. 5 and 6). In contrast, the Co-complexes are substitutionally labile [43,44].

The formation of the *O,O*-*o*-SQ chelate ring is always associated with an increase in the a_M-value, a decrease in the *g*-factor (although still close to that of the free semiquinone) and with a remarkable increase in stability with respect to the *O*-*o*-SQ complexes. This is caused by the formation of a stable 5-membered chelate ring with the metal atom lying in the semiquinone plane. The crystal structure of $Re(CO)_3(PPh_3)$(*O,O*-*o*-DBSQ) gives a representative example of this [25]. The d_π-orbitals now overlap directly with the SOMO and, as a result, the unpaired electron becomes partly delocalized over the metal. The decrease of the *g*-factor points to a strong interaction of the SOMO with higher-lying empty levels of the metal [47]. The chelated *O,O*-*o*-SQ ligands thus appear to be weak π-donors.

The *cis*-CO ligand in $M(CO)_4$(*O,O*-*o*-SQ) is labile with respect to both photochemical and thermal substitution. The replacement of this ligand by a Lewis base leads, in the case of Re, usually to an increase in the a_{Re}-value [23]. This points to a larger delocalization within the Re(*O,O*-*o*-SQ) chelate ring for the substituted $Re(CO)_3L$(*O,O*-*o*-SQ) complexes than for the tetracarbonyl species. In the case of Mn, the changes in the *g*- and a_{Mn}-values caused by the substitution appeared to be strongly dependent on the ligand L [20]. For both Mn and Re, the substitution of *cis*-CO in $M(CO)_4$(*O,O*-*o*-DBSQ) resulted in a sharp decrease in the ν(CO) frequencies. Obviously, the *O,O*-*o*-DBSQ ligand cannot accommodate the increased electron density at the metal atom. The ν(CO) frequencies of $Mn(CO)_3L$(*O,O*-*o*-DBSQ) are comparable with those of $Mn(CO)_3L_3^+$ complexes in which L is a ligand without pronounced π-bonding ability, such as pyridine, CH_3CN, or acetone (see Table 1). Apparently, the π-delocalization in the M(*O,O*-*o*-DBSQ) ring is rather limited and the *o*-semiquinone anion-radical retains its identity upon complexation. Interestingly, the corresponding dianion *o*-DBQ^{2+} = *o*-catecholate acts as very strong π-donor towards a $Mn(CO)_3^+$ structural unit [48].

Conclusions

Quinones have been found to react with both primary photoproducts of $M_2(CO)_{10}$ (M = Mn, Re), i.e., with $M(CO)_5$ radicals as well as with $M_2(CO)_9$. There appeared to be no difference in reactivity of primary photoproducts towards the *ortho*- and *para*-quinone isomers. The quinones reacted with $M(CO)_5$ by a one-electron oxidative addition that is typical for d^7 metal centred radicals [43,44]. Towards $M_2(CO)_9$ they behave as simple Lewis bases. The *o*-semiquinones can, for steric reasons, form a stable 5-membered M(*O,O*-*o*-SQ) chelate ring, the formation of which has a large driving force. The primarily produced $M(CO)_5$(*O*-*o*-SQ) complex thus underwent a thermal as well as photochemical intramolecular substitution of CO with formation of $M(CO)_4(O,O\text{-}o\text{-}SQ)$. In $M_2(CO)_9(O\text{-}o\text{-}SQ)$ an intramolecular electron transfer took place, resulting also in the formation of $M(CO)_4(O,O\text{-}o\text{-}SQ)$. The substitution of a *cis*-CO ligand by a Lewis base (THF, PPh_3, CH_3CN, pyridine) leading to the formation of a more stable $M(CO)_3L(O,O\text{-}o\text{-}DBSQ)$ complex occurred both thermally and photochemically. The chelated *O,O-o*-SQ ligands appeared to act as π-donors toward the Mn(I) and Re(I) central atoms, but the π-interaction is rather weak.

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