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Metal to ligand charge-transfer photochemistry of metal–metal bonded complexes
9*. Photochemistry of $CpFe(CO)_2Re(CO)_3L$ ($L = 4,4'$-Me_2-bpy; pyridine-2-carbaldehyde *N*-isopropylimine)

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Abstract

In this article we report the photochemistry of the two metal–metal-bonded complexes $CpFe(CO)_2Re(CO)_3$(α-diimine) (α-diimine = 4,4'-dimethyl-2,2'-bipyridine (bpy'), pyridine-2-carbaldehyde *N*-isopropylimine (iPr-PyCa)) which are characterized by strongly allowed metal to ligand charge-transfer (MLCT) transitions in the visible region. At 218 K the bpy' complex (**1**) showed a wavelength dependent photochemistry. Low-energy excitation into the MLCT band produced homolysis products, irradiation with UV light gave rise to release of CO and to the formation of a CO-bridged photoproduct. The iPr-PyCa complex (**2**) showed a wavelength dependent photochemistry already at r.t. Again, homolysis of the metal–metal bond occurred upon low-energy excitation. UV irradiation of **2** also resulted in release of CO but in this case an iPr-PyCa bridged complex was formed. In this photoproduct, which could also be formed via a radical coupling mechanism upon prolonged irradiation of **2**, the iPr-PyCa ligand is most probably σ-N,σ-N' coordinated to Re and η^2-CN to Fe. From the experimental data it was concluded that the homolysis reaction occurred from the repulsive $^3\sigma\sigma^*$ state of the metal–metal bond and release of CO from a ^{3}LF state at higher energy, localized at the $CpFe(CO)_2$ fragment.

Introduction

Mechanistic studies in the field of organometallic photochemistry have mainly been confined to mono- and dinuclear transition-metal carbonyls. For the metal–metal bonded complexes, most mechanistic information is available for the carbonyl dimers $M_2(CO)_{10}$ (M = Mn, Re), $Cp_2Fe_2(CO)_4$, $Cp_2M_2(CO)_6$ (M = Mo, W) and their derivatives [2–8]. Several review articles dealing with the photochemistry of these complexes, have already appeared [9–11]. All homo- and heterodinuclear carbonyls display similar primary photoprocesses, viz. homolysis of the metal–metal bond and/or release of CO. For the above-mentioned carbonyl dimers the homolysis reaction was assumed to occur from the $^3\sigma\sigma^*$ state of the metal–metal bond, the CO-loss reaction from a close-lying ^{3}LF state [9].

A similar homolysis reaction was observed for the substituted complexes $L_m'M'M(CO)_3$(α-diimine) ($L_m'M' = (CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, Ph_3Sn; M = Mn, Re) upon irradiation into the low-energy M(d) → α-diimine (π^*) (MLCT) band [1, 3, 12–15]. This reaction also most probably occurs from the $^3\sigma\sigma^*$ state after intersystem crossing/internal conversion from the non-reactive MLCT states. Quite recently it was, however, shown by us that occupation of the $^3\sigma\sigma^*$ state not only leads to a homolysis reaction but can also give rise to release of CO [1, 15]. For both reactions the quantum yield was found to be wavelength independent throughout the MLCT band, in agreement with energy transfer to a repulsive $^3\sigma\sigma^*$ state. Whether metal–metal bond homolysis or CO-loss dominates, will depend on the relative strengths of the M–M' and M–CO bonds in the $^3\sigma\sigma^*$ state. Thus, both release of CO and homolysis

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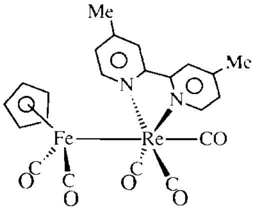

Fig. 1. Proposed structure of $CpFe(CO)_2Re(CO)_3(bpy')$.

of the metal–metal bond occur for the complexes $(CO)_5MnMn(CO)_3(\alpha$-diimine), which possess both a weak Mn–Mn bond and a $Mn(CO)_3(\alpha$-diimine) fragment with weak Mn–CO bonds [1, 3]. Since the Re–CO bond is about twice as strong as the Mn–CO bond, only homolysis of the M'–Re bond was observed for all metal–metal bonded complexes $L_m'M'Re(CO)_3(\alpha$-diimine) ($L_m'M' = (CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, Ph_3Sn) studied so far [3, 11, 13–15].

This article describes the synthesis, spectroscopic properties and photochemistry of two novel complexes $CpFe(CO)_2Re(CO)_3(\alpha$-diimine) ($\alpha$-diimine = 4,4'-dimethyl-2,2'-bipyridine (bpy') and pyridine-2-carbaldehyde*N*-isopropylimine (iPr-PyCa; C_5H_4N–CH=N–iPr)). They show, in contrast to all other $L_m'M'Re(CO)_3(\alpha$-diimine) complexes mentioned above, both homolysis and release of CO as primary photoprocesses. It will be shown, however, that these reactions do not occur from the same excited state.

The structure proposed for these complexes is presented in Fig. 1 for bpy'. It is based on previous (NMR and X-ray) structural data of other $XRe(CO)_3(\alpha$-diimine) (X = Br, $Mn(CO)_5$, $Re(CO)_5$, Ph_3Sn, $Co(CO)_4$) complexes, all having the α-diimine ligand in the equatorial plane of the $Re(CO)_3(\alpha$-diimine) fragment [13, 16–20].

Experimental

Materials

The solvents 2-MeTHF, THF and toluene were all of spectroscopic grade and they were distilled several times from Na and deoxygenated prior to use. $Re_2(CO)_{10}$, $Cp_2Fe_2(CO)_4$ and bpy' were obtained commercially and used without further purification. iPr-PyCa [21] and the complexes $Re(CO)_3LBr$ (L = bpy', iPr-PyCa) [22] were prepared by literature procedures. CCl_4 was distilled from P_2O_5 and kept under nitrogen before use. All spectroscopic samples were prepared by standard inert gas techniques.

Preparation of $CpFe(CO)_2Re(CO)_3(bpy')$ (1)

An excess of $NaK_{2.8}$ was added to a THF solution of $Cp_2Fe_2(CO)_4$ and after stirring for 2 h filtration yielded $Na^+[CpFe(CO)_2]^-$ (IR (ν(CO), THF): 1868 and 1793 cm^{-1}). An equimolar amount of $Re(CO)_3(bpy')Br$ was then added to the THF solution of $Na^+[CpFe(CO)_2]^-$. The reaction mixture was stirred for 1.5 h under exclusion of light and evaporated to dryness. The residue was dissolved in a minimal volume of THF and then chromatographed in the dark on Silica 60 with gradient elution of n-hexane–THF. Elution with 100% THF yielded a green band, which eluted after the residual $Cp_2Fe_2(CO)_4$. After removing the solvent by vacuum a deep green powder was obtained, which was washed several times with n-hexane. Yield: 30%. *Anal.* Found: C, 41.51; H, 2.87; N, 4.34; O, 12.17. Calc. for $CpFe(CO)_2Re(CO)_3(bpy')$: C, 41.81; H, 2.71; N, 4.44; O, 12.67%.

Preparation of $CpFe(CO)_2Re(CO)_3(iPr\text{-}PyCa)$ (2)

$[Re(CO)_3(iPr\text{-}PyCa)]^+OTF^-$ ($OTF^- = [O_3S\text{-}CF_3]^-$) was synthesized analogous to $[Mn(CO)_3(iPr\text{-}DAB)]^+OTF^-$ (DAB = 1,4-diaza-1,3-butadiene) described in the literature [3]. Complex **2** was prepared from $[Re(CO)_3(iPr\text{-}PyCa)]^+OTF^-$ and $Na^+[CpFe(CO)_2]^-$ using the method described above for complex **1**. Yield: 19%.

Spectroscopic measurements and photochemistry

UV–Vis absorption spectra were recorded on a Perkin-Elmer Lambda 5 spectrophotometer, equipped with a 3600 data station. IR spectra were measured with a Nicolet 7199 B FT-IR interferometer provided with a liquid nitrogen cooled MCT detector (32 scans, resolution 1.0 cm^{-1}). The spectroscopic solutions were irradiated by one of the lines of an SP model 2020 Ar^+ laser, a Coherent CR 8 Ar^+ laser or a CR 490 tunable dye laser with Rhodamine 110 as a dye, which was pumped by an SP model 171 Ar^+ laser. The reactions, which only proceeded upon exposure to light, were followed by IR and UV–Vis spectroscopy.

Results and discussion

Spectroscopic properties

The IR and UV–Vis data of the relevant compounds of this study are collected in Table 1. For the complexes $CpFe(CO)_2Re(CO)_3(L)$ (L = bpy', iPr-PyCa) four bands are observed at r.t. in the IR CO-stretching region. Figure 2 shows the IR and UV–Vis spectra of $CpFe(CO)_2Re(CO)_3(bpy')$ (**1**) at 293 K in THF. The assignment of the IR frequencies at

TABLE 1. IR ν(CO) frequencies (cm^{-1}) and λ_{max} (nm) of the lowest energy absorption bands of complexes **1** and **2** and their photoproducts

Complex	ν(CO) (cm^{-1})	λ_{max} (nm)
$CpFe(CO)_2Re(CO)_3(bpy')$ (**1**)	1989, 1927, 1895, 1872^a	406(sh), 625^a
	1989, 1926, 1892, 1868^b	400(sh), 610^b
	1988, 1924, 1892, 1871, 1864^c	475(sh), 598^c
$CpFe(CO)_2Re(CO)_3$(iPr-PyCa) (**2**)	1990, 1931, 1899, 1880^a	366, 410(sh), 700(sh), 770
	1988, 1929, 1896, 1874^b	
$Cp_2Fe_2(CO)_4$	1992, 1952, 1782^a	507^a
	1990, 1947, 1777^b	
$Re_2(CO)_6(bpy')_2$ ^{d}	1983, 1946, 1881, 1853^a	610, 810^a
$Re(CO)_3(bpy')$	2017, 1915, 1892^a	370^a
$Re(CO)_3(bpy')S$	2004, 1890, 1877^b	
$Re(CO)_3(bpy')Cl$	2018, 1915, 1891^a	375^a
$CpFe(CO)_2Cl$	2042, 1994^a	
$CpFe(CO)(\mu\text{-}CO)Re(CO)_2(bpy')$	1887, 1855, 1676^b	614^b
$Re(CO)_3$(iPr-PyCa)	2020, 1918, 1891^a	
$Re(CO)_3$(iPr-PyCa)Cl	2020, 1918, 1895^a	
$CpFe(CO)(\sigma,\sigma,\eta^2$-iPr-PyCa)$Re(CO)_3$	2006, 1907, 1896^a	390(sh)^a
	2004, 1904, 1891^b	382(sh)^b

^{a}Measured in THF at 293 K. ^{b}Measured in THF at 218 K. ^{c}Measured in 2-MeTHF at 133 K. ^{d}Made by electrochemical synthesis (see text).

1989, 1927, 1895 and 1872 cm^{-1} is not straightforward, since the coupling between two metal–carbonyl fragments frequently results in more complicated spectra in the CO-stretching region [23]. Furthermore the spectrum of **1** taken at 133 K in 2-MeTHF, reveals a more structured band pattern (ν(CO) frequencies: 1988, 1924, 1892, 1871 and 1864 cm^{-1}). The UV–Vis spectrum of **1** exhibits a distinct band in the visible region ($\lambda_{max}^{THF}=625$ nm). This intense band ($\epsilon=4\times10^3$ M^{-1} cm^{-1}), which is common for metal–metal bonded complexes possessing an α-diimine ligand [11], belongs to one or more metal–d to bipyridine–π^* (MLCT) transitions. This assignment is supported by the observation of a positive solvatochromism, characteristic for MLCT transitions ($\sigma_{max}(CH_3CN)-\sigma_{max}$(toluene) = 1.84 kK). At higher energy shoulders are observed at 406 and 355 nm, probably belonging to MLCT transitions to the second π^* orbital of bpy' and to the $\sigma\rightarrow\sigma^*$ transition of the metal–metal bond, respectively. Figure 3 shows the IR and UV–Vis spectra of $CpFe(CO)_2Re(CO)_3$(iPr-PyCa) (**2**). Whereas the IR spectrum of **2** closely resembles that of the bpy' complex, the UV–Vis spectrum shows a more structured MLCT band. The maximum of this band in THF occurs at 768 nm, while a shoulder is observed at 698 nm. Thus, the main MLCT transition of **2** is shifted appreciably to lower energy compared to that of complex **1**. It clearly demonstrates that the energy of the LUMO π^* orbital is lowered on going from bpy' to iPr-PyCa [24].

Photochemical reactions

$CpFe(CO)_2Re(CO)_3(bpy')$ (1)

Photolysis at 293 K. At room temperature a THF solution of **1** underwent an efficient photochemical reaction subsequent to irradiation with visible light. The IR spectral changes in the CO-stretching region accompanying this reaction are shown in Fig. 4 ($\lambda_{irr}=630$ nm; dye laser). It should be noted that no excitation wavelength dependence was observed for this reaction. Several new bands showed up from which those at 1992, 1952 and 1782 cm^{-1} are characteristic for the dimer $Cp_2Fe_2(CO)_4$ [8], the terminal CO-stretching frequencies at 1992 and 1952 cm^{-1} belonging to its *cis*- and *trans*-isomer, respectively. In polar media such as THF the dimer is mainly in its *cis*-conformation [25]. The formation of this product implies that a rapid recombination of $CpFe(CO)_2$ radicals has occurred after photochemical homolysis of the metal–metal bond (eqns. (1) and (2)).

$$CpFe(CO)_2Re(CO)_3(bpy') \xrightarrow{h\nu} CpFe(CO)_2 + Re(CO)_3(bpy') \quad (1)$$

$$2CpFe(CO)_2 \longrightarrow Cp_2Fe_2(CO)_4 \quad (2)$$

This homolysis reaction was further evidenced by the photoreaction of a solution of **1** and 0.05 M CCl_4 in degassed THF (eqn. (3)).

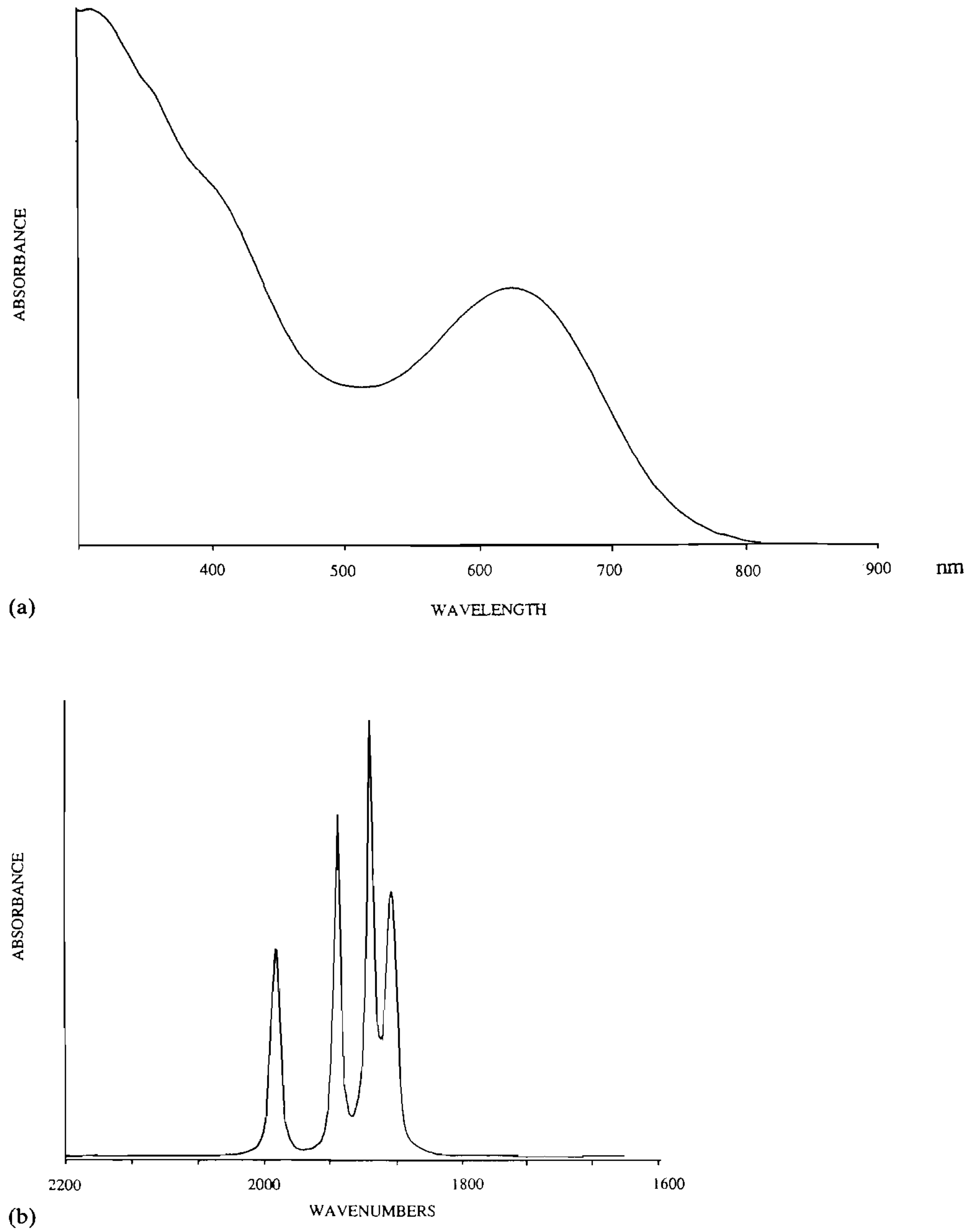

Fig. 2. (a) UV–Vis and (b) infrared (CO-stretching region) spectrum of $CpFe(CO)_2Re(CO)_3(bpy')$ (1) at 293 K in THF.

$$CpFe(CO)_2Re(CO)_3(bpy') \xrightarrow[0.05\ M\ CCl_4]{h\nu} CpFe(CO)_2Cl + Re(CO)_3(bpy')Cl \quad (3)$$

A noticeable thermal conversion to the same products occurred when higher concentrations of CCl_4 were employed.

When the CO-stretching frequencies of $Cp_2Fe_2(CO)_4$ are subtracted from the product spectrum in Fig. 4, five bands remain, at 2017(s), 1996(m), 1915(s), 1892(s) and 1876(s, broad) cm^{-1}, respectively. Three of them, at 2017, 1915 and 1892 cm^{-1}, are assigned to the radical complex $Re(CO)_3(bpy')$, formed according to reaction (1). This assignment is supported by the IR spectral data of the pho-

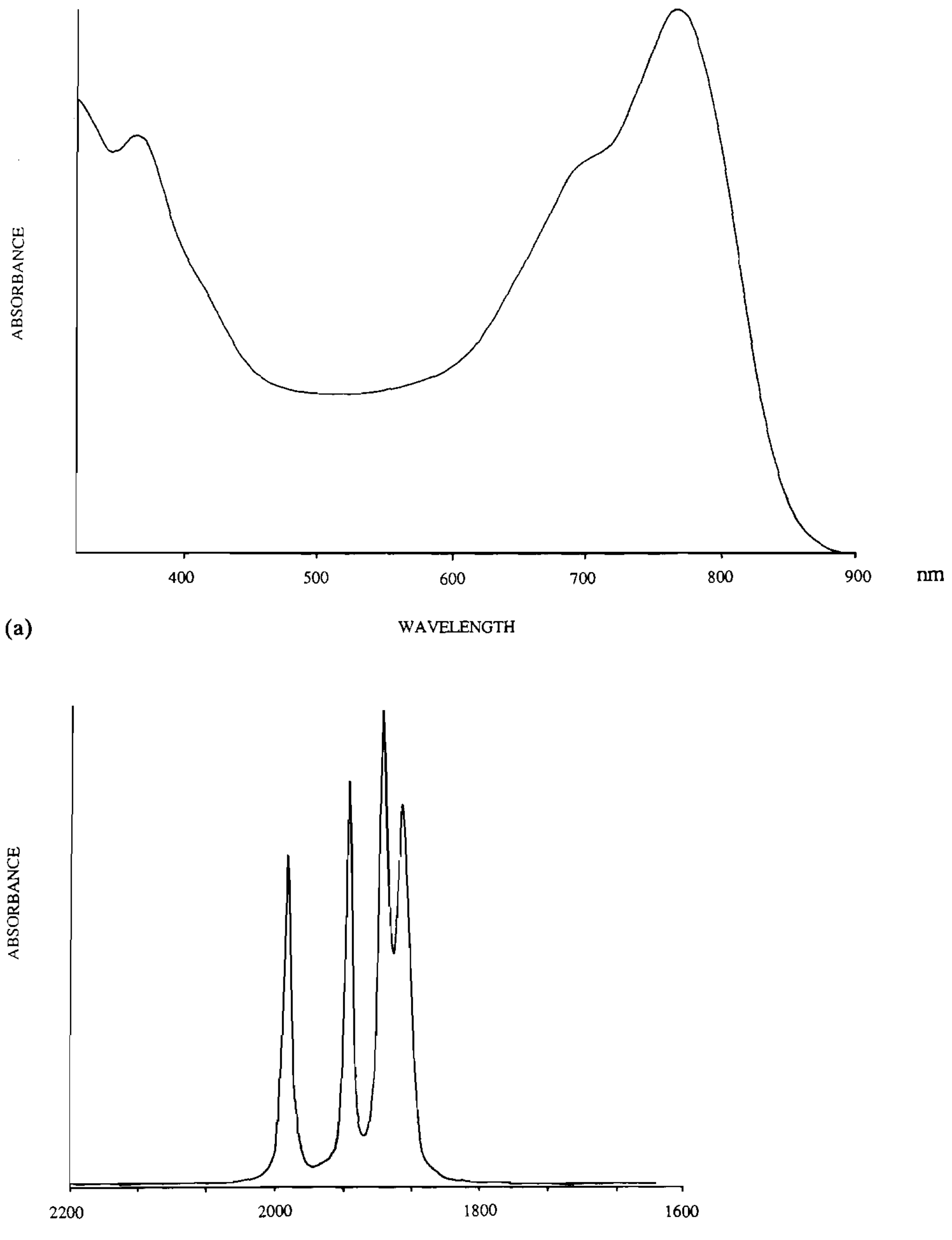

Fig. 3. (a) UV–Vis and (b) infrared (CO-stretching region) spectrum of $CpFe(CO)_2Re(CO)_3(iPr\text{-}PyCa)$ (**2**) at 293 K in THF.

toproduct of $Ph_3SnRe(CO)_3(tBu\text{-}DAB)$ (DAB = 1,4-diaza-1,3-butadiene) [15] and of the radical complexes obtained by reduction of a series of $(\mu\text{-}L)[Re(CO)_3Hal]_2$ (Hal = Cl, Br; L = bis-chelating α-diimine) complexes [26].

Irradiation of a benzene solution of $Ph_3SnRe(CO)_3(tBu\text{-}DAB)$ into its MLCT band gave rise to the formation of a paramagnetic photoproduct having no low-energy absorption band and CO-stretching frequencies at 2023, 1917 and 1897 cm^{-1} [15]. These IR bands were then assigned to the radical $Re(CO)_3(tBu\text{-}DAB)$, which was identified as a $16e\text{-}Re^{+}(CO)_3(tBu\text{-}DAB)^{\bullet -}$ radical complex with ESR.

Similar IR results were obtained recently by Kaim and Kohlmann [26], who studied the reduction products of several $(\mu\text{-}L)[Re(CO)_3Hal]_2$ (Hal = Cl, Br; L = 3,6-bis(2-pyridyl)tetrazine (bptz), 2,2′-bipyrimi-

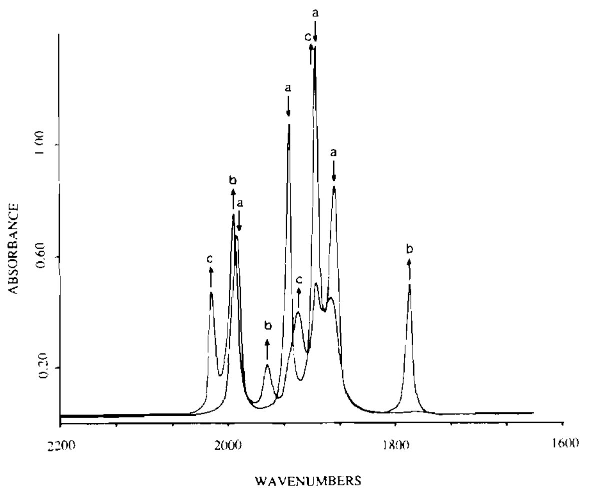

Fig. 4. Infrared spectral changes upon photolysis of complex **1** with $\lambda = 630$ nm ($P = 35$ mW) in THF at 293 K: (a) **1**; (b) $Cp_2Fe_2(CO)_4$; (c) $Re(CO)_3(bpy')$.

dine (bpym), etc) complexes. For the radical complex $(bptz^-)[Re(CO)_3Cl]_2$ in THF CO-stretching vibrations were found at 2015, 1918 and 1898 cm^{-1}, very close in frequency to those of the above-mentioned $Re(CO)_3$(α-diimine) radical complexes.

The same radicals have been produced by irradiation of other complexes L_m'M'$Re(CO)_3$(α-diimine) (L_m'M' = $(CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, Ph_3Sn). In this respect the Re complexes deviate in their behaviour from the corresponding Mn complexes, in which homolysis of the metal–metal bond is followed by dimerization of the $Mn(CO)_3$(α-diimine) radicals to give the photostable complexes $Mn_2(CO)_6$(α-diimine)$_2$. These dimers have a characteristic MLCT band at very low energy ($\lambda_{max} > 800$ nm) and typical IR bands in the CO-stretching region ($Mn_2(CO)_6(bpy')_2$ in 2-MeTHF at 293 K: 1979, 1932, 1882 and 1863 cm^{-1} [11]). No such low-energy band was observed upon photolysis of **1** and the two remaining IR bands in its product spectrum of Fig. 4 (1996 and 1876 cm^{-1}) do not belong to $Re_2(CO)_6(bpy')_2$ (*vide infra*). Yet, $Re_2(CO)_6(bpy')_2$ is a thermally stable complex which has been prepared electrochemically by Breikss and Abruna [27]. These authors studied the electrochemistry of $Re(CO)_3(bpy')Cl$ and observed the formation of $Re_2(CO)_6(bpy')_2$ when a solution of this complex with 0.4 M TBAP in CH_3CN was held for some time at a potential of -1.7 V versus SSCE. The dimer showed characteristic MLCT transitions at 598 and 792 nm. In order to obtain the IR frequencies of this dimer, we performed the same reaction in TBAP/THF at a potential of -1.5 V in the dark. After 16 h the solution had obtained a green colour and the UV–Vis ($\lambda_{max}^{THF} = 610$ nm, 810 nm) and IR (ν(CO) = 1983, 1946, 1881 and 1853 cm^{-1}) spectral data showed that $Re_2(CO)_6(bpy')_2$ had been formed. The complex was, however, very light sensitive and photodecomposed rapidly. The major decomposition product, having its CO-stretching frequencies at 1995, 1880 and 1867 cm^{-1}, slowly reacted back on standing in the dark to give the dimer. These results demonstrate that, whenever a $Re_2(CO)_6$(α-diimine)$_2$ complex is formed in a photochemical reaction, it will rapidly photodecompose. The composition and structure of this decomposition product, which also showed up in the product IR spectrum upon irradiation of complex **1** (1996 (m) and 1876 (s, broad) cm^{-1}), was not further investigated.

The attempted thermal synthesis of $Re_2(CO)_6(bpy')_2$ by refluxing for 48 h in the dark a THF solution of $Re_2(CO)_{10}$ containing a threefold excess of bpy', only resulted in the formation of a very small amount of the dimer. The main product isolated by column chromatography (Silica 60; gradient elution of n-hexane-THF) with a yield of 6%, was a yellowish solid substance. The IR spectrum of a THF solution of this product showed the three CO-stretching frequencies at 2017, 1915 and 1892 cm^{-1} belonging to the radical complex $Re(CO)_3(bpy')$ (*vide supra*). The UV–Vis spectrum of this complex consisted of a single band with a maximum at 370 nm. In conclusion it can be said that complex **1** photoreacts at r.t. according to reactions (1) and (2) and that the $Re(CO)_3(bpy')$ radicals partly dimerize to give $Re_2(CO)_6(bpy')_2$, a product which could not, however, be detected in the reaction mixture due to its photolability.

Photolysis at 218 K. Irradiation of **1** in THF at 218 K gave rise to different reactions depending on the wavelength of excitation. The IR spectral changes, observed upon irradiation with 630 nm light into the low-energy MLCT band, are shown in Fig. 5. The major photoproduct formed was $Cp_2Fe_2(CO)_4$ (1990, 1947 and 1777 cm^{-1}), which means that the photochemistry of **1** under these conditions is still dominated by homolysis of the metal–metal bond. Contrary to the reaction at 293 K, however, no IR bands belonging to $Re(CO)_3(bpy')$ were observed. Instead, another tricarbonyl species was formed with IR frequencies at 2002, 1890 and 1877 cm^{-1}. Raising the temperature caused the gradual transformation of this product into the $Re(CO)_3(bpy')$ radical complex. From this observation and from the frequencies of the CO-stretching vibrations, we conclude that this photoproduct represents the solvated radical $Re(CO)_3(bpy')S$ (S = THF). Further support for this

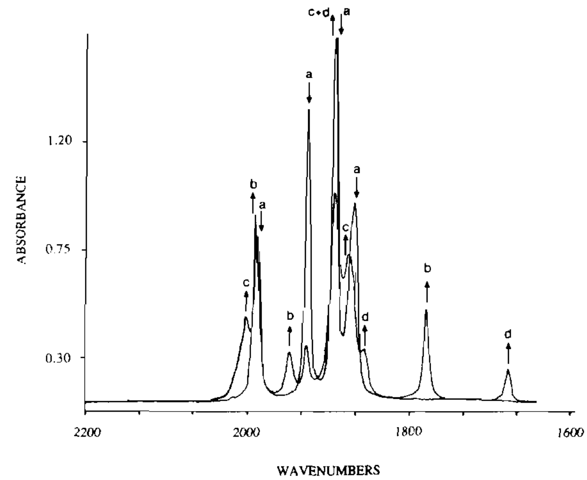

Fig. 5. Infrared spectral changes upon photolysis of complex 1 with $\lambda = 630$ nm ($P = 60$ mW) in THF at 218 K: (a) 1: (b) $Cp_2Fe_2(CO)_4$; (c) $Re(CO)_3(bpy')S$ (S = THF); (d) $CpFe(CO)(\mu\text{-}CO)Re(CO)_2(bpy')$.

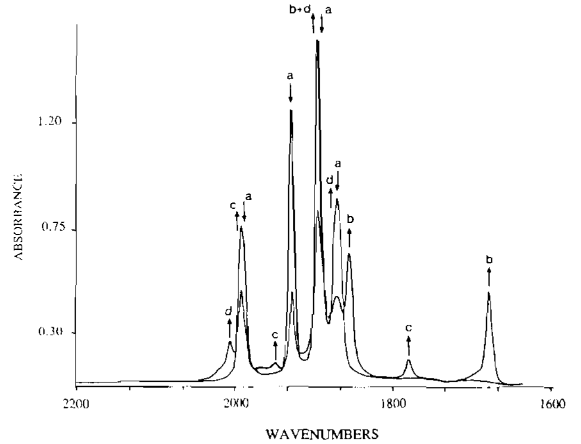

Fig. 6. Infrared spectral changes upon photolysis of complex 1 with $\lambda = 353/365$ nm ($P = 25$ mW) in THF at 218 K: (a) 1; (b) $CpFe(CO)(\mu\text{-}CO)Re(CO)_2(bpy')$; (c) $Cp_2Fe_2(CO)_4$; (d) $Re(CO)_3(bpy')S$ (S = THF).

assignment is provided by the observation that in the case that 2-MeTHF was used instead of THF both $Re(CO)_3(bpy')$ and its solvated complex were formed due to the weaker coordinating properties of 2-MeTHF at 218 K.

Apart from these two photoproducts a third complex was formed to a much smaller extent. Its CO-stretching frequencies at 1887, 1855 and 1676 cm^{-1}, respectively, point to a dinuclear species containing a bridging carbonyl group. Upon irradiation with shorter wavelengths the formation of this product became more pronounced and dominated the photochemistry after short irradiation times. This is clearly demonstrated in Fig. 6, which presents the initial IR spectral changes upon irradiation of 1 with the 353/365 nm lines of the Ar^+ laser. A radical mechanism (viz. homolysis of the Fe–Re bond) cannot account for this reaction since the product formation was not influenced by adding 0.05 M CCl_4 to the starting solution. The reaction most probably occurs via release of CO, although at 218 K no free carbon monoxide could be detected in the IR spectra. The dinuclear photoproduct still contained the N,N′-chelating bipyridine ligand, since the position and intensity of the MLCT band hardly changed during the photoreaction. The photoproduct is, therefore, assumed to be $CpFe(CO)(\mu\text{-}CO)Re(CO)_2(bpy')$.

A similar CO-loss photoreaction has been reported by Pope and Wrighton for the complexes $CpMo(CO)_3Mn(CO)_5$ [28] and $CpFe(CO)_2Mn(CO)_5$ [29] in rigid alkane glasses at 93 K. The latter complex only produced a coordinatively unsaturated species, whereas $CpMo(CO)_3Mn(CO)_5$ gave rise to the formation of two CO-bridged isomers from which the more stable one contained a similar fully bridging CO ligand ($\nu(CO) = 1680$ cm^{-1}) as the photoproduct of 1 ($\nu(CO) = 1676$ cm^{-1}). Unfortunately, due to the restricted solubility of 1, a comparative photochemical study of this complex in such an alkane glass could not be executed.

This CO-bridged photoproduct of 1 appeared to be thermally unstable and could not therefore be isolated. Besides, prolonged irradiation with UV-light caused its disappearance and the concomitant formation of $Cp_2Fe_2(CO)_4$, $Re(CO)_3(bpy')$ and $Re(CO)_3(bpy')S$ as the major photoproducts. Summarizing the above results it can be concluded that complex 1 undergoes the following photoreactions at 218 K.

$$CpFe(CO)_2Re(CO)_3(bpy') \xrightarrow[630\ \text{nm}]{h\nu} Cp_2Fe_2(CO)_4 + Re(CO)_3(bpy')S \quad (4)$$

$$CpFe(CO)_2Re(CO)_3(bpy') \xrightarrow[\substack{\text{UV}\\ \text{short irr.}\\ \text{times}}]{h\nu} CpFe(CO)(\mu\text{-}CO)Re(CO)_2(bpy') \quad (5)$$

CpFe(CO)₂Re(CO)₃(iPr-PyCa) (2)

Several new bands showed up in the IR CO-stretching region when 2 was irradiated with $\lambda = 514.5$ nm in THF at 293 K. At short irradiation times an almost identical band pattern was obtained as in the case of complex 1 at 293 K. Apart from the bands belonging to $Cp_2Fe_2(CO)_4$ and the 16e-radical complex $Re(CO)_3(iPr\text{-}PyCa)$ two bands showed up at 1993 and 1876 cm^{-1}, which are again assigned to a photodecomposition product, in this case of the dimer $Re_2(CO)_6(iPr\text{-}PyCa)_2$. The formation of these products confirms that a homolytic splitting of the Fe–Re bond has occurred, according to eqn. (6).

$$CpFe(CO)_2Re(CO)_3(iPr\text{-}PyCa) \xrightarrow{h\nu} CpFe(CO)_2 + Re(CO)_3(iPr\text{-}PyCa) \quad (6)$$

Upon prolonged irradiation, the bands of $Cp_2Fe_2(CO)_4$ and $Re(CO)_3(iPr\text{-}PyCa)$ slowly disappeared and three strong bands showed up at 2006, 1907 and 1896 cm^{-1}, respectively. This species was also the major photoproduct when **2** was irradiated with the UV-lines of the Ar^+ laser. When this latter reaction was followed with UV–Vis spectroscopy, the low-energy MLCT band disappeared, indicative of a change in coordination of the α-diimine ligand. Until now, only a very small amount of this product could be isolated and no single crystals have yet been obtained for an X-ray structure determination. A similar reaction has, however, recently been observed for the complex $(CO)_5MnMn(CO)_3(iPr\text{-}PyCa)$ and in this case the crystal structure of the photoproduct was determined [1]. The product was shown to be $(CO)_4Mn(\sigma,\sigma,\eta^2\text{-}iPr\text{-}PyCa)Mn(CO)_3$ with the iPr-PyCa ligand σ,σ-coordinated to one Mn atom and η^2-bonded to the other. The η^2-coordination is responsible for the loss of a CN double bond and of the low-lying π^*-orbital. As a result also the MLCT transitions to this orbital will disappear. The same reaction has most probably occurred for **2** and the proposed structure of the α-diimine bridged photoproduct is shown in Fig. 7. Thus, the second reaction observed for complex **2**, can be presented by eqn. (7).

$$CpFe(CO)_2Re(CO)_3(iPr\text{-}PyCa) \xrightarrow{h\nu} CpFe(CO)(\sigma,\sigma,\eta^2\text{-}iPr\text{-}PyCa)Re(CO)_3 + CO \quad (7)$$

Two possible mechanisms can account for this reaction, viz. direct loss of CO followed by attack of the iPr-PyCa ligand at the open coordination site or homolysis of the Fe–Re bond followed by a radical coupling reaction between the $Re(CO)_3(iPr\text{-}PyCa)$ and $CpFe(CO)_2$ radicals formed. From the observation that prolonged irradiation of **2** with 514.5 nm light caused the formation of the bridged species at the expense of the $Re(CO)_3(iPr\text{-}PyCa)$ radical and $Cp_2Fe_2(CO)_4$ we can conclude that the reaction proceeds at least to some extent via the latter mechanism. The reaction will start as soon as an appreciable amount of $Cp_2Fe_2(CO)_4$ is formed, which will absorb the 514.5 nm light and photoreact to give the $CpFe(CO)_2$ radicals necessary for the radical coupling reaction. A similar radical mechanism has recently been established for the photochemical formation of $(CO)_4Mn(\sigma,\sigma,\eta^2\text{-}iPr\text{-}PyCa)Mn(CO)_3$ out of $(CO)_5MnMn(CO)_3(iPr\text{-}PyCa)$ [1].

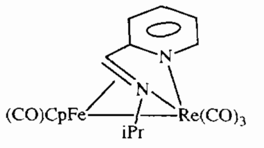

Fig. 7. Proposed structure of $CpFe(CO)(\sigma,\sigma,\eta^2\text{-}iPr\text{-}PyCa)Re(CO)_3$.

On the other hand, irradiation of **2** with the UV-lines of the Ar^+ laser in the presence of 0.05 M CCl_4 still caused the formation of the bridged species. This shows that upon higher energy excitation release of CO is the main primary photoprocess responsible for the formation of this photoproduct. This latter reaction in the presence of CCl_4 had to be performed at lower temperatures ($T = 218$ K) since a fast thermal reaction occurs between **2** and CCl_4 at 293 K. In contrast to complex **1**, complex **2** did not show a different photochemistry upon varying the temperature. This different behaviour between **1** and **2** will be discussed hereafter.

Photochemical mechanism

Both complexes show homolysis of the Fe–Re bond upon irradiation at r.t. into their MLCT band. This behaviour is analogous to that of other $L_m'M'Re(CO)_3(\alpha\text{-diimine})$ ($L_m'M' = (CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, Ph_3Sn) complexes studied so far. It is now well accepted that this reaction occurs from the ${}^3\sigma\sigma^*$ state after intersystem crossing/internal conversion from the MLCT state(s) [9, 11]. Due to its repulsive character this surface crossing to ${}^3\sigma\sigma^*$ can occur even at very low energy excitation. This explains why the photoreaction of **1** was still very efficient upon irradiation with 630 nm light. Figure 8 presents a qualitative diagram showing the potential energy curves of the MLCT and $\sigma\sigma^*$ states. Although occupation of the ${}^3\sigma\sigma^*$ state may also lead to release of CO, this reaction can only compete with homolysis of the metal–metal bond for complexes containing a $M(CO)_3(\alpha\text{-diimine})$ fragment having relatively weak M–CO bonds. This is the case for M = Mn but, due to the much stronger Re–CO bonds, such a CO-loss reaction from the ${}^3\sigma\sigma^*$ state has never been observed for any of the above-mentioned $L_m'M'Re(CO)_3(\alpha\text{-diimine})$ complexes. Also for **1** and **2** release of CO does not occur from the ${}^3\sigma\sigma^*$ state since in that case the quantum yield of the reaction would have been hardly wavelength dependent.

For complex **1** at T = 218 K and for **2** at r.t. release of CO became the major reaction upon UV irradiation. This means that the reaction most likely occurs from a reactive ${}^3LF$ state at somewhat higher energy. Since this reaction has not been observed

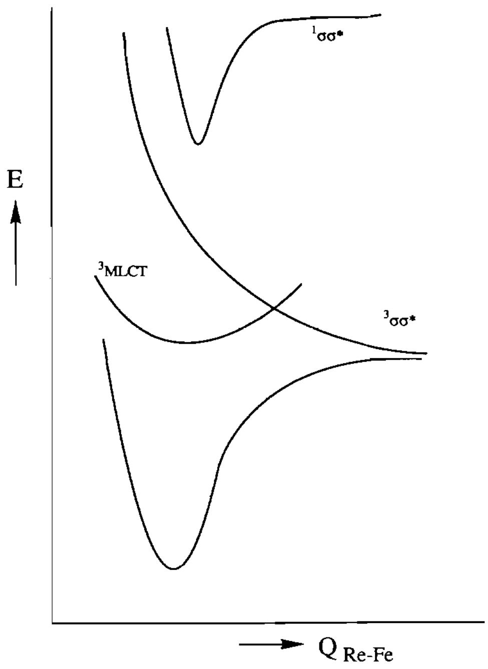

Fig. 8. Schematic potential energy-coordinate diagram showing the crossing between the MLCT and $^3\sigma\sigma^*$ states.

for any L_m'M'Re(CO)$_3$(α-diimine) complex, release of CO most likely occurs from the CpFe(CO)$_2$ fragment.

Contrary to complex **2**, complex **1** does not show a wavelength dependent photochemistry upon irradiation at r.t. This difference in behaviour is most likely due to the fact that in the case of **1** a fast backreaction of the CO-loss product with CO takes place. This backreaction was indeed observed when a solution containing the photoproduct formed by UV irradiation at 218 K was raised in temperature.

A similar behaviour has been observed for the complexes (CO)$_5$MnMn(CO)$_3$(α-diimine), which only give rise to the formation of homolysis products upon irradiation at r.t. [1, 3, 11, 12]. Nanosecond flash-photolysis of one of these complexes, viz. (CO)$_5$MnMn(CO)$_3$(phen), has, however, been shown to result in the formation of both a homolysis and CO-loss product [30]. The latter one reacted, however, back with CO to give the parent compound.

In the case of **2**, release of CO from the CpFe(CO)$_2$ fragment is, apparently, followed by attack of the CN group of the iPr-PyCa ligand at the Fe atom giving rise to the formation of the (photo) stable reaction product CpFe(CO)(σ,σ,η^2-iPr-PyCa)-Re(CO)$_3$. Since this reaction cannot occur for the bpy' ligand, release of CO from **1** gives rise to the formation of a CO-bridged photoproduct, which is, however, only stable at lower temperatures.

Conclusions

The above results clearly show that the complexes CpFe(CO)$_2$Re(CO)$_3$L (L = bpy', iPr-PyCa) undergo a wavelength dependent photochemistry. Irradiation into the low-energy MLCT band gave rise to homolysis of the Fe–Re bond and to the formation of 16e-radical complexes Re(CO)$_3$L, which were characterized with IR.

Low-temperature irradiation with the UV-lines of an argon ion laser gave instead release of CO, presumably from a LF state of the CpFe(CO)$_2$ fragment. This reaction led to the formation of the bridged dinuclear complexes CpFe(CO)(μ-CO)Re(CO)$_2$(bpy') and CpFe(CO)(σ,σ,η^2-iPr-PyCa)Re(CO)$_3$, respectively.

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