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Metal to ligand charge-transfer photochemistry of metal–metal-bonded complexes
11*. Halogen atom and electron transfer reactions of $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ (M, M' = Mn, Re) complexes

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Abstract

This article describes three types of photoreactions of the complexes $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ (M, M' = Mn, Re). First of all, halogen atom transfer reactions are discussed which take place in the presence of halocarbons. Reactions with CCl_4 and CBr_4 appeared to proceed by a radical chain mechanism. This catalytic behaviour was ascribed to the CX_3 radicals, formed out of CX_4 which can initiate secondary halogen atom transfer reactions. Quantum yields for the reactions with halocarbons were therefore determined for CH_2Cl_2 which did not show a catalytic behaviour because of its higher C–Cl bond dissociation energy. For all complexes high quantum yields were obtained (0.3–0.7) and variations of these values throughout the series of complexes were ascribed to changes in spin–orbit coupling and rates of non-radiative decay processes. The photoreactions were also studied in the presence of 9,10-phenanthrenequinone in order to confirm that these quantum yields were indeed a measure for the photolysis of the parent compounds. Quinones are known to react with the primary photoproducts of both the CO loss and M–M' bond homolysis reactions. From the agreement between the quantum yield data for the reactions with CH_2Cl_2 and 9,10-phenanthrenequinone, it was concluded that the CO loss products of the $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ compounds, contrary to those of the $Ph_3SnMn(CO)_3(\alpha\text{-diimine})$ complexes, also react with halocarbons. Finally, the complexes $(CO)_5MRe(CO)_3(\alpha\text{-diimine})$ photodisproportionate in the presence of 2e-donors L (L = THF, PR_3) into $M(CO)_5^-$ and $Re(CO)_3(\alpha\text{-diimine})(L)^+$ ions. Irradiation of the complexes in toluene at 183 K gave rise to another electron transfer reaction, viz. the formation of a contact ion-pair (CIP). The CIPs $[M(CO)_5^- \text{---} Re(CO)_3(\alpha\text{-diimine})^+]$ showed a characteristic low frequency $\nu(CO)$ band of a bridging CO ligand that was not present in the spectra of solvent-separated ion-pairs.

Introduction

The metal–metal bonded complexes $M_2(CO)_{10}$ (M = Mn, Re) are characterized by an intense absorption band between 300 and 350 nm belonging to the $\sigma_b \rightarrow \sigma^*$ transition of the metal–metal bond [1–3]. Laser-flash photolysis studies have shown that irradiation into this band gives rise to both homolysis of the metal–metal bond and release of CO [4–9]. $M(CO)_5$ radicals were proposed to be formed by a homolysis reaction from the $^3\sigma_b\sigma^*$ state of the metal–metal bond; $Mn_2(CO)_9$ was assumed to be the photoproduct of a CO loss reaction from a LF state [10, 11].

Similar photoreactions have been observed for the substituted complexes $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ (M, M' = Mn, Re) [12] which show in addition to the $\sigma_b \rightarrow \sigma^*$ transition in the near UV, an intense $d_\pi(M) \rightarrow \pi^*(\alpha\text{-diimine})$ charge transfer (MLCT) band in the visible region [13]. Upon irradiation into this latter electronic transition, again, both homolysis and release of CO were observed as primary photoprocesses although the relative quantum yields of these reactions strongly depended on M and M' [14–18].

Since the MLCT states themselves are normally not reactive [19], both reactions were proposed to occur from the repulsive $^3\sigma_b\sigma^*$ state after surface crossing from the MLCT state(s) [10, 11]. A CO

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loss reaction taking place from a low-lying ^{3}LF state, as proposed by Meyer and Caspar for the $M_2(CO)_{10}$ complexes [10], was discarded here in view of the fact that these reactions even proceed with high quantum yield upon excitation with $\lambda_{irr} > 600$ nm. A low-lying ^{3}LF state is not expected to be occupied at such low energies.

In previous articles we have reported in detail the photochemistry [17] and photocatalysis [20] of the complexes $(CO)_5MnMn(CO)_3(\alpha\text{-diimine})$. In addition, the primary photoreaction of the complexes $(CO)_5ReMn(CO)_3(\alpha\text{-diimine})$ has been elucidated by a combined flash photolysis, and temperature- and pressure-dependent photochemical study [18]. In contrast to all other $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ (M, M' = Mn, Re) complexes, these compounds only showed release of CO. This exceptional behaviour was ascribed to the weakness of the Mn–CO bonds with respect to the strong Re–Mn bond.

In this article we report the photochemical reactions of several $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ complexes with chlorocarbons and with 9,10-phenanthrenequinone (Phen-Q). Attention will also be paid to the exceptional behaviour of the complexes $(CO)_5MRe(CO)_3(\alpha\text{-diimine})$ in toluene at 183 K, which provide upon irradiation into their MLCT band the contact ion-pair $[M(CO)_5^- \text{--} Re(CO)_3(\alpha\text{-diimine})^+]$. The α-diimine ligands used throughout this article are 4,4'-dimethyl-2,2'-bipyridine (bpy'), 1,10-phenanthroline (phen) and 1,4-di-*p*-tolyl-1,4-diaza-1,3-butadiene (pTol-DAB).

Experimental

Materials and preparations

THF, 2-MeTHF, toluene, CH_2Cl_2, $CHCl_3$, 2-Cl-butane and CCl_4 were carefully dried and stored under nitrogen. CBr_4 was recrystallized from hexane. Phen-Q (Aldrich), bpy' (Merck) and phen (Merck) were used as received. The pTol-DAB ligand [21] and the complexes $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ (M, M' = Mn, Re) [14, 22] and $Ph_3SnMn(CO)_3(\alpha\text{-diimine})$ [23, 24] were synthesized according to literature procedures.

Spectroscopic measurements

IR spectra were recorded on a Nicolet 7199 B FTIR spectrometer equipped with a liquid-nitrogen-cooled MCT detector (resolution 1.0 cm^{-1}). Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 UV–Vis spectrometer connected to a model 3600 data station. Low-temperature UV–Vis and IR measurements were performed by using an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat.

Photochemistry

An SP 2025 argon-ion laser was used as the light source in the photochemical experiments. Unless otherwise stated, the 514.5 nm line was selected for excitation. Photon fluxes for the quantum yield determinations were measured with Coherent model 210 and 212 power meters. The handling of the light-sensitive samples for the IR and UV–Vis experiments and the procedure used for the quantum yield determinations have been described elsewhere [20]. All quantum yields were determined in duplicate.

Results and discussion

Halogen atom transfer reactions

Morse and Wrighton have shown that $(CO)_5MnMn(CO)_3(\alpha\text{-diimine})$ complexes photoreact in the presence of excess CCl_4 according to reaction (1) [14].

$$(CO)_5MnMn(CO)_3(\alpha\text{-diimine}) \xrightarrow[CCl_4]{h\nu} Mn(CO)_5Cl + Mn(CO)_3(\alpha\text{-diimine})Cl \quad (1)$$

The reaction was proposed to proceed by a halogen atom transfer from the chlorocarbon to the radicals formed upon homolysis of the metal–metal bond. Just as in the case of $Mn_2(CO)_{10}$ [25] the CO loss products were not expected to react thermally with CCl_4. This assumption was confirmed by more recent experiments on the complexes $Ph_3SnMn(CO)_3(\alpha\text{-diimine})$, which undergo release of CO as the only primary photoprocess and which were found not to react with CCl_4 [25]. On the other hand, the CO loss products of complexes $(CO)_5ReMn(CO)_3(\alpha\text{-diimine})$ reacted rather efficiently with CCl_4 [18].

We have observed that reaction (1) also proceeds for all other $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ (M, M' = Mn, Re) complexes and that similar halogen abstraction products are formed by reaction of these complexes with CBr_4 and $CHCl_3$. The photoreactions in CH_2Cl_2 depended, however, on the complex used (reaction (2)). The $Re(CO)_5$ radicals reacted with

$$(CO)_5MM'(CO)_3(\alpha\text{-diimine}) \xrightarrow[CH_2Cl_2]{h\nu} M(CO)_5Cl\ (M = Re),\ M_2(CO)_{10}\ (M = Mn) + M'(CO)_3(\alpha\text{-diimine})Cl \quad (2)$$

CH_2Cl_2 to give the chlorine abstraction product whereas the $Mn(CO)_5$ radicals showed a radical coupling reaction. All products were characterized by IR and UV–Vis spectroscopy and relevant data are collected in Table 1. Figure 1 presents the UV–Vis spectral changes accompanying the photoreaction of

TABLE 1. CO stretching frequencies of the photoproducts of $(CO)_5MM'(CO)_3$(α-diimine) (M, M' = Mn, Re)

Complex	Solvent, temperature	ν(CO) (cm^{-1})					
$Mn_2(CO)_{10}$	CH_2Cl_2, r.t.[a]		2046	2011	1979		
$Re_2(CO)_{10}$	CH_2Cl_2, r.t.		2068	2009	1981		
$Mn(CO)_5Cl$	THF, r.t.	2139	2086	2050	2003		
$Re(CO)_5Cl$	CH_2Cl_2, r.t.	2143	2084	2046	1986		
$Mn(CO)_3$(bpy')Cl	CH_2Cl_2, r.t.		2028	1936	1918		
$Re(CO)_3$(bpy')Cl	$CHCl_2$, r.t.		2022	1918	1894		
$Mn(CO)_3$(Phen-SQ)(THF)	THF, r.t.		2032	1926			
$Re(CO)_3$(Phen-SQ)(THF)	THF, r.t.		2021	1928	1901		
$Re_2(CO)_7$(Phen-SQ)$_2$	KBr, r.t.[b]	2113	2015	1985	1933	1914	1894
$Mn(CO)_3$(bpy')(Phen-SQ)	THF, r.t.		2022	1929	1909		
$Re(CO)_3$(bpy')(Phen-SQ)	THF, r.t.		2028	1921	1909		
$Re(CO)_3$(bpy')(THF)$^+$	THF, r.t.		2034	1922	1916		
$Re(CO)_3$(bpy')(2-MeTHF)$^+$	2-MeTHF, 183 K		2032	1924	1917		
$Re(CO)_3$(bpy)$^+$	toluene, 230 K[c, d]		2033	1930	1919		
$Mn(CO)_5^-$	2-MeTHF, 183 K		1897	1864	1855		
$Re(CO)_5^-$	2-MeTHF, 183 K		1894	1862	1852		
$Mn(CO)_5^-$	toluene-d^8, 193 K[c]		1894	1867	1844		
$Re(CO)_5^-$	toluene-d^8, 193 K[c]		1892	1865	1841		

[a] Room temperature. [b] Ref. 27. [c] In CIP. [d] Ref. 28.

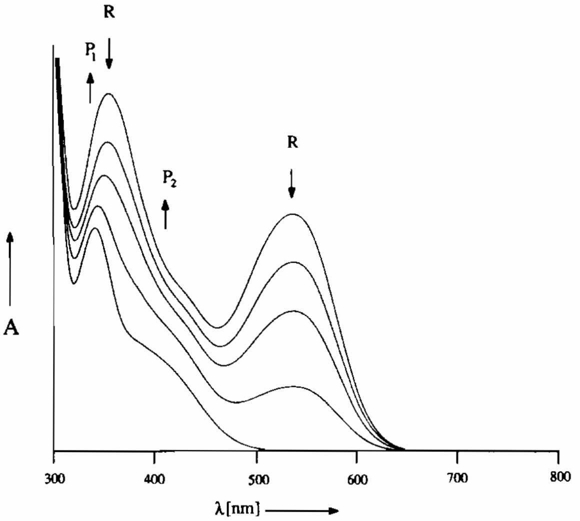

Fig. 1. UV–Vis spectral changes accompanying the photoreaction of $(CO)_5MnMn(CO)_3$(bpy') in CH_2Cl_2 (λ_{irr} = 514.5 nm) (R = $(CO)_5MnMn(CO)_3$(bpy'), P_1 = $Mn_2(CO)_{10}$, P_2 = $Mn(CO)_3$(bpy')Cl).

$(CO)_5MnMn(CO)_3$(bpy') in CH_2Cl_2. It clearly shows the formation of $Mn_2(CO)_{10}$ and $Mn(CO)_3$(bpy')Cl by the appearance of the $\sigma_b \rightarrow \sigma^*$ transition of the decacarbonyl at 340 nm and the MLCT band of the latter complex at *c.* 400 nm.

The results of reaction (2) agree with those obtained by Brown and coworkers for the reactions of $M(CO)_{5-x}(PR_3)_x$ (x = 0, 1, 2; M = Mn, Re) radicals with halocarbons [29, 30]. These authors ascribed the more facile chlorine atom transfer in the case of $Re(CO)_5$ to electronic effects and the decreasing tendency for halogen abstraction upon going from CBr_4 and CCl_4 to $CHCl_3$ and CH_2Cl_2, to an increase of the C–halogen bond dissociation energy.

Comparing the $M(CO)_3$(α-diimine) and $M(CO)_5$ radicals, the unpaired electron occupies an energetically more favourable orbital in the former type of radical; $M(CO)_3$(α-diimine) radicals are 16e-ligand centred radicals with a π^*(α-diimine) singly occupied molecular orbital (SOMO) [31] whereas $M(CO)_5$ radicals are 17e-metal centred radicals with a d_{z^2}(M) SOMO [32]. The dimerization of the $Mn(CO)_3$(α-diimine) species is therefore much slower than that of $Mn(CO)_5$ and this results in the simultaneous formation of $Mn(CO)_3$(α-diimine)Cl and $Mn_2(CO)_{10}$.

Halogen abstraction did not occur in 2-Cl-butane since the C–Cl bond dissociation energy of this molecule is even higher than that of CH_2Cl_2. Table 2 summarizes the above results for the complex $(CO)_5MnMn(CO)_3$(bpy').

TABLE 2. The photoproducts of $(CO)_5MnMn(CO)_3$(bpy') in some chlorocarbons

Chlorocarbon	Products
CCl_4	$Mn(CO)_5Cl + Mn(CO)_3$(bpy')Cl
$CHCl_3$	$Mn(CO)_5Cl + Mn(CO)_3$(bpy')Cl (+traces of $Mn_2(CO)_{10}$)
CH_2Cl_2	$Mn_2(CO)_{10} + Mn(CO)_3$(bpy')Cl
2-Cl-butane	$Mn_2(CO)_{10} + Mn_2(CO)_6(bpy')_2$

Preliminary quantum yield determinations of the halogen atom transfer were performed by irradiating the complexes in CCl_4 and by measuring the decay of the MLCT band. However, values of ϕ higher than unity were then obtained. For instance, for the reaction of $(CO)_5MnMn(CO)_3(bpy')$ in neat CCl_4 $\phi = 1.18$, and for that of a $(CO)_5MnMn(CO)_3(bpy')/CBr_4$ mixture (molar ratio 1:200) in THF $\phi = 1.41$. A quantum yield higher than unity has been reported before for the reaction of $(CO)_5MnMn(CO)_3(phen)$ in a degassed CCl_4/CH_2Cl_2 (1:1) solution and has then been ascribed to a catalytic reaction initiated by traces of oxygen [14]. We could, however, not obtain any evidence of an irregular influence of oxygen impurities during the reactions in toluene, THF or CH_2Cl_2 and therefore present the following alternative explanation. Halogen atom transfer from CX_4 (X = Cl, Br) will give rise to the formation of CX_3 radicals which may either dimerize or react with yet another $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ complex. The rates of such secondary reactions are expected to increase for halocarbons with low C–X bond dissociation energies; the higher value of ϕ for X = Br than for X = Cl agrees with this expectation.

The mechanism of these processes has not been further studied and their occurrence has been avoided by using instead CH_2Cl_2 as the radical scavenging agent in the quantum yield determinations. In addition, the $M(CO)_5$ and $M'(CO)_3(\alpha\text{-diimine})$ radicals, intermediates in reaction (1), have also been trapped by using Phen-Q as a radical scavenger (*vide infra*). Quantum yield data for the reactions with CH_2Cl_2 are collected in Table 3. The values, which vary between 0.3 and 0.7, will strongly be influenced by the competition between the surface crossing from the MLCT state(s) to the reactive $^3\sigma_b\sigma^*$ state and the radiationless transfer to the ground state. The rate of the latter process will increase going from M' = Mn to M' = Re because of an increase in the spin–orbit coupling, and by replacing phen or bpy' by pTol-DAB (energy-gap law). The influences are indeed clearly perceptible in the values of ϕ.

TABLE 3. Quantum yields of the photoreactions of several complexes $L_nMM'(CO)_3(\alpha\text{-diimine})$ with CH_2Cl_2 (ϕ_1) and Phen-Q (ϕ_2), respectively

L_nM	M'	α-diimine	$\phi_1^{a,b}$	$\phi_2^{a,c}$
$(CO)_5Mn$	Mn	phen	0.67	
$(CO)_5Mn$	Mn	bpy'	0.52	0.46
$(CO)_5Mn$	Mn	pTol-DAB	0.37	
$(CO)_5Re$	Mn	bpy'	0.46	0.34
$(CO)_5Re$	Mn	pTol-DAB	0.42	0.51
$(CO)_5Mn$	Re	bpy'	0.30	0.23
$(CO)_5Re$	Re	bpy'	0.38	0.42
Ph_3Sn	Mn	bpy'	3.610^{-3}	c. 0.3[d]

[a] $\lambda_{irr} = 514.5$ nm; $P_\lambda = 11$ mW; $T = 293$ K. [b] In CH_2Cl_2; values ±5%. [c] In THF; molar ratio $L_nMM'(CO)_3(\alpha\text{-diimine})$: Phen-Q = 1.50; values ±10%. [d] Estimated from decrease of CO bands in IR.

Table 3 also presents the quantum yield data for the complexes $(CO)_5ReMn(CO)_3(\alpha\text{-diimine})$ (α-diimine = bpy', pTol-DAB) and $Ph_3SnMn(CO)_3(bpy')$, which complexes are exceptional in losing CO as the only primary photoprocess [18, 26]. The two types of complexes have remarkably differing photoreactivities. For $Ph_3SnMn(CO)_3(bpy')$ the quantum yield of the halogen abstraction is about two orders lower than that of the CO substitution whereas these two reactions have almost the same quantum yield in the case of $(CO)_5ReMn(CO)_3(\alpha\text{-diimine})$. The low yields of the Sn–Mn homolysis reactions were ascribed to the high Sn–Mn bond strength [26]. For instance, compounds such as $Ph_3SnMn(CO)_5$ are known to be chemically inert even upon attack by chlorine [33].

Electron transfer reactions

Reactions with Phen-Q

Quinones (Q) are efficient radical scavengers since they can easily be reduced in a one electron process, forming a semi-quinone (SQ) ligand of which the unpaired electron resides in the $\pi^*(Q)$ orbital. These molecules can be used to determine the overall photoreactivity of metal–metal bonded complexes since they can react with both the homolysis and CO loss products. This has recently been demonstrated for the photoreactions of $Mn_2(CO)_{10}$ with *ortho-* and *para*-quinones [34]. The homolysis product $Mn(CO)_5$ reacted with *ortho*-quinones to give $Mn(CO)_4(SQ)$ and the same complexes were obtained in the reaction between the *ortho*-quinones and the CO loss photoproduct $Mn_2(CO)_9$ via formation of the intermediate $Mn_2(CO)_9(Q)$.

For all experiments Phen-Q has been used as a reactant because it is one of the few *ortho*-quinones for which the lowest-energy ($n \rightarrow \pi^*(Q)$) absorption band does not overlap with the MLCT bands of the $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ complexes under study. This facilitated the determination of the $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$ photoreactivity by following the decay of their MLCT bands. For solubility reasons the photoreactions of $(CO)_5MM'(CO)_3(\alpha\text{-diimine})$/Phen-Q mixtures (molar ratio 1:50) were performed in THF.

Equation (3) shows that the photoproducts formed depend on M and M′. First of all the $M(CO)_5$ radicals react differently with Phen-Q. The $Mn(CO)_5$ radicals produce $Mn(CO)_3$(THF)(Phen-SQ) which

$$(CO)_5MM'(CO)_3(\alpha\text{-diimine}) + \text{Phen-Q} \xrightarrow[\text{THF}]{h\nu}$$
$$\begin{aligned} &M(CO)_3(\text{THF})(\text{Phen-SQ})\ (M = Mn)\\ &+ M_2(CO)_7(\text{Phen-SQ})_2\ (M = Re)\\ &+ M'(CO)_3(\alpha\text{-diimine})(\text{Phen-SQ})\\ &+ M'(\alpha\text{-diimine})(\text{Phen-SQ})_2\ (M' = Mn) \end{aligned} \quad (3)$$

was characterized by analogy with the photoproducts $Mn(CO)_3$(THF)(DBSQ)(DBQ = 3,5-tBu_2-1,2-benzoquinone) formed in the reaction of $Mn_2(CO)_{10}$ with DBQ [34]. This assignment was supported by the crystal structure of the related complex $Re(CO)_3(PPh_3)$(DBSQ) [35]. The $Re(CO)_5$ radicals gave rise to the formation of the binuclear complex $Re_2(CO)_7$(Phen-SQ)$_2$ for which the structure had already been determined by X-ray diffraction [27].

The $M'(CO)_3$(α-diimine) moieties of the starting complexes were converted into the $M'(CO)_3$(α-diimine)(Phen-SQ) and, for M′ = Mn, M′(α-diimine)(Phen-SQ)$_2$ photoproducts. The former complexes could easily be identified by comparing their CO-stretching frequencies with those of $M'(CO)_3$(α-diimine)X (X = Cl, Br) (Table 1). The Mn(α-diimine)(Phen-SQ)$_2$ complexes were identified by their characteristic absorption bands at 500 and 710 nm, which closely correspond to those of $Mn(py)_2(DBSQ)_2$ [36].

The mechanisms of the reactions between the $Mn(CO)_3$(α-diimine) groups and Phen-Q were established by comparing the reactions of the $(CO)_5MMn(CO)_3$(α-diimine) and $Ph_3SnMn(CO)_3$(bpy′) complexes. Irradiation of the latter complex in the presence of Phen-Q only afforded Mn(bpy′)(Phen-SQ)$_2$ and no $Mn(CO)_3$(bpy′)(Phen-SQ). Apparently, the attack of Phen-Q on the CO loss photoproduct $Ph_3SnMn(CO)_2$(bpy′) is followed by chelate formation, electron transfer and Sn–Mn bond splitting. Further substitution of CO by Phen-Q is then facilitated by the weakening of the Mn–CO bonds as result of the electron transfer to the quinone ligand. A similar reaction sequence has been observed for the photoreaction of $Cr(CO)_6$ with DBQ in CH_2Cl_2 [37]. During irradiation of this solution at 223 K, $Cr(CO)_5$(DBQ) was formed in which the quinone is coordinated to the metal as a monodentate ligand. Raising the temperature gave rise to chelation of the quinone with a concomitant electron transfer. The $Cr(CO)_4$(DBSQ) thus formed appeared to be unstable with respect to attack by a second quinone and it transformed into the stable complex $Cr(DBSQ)_3$. In a recent article we have shown that $Mn(CO)_3$(α-diimine) radicals do not react with *ortho*-quinones by such a quinone-chelation/CO-substitution reaction sequence [34]. Instead [$Mn(CO)_3$(α-diimine)][*o*-SQ] ion-pairs were formed by an electron transfer from the α-diimine radical anion to the *ortho*-quinone.

Since MLCT excitation of metal–metal bonded L_nM–$Re(CO)_3$(α-diimine) ($L_nM = (CO)_4Co$ [28], $Cp(CO)_2Fe$ [38], Ph_3Sn [26]) compounds only afforded M–Re bond splitting, due to the strength of the Re–CO bond, the above mentioned processes also explain why $Re(CO)_3$(α-diimine)(Phen-SQ) is formed and no decarbonylized rhenium ion. Both Mn(α-diimine)(Phen-SQ)$_2$ and $Mn(CO)_3$(α-diimine)(Phen-SQ) compounds were obtained upon photolysis of $(CO)_5ReMn(CO)_3$(α-diimine)/Phen-Q mixtures. The formation of such $Mn(CO)_3$(α-diimine) radical products was also noted in the photoreactions of $(CO)_5ReMn(CO)_3$(α-diimine)/CH_2Cl_2 (*vide supra*) and $(CO)_5ReMn(CO)_3$(α-diimine)/PPh_3/CCl_4 [18] mixtures, in spite of the fact that loss of CO is the only primary photoprocess for $(CO)_5ReMn(CO)_3$(α-diimine). Once more, this finding confirms that the CO loss product of $(CO)_5ReMn(CO)_3$(α-diimine) contains a much weaker metal–metal bond than that of $Ph_3SnMn(CO)_3$(α-diimine). This behaviour is evident from Table 3 which presents the quantum yields of the $(CO)_5MM'(CO)_3$(α-diimine)/Phen-Q photoreactions. The rather good agreement with the values determined for the reactions with CH_2Cl_2 is not surprising for the $(CO)_5MRe(CO)_3$(α-diimine) complexes since these compounds only give rise to the formation of radicals which are scavenged by CH_2Cl_2 as well as Phen-Q. It is, however, noteworthy that the quantum yields of both reactions are also similar for $(CO)_5MnMn(CO)_3$(bpy′), which is known to afford both homolysis and CO loss products [15, 17]. Since Phen-Q reacts with both these primary photoproducts, the same will hold for CH_2Cl_2. The quantum yields obtained for $Ph_3SnMn(CO)_3$(bpy′) show that this complex has a completely different reactivity towards halocarbons. It hardly reacts with CH_2Cl_2 although the quantum yield of its reaction with Phen-Q is comparable to that of its CO substitution [26] and that of the corresponding reactions of the $(CO)_5MM'(CO)_3$(α-diimine) complexes.

In conclusion it can be said that the quantum yields for the reaction with CH_2Cl_2 reflect the extent to which the $(CO)_5MM'(CO)_3$(α-diimine) complexes photodecompose since the chlorocarbon reacts with both types of primary photoproducts. The results obtained for $Ph_3SnMn(CO)_3$(bpy′) demonstrate, however, that one has to be very careful with extending this conclusion to other metal–metal bonded complexes.

Photodisproportionation and ion-pair formation

In a previous article we have discussed in detail the photochemical reactions of the complexes $(CO)_5MnMn(CO)_3(\alpha\text{-diimine})$ with various oxygen-, nitrogen- and phosphorus-donor ligands [20]. Irradiation of a complex in neat THF only gave rise to the formation of radical coupling reactions according to eqn. (4). Apparently, THF has no direct

$$(CO)_5MnMn(CO)_3(\alpha\text{-diimine}) \xrightarrow[\text{THF}]{h\nu} Mn_2(CO)_{10} + Mn_2(CO)_6(\alpha\text{-diimine})_2 \quad (4)$$

influence on this photoreaction since the same products were obtained upon irradiation in a non-coordinating solvent such as toluene. In the presence of phosphine ligands, however, reaction (4) was suppressed by the photodisproportionation reaction (5).

$$(CO)_5MnMn(CO)_3(\alpha\text{-diimine}) + L \xrightarrow[L]{h\nu} Mn(CO)_5^- + Mn(CO)_3(\alpha\text{-diimine})(L)^+ \quad (5)$$

$L =$ pyridine, PR_3

In fact, reaction (5) was a photocatalytic process that was triggered by a short light-pulse and proceeded in the dark. The catalysis is initiated by the highly reducing 18e-$Mn(CO)_3(\alpha\text{-diimine})(L)$ radicals that are formed by the addition of L to the 16e-$Mn(CO)_3(\alpha\text{-diimine})$ radicals. These species reduce the starting compound and thereby start a radical chain reaction. The yield of the 18e-radicals, hence of the photodisproportionation (5), mainly depends on the electronic properties of L. Hard bases like THF or nitrogen-donor ligands like pyridine can only weakly coordinate to the 16e-radical whereas the catalytic reaction persists in the presence of only a moderate excess of phosphine ligands. It is evident that in the absence of 2e-donor ligands, in non-coordinating solvents like toluene, reaction (5) will not take place. The complexes $(CO)_5MnRe(CO)_3(\alpha\text{-diimine})$ have a somewhat different photochemical behaviour and this will be illustrated for the reactions of $(CO)_5MnRe(CO)_3(bpy')$. Irradiation of this complex in THF gave rise to a photodisproportionation (6) of which the ionic products are similar to those formed in reaction (5).

$$(CO)_5MnRe(CO)_3(bpy') \xrightleftharpoons{h\nu,\text{THF}} Mn(CO)_5^- + Re(CO)_3(bpy')(THF)^+ \quad (6)$$

Reaction (6) was, however, reversible and the ionic species formed reacted back to give the parent complex. In addition a small amount of homolysis products was formed. No such backreaction was observed when the complex was irradiated in the presence of a phosphine ligand (reaction (7)). The quantum yield of this reaction was determined for a $(CO)_5MnRe(CO)_3(bpy')/PPh_3$ (molar ratio 1:200) mixture in THF. Its value (0.28) almost equalled

$$(CO)_5MnRe(CO)_3(bpy') \xrightarrow{h\nu,\ PPh_3} Mn(CO)_5^- + Re(CO)_3(bpy')(PPh_3)^+ \quad (7)$$

that of the corresponding halogen atom abstraction (2). This proves that, unlike the corresponding dimanganese compounds, $(CO)_5MnRe(CO)_3(bpy')$ complexes photodisproportionate by a stoichiometric process.

An interesting reaction was observed upon irradiation of these complexes in toluene at 183 K. IR bands showed up which were close in frequency to those of the ionic species formed in reaction (6). This result was rather surprising since toluene is known to have no coordinating ability for such a photodisproportionation [39]. The reaction was also observed for the corresponding $(CO)_5Re$-$Re(CO)_3(bpy')$ complex but not for any of the $(CO)_5MnMn(CO)_3(\alpha\text{-diimine})$ compounds discussed before. A similar reaction had been observed by us for the related complex $(CO)_4CoRe(CO)_3(bpy)$ in toluene at 230 K [28]. This reaction was then explained by the formation of a contact ion-pair (CIP) $[Co(CO)_4^-\text{---}Re(CO)_3(bpy)^+]$. This interpretation was supported by the observation of a splitting of the normally degenerate CO stretching modes of the $Co(CO)_4^-$ ion at 1885 cm^{-1}. It is assumed that a similar reaction has taken place for the corresponding $(CO)_5M$ complexes according to reaction (8).

$$(CO)_5MRe(CO)_3(bpy') \xrightarrow[\text{toluene, 183 K}]{h\nu} [M(CO)_5^-\text{---}Re(CO)_3(bpy)^+] \quad (8)$$

The CIPs $[Mn(CO)_5^-\text{---}M^+]$ ($M =$ Na, Li) have already been identified at r.t. in THF and ether [40, 41]. It was shown that they are kept together by a weak bond between M^+ and an equatorial CO ligand of $Mn(CO)_5^-$. This interaction gave rise to small shifts of the CO stretching frequencies. The CO bands of $Mn(CO)_5^-$ had shifted from 1897.0 to 1901.7 cm^{-1} and from 1862.3 to 1875.1 cm^{-1}, respectively, upon formation of $[Mn(CO)_5^-\text{---}Na^+]$. A third band at 1828.6 cm^{-1} was assigned to the stretching vibration of the carbonyl ligand that interacts with Na^+. In order to search for this CO band of the CIPs $[M(CO)_5^-\text{---}Re(CO)_3(bpy')^+]$, the photoreaction was instead performed in toluene-d^8 at 193 K (reactions could not take place at 183 K since toluene-d^8 freezes already at 189 K) since this part of the IR spectrum is obscured by strong absorptions in the case of non-deuterated toluene. New bands were then observed at 1844 (M = Mn) and 1841 (M = Re) cm^{-1}. They are assigned to the bridging equatorial carbonyl of the CIP, since such a band is not present in the spectrum of the solvent separated ion-pair $Mn(CO)_5^-$-$Re(CO)_3$(bpy')(2-MeTHF)$^+$ (Fig. 2).

The question remains whether metal–metal bond heterolysis or homolysis is the primary photoreaction of reaction (8). For the complex $(CO)_4CoRe(CO)_3$(bpy), CIP formation was quenched by addition of a 200-fold excess of the CBr_4 radical scavenger. This proved that the CIP results from a photochemical metal–metal bond homolysis followed by an electron transfer reaction since it was established that $Re(CO)_3(bpy)^+$ did not react under the reaction conditions with CBr_4. A similar experiment was done for the $(CO)_5MnRe(CO)_3$(bpy') complex. Irradiation of a $(CO)_5MnRe(CO)_3$(bpy')/CBr_4 (molar ratio 1:200) mixture in toluene at 183 K afforded exclusively $Mn(CO)_5Br$ and $Re(CO)_3$(bpy')Br. Apparently, reaction (8) starts by the homolysis of the metal–metal bond followed by an electron transfer from the $Re(CO)_3$(bpy') to the $Mn(CO)_5$ radical.

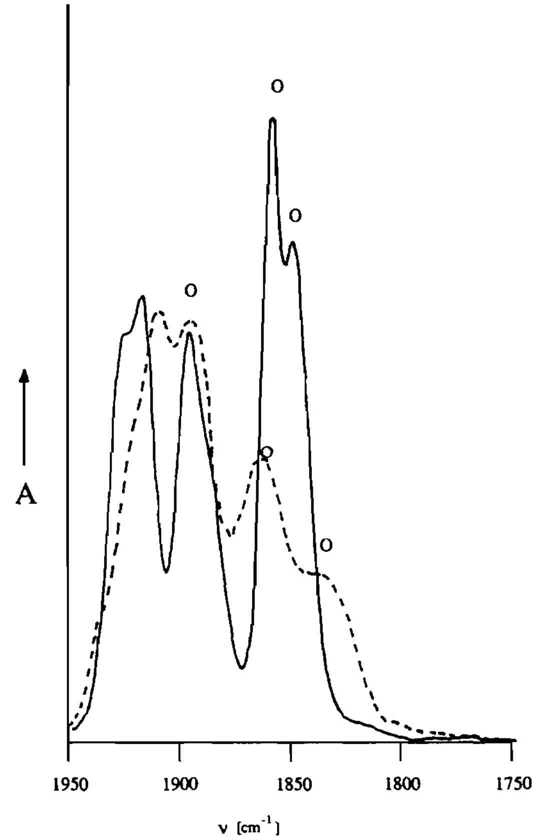

Fig. 2. IR spectra between 1750 and 1950 cm^{-1} of the $(CO)_5MnRe(CO)_3$(bpy') photoproduct in 2-MeTHF at 183 K (——) and in toluene-d^8 at 193 K (- - -) (O = $Mn(CO)_5^-$).

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References

1 R. A. Levenson, H. B. Gray and G. P. Ceasar, *J. Am. Chem. Soc., 92* (1970) 3653.
2 M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc., 97* (1975) 2065.
3 R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc., 97* (1975) 6042.
4 H. Yesaka, T. Kobayashi, K. Yasufuku and S. Nagakura, *J. Am. Chem. Soc., 105* (1983) 6249.
5 L. J. Rothberg, N. J. Cooper, K. S. Peters and V. Vaida, *J. Am. Chem. Soc., 104* (1982) 3536.
6 S. P. Church, H. Hermann, F.-W. Grevels and K. Schaffner, *J. Chem. Soc., Chem. Commun.,* (1984) 785.
7 K. Yasufuku, H. Noda, J. Iwai, H. Ohtani, M. Hoshino and T. Kobayashi, *Organometallics, 4* (1985) 2174.
8 T. Kobayashi, H. Ohtani, H. Noda, S. Teratani, H. Yamazaki and K. Yasufuku, *Organometallics, 5* (1986) 110.
9 T. A. Seder, S. P. Church and E. Weitz, *J. Am. Chem. Soc., 108* (1986) 7518.
10 T. J. Meyer and J. V. Caspar, *Chem. Rev., 85* (1985) 187.
11 D. J. Stufkens, in I. Bernal (ed.), *Stereochemistry of Organometallic and Inorganic Compounds,* Vol. 3, Elsevier, Amsterdam, 1989, p. 226.
12 D. J. Stufkens, *Coord. Chem. Rev., 104* (1990) 39.
13 M. W. Kokkes, Th. L. Snoeck, D. J. Stufkens, A. Oskam, M. Cristophersen and C. H. Stam, *J. Mol. Struct., 131* (1985) 11.
14 D. L. Morse and M. S. Wrighton, *J. Am. Chem. Soc., 98* (1976) 3931.
15 M. W. Kokkes, D. J. Stufkens and A. Oskam, *Inorg. Chem., 24* (1985) 2934.
16 M. W. Kokkes, W. G. J. de Lange, D. J. Stufkens and A. Oskam, *J. Organomet. Chem., 294* (1985) 59.
17 T. van der Graaf, D. J. Stufkens, A. Oskam and K. Goubitz, *Inorg. Chem., 30* (1991) 599.
18 T. van der Graaf, R. van Eldik, C. H. Langford, K. Bal Reddy, A. van Rooy, D. J. Stufkens and A. Vlcek, Jr., to be published.
19 T. J. Meyer, *Pure Appl. Chem., 58* (1986) 1193.
20 T. van der Graaf, R. Hofstra, P. G. M. Schilder, M. Rÿkhoff, D. J. Stufkens and J. G. M. van der Linden, *Organometallics,* in press.
21 H. Bock and H. tom Dieck, *Chem. Ber., 100* (1967) 228.
22 L. H. Staal, G. van Koten and K. Vrieze, *J. Organomet. Chem., 75* (1979) 73.
23 J. C. Luong, R. A. Faltynek and M. S. Wrighton, *J. Am. Chem. Soc., 102* (1980) 7892.

24 R. R. Andréa, W. G. J. de Lange, D. J. Stufkens and A. Oskam, *Inorg. Chim. Acta, 149* (1988) 77.

25 A. F. Hepp and M. S. Wrighton, *J. Am. Chem. Soc., 105* (1983) 5934.

26 R. R. Andréa, W. G. J. de Lange, D. J. Stufkens and A. Oskam, *Inorg. Chem., 28* (1989) 318.

27 L. A. deLearie and C. G. Pierpont, *J. Am. Chem. Soc., 109* (1987) 703.

28 H. K. van Dijk, J. van der Haar, D. J. Stufkens and A. Oskam, *Inorg. Chem., 28* (1989) 75.

29 R. S. Herrick, Th. R. Herrinton, H. W. Walker and Th. L. Brown, *Organometallics, 4* (1985) 42.

30 J. M. Hanckel, K.-W. Lee, P. Rushman and Th. L. Brown, *Inorg. Chem., 25* (1986) 1852.

31 R. R. Andréa, W. G. J. de Lange, T. van der Graaf, M. Rijkhoff, D. J. Stufkens and A. Oskam, *Organometallics, 7* (1988) 1100.

32 M. C. Baird, *Chem. Rev., 88* (1988) 217, and refs. therein.

33 J. R. Chipperfield, J. Ford and D. E. Webster, *J. Organomet. Chem., 102* (1975) 417.

34 T. van der Graaf, D. J. Stufkens, J. Víchová and A. Vlček, Jr., *J. Organomet. Chem., 401* (1991) 305.

35 C. P. Cheng, S. R. Wang, J. C. Lin and S.-L. Wang, *J. Organomet. Chem., 249* (1988) 375.

36 M. W. Lynch, D. N. Hendrickson, B. J. Fitzgerald and C. G. Pierpont, *J. Am. Chem. Soc., 249* (1984) 375.

37 R. R. Andréa, D. J. Stufkens, F. Hartl and A. Vlček, Jr., *J. Organomet. Chem., 359* (1989) 49.

38 P. C. Servaas, G. Stor, D. J. Stufkens and A. Oskam, *Inorg. Chim. Acta, 178* (1991) 185.

39 R. Schmid, *J. Solution Chem., 12* (1983) 2.

40 C. D. Pribula and T. L. Brown, *J. Organomet. Chem., 71* (1974) 415.

41 M. York Darensbourg, D. J. Darensbourg, D. Burns and D. A. Drew, *J. Am. Chem. Soc., 98* (1976) 3127.