

MLCT and LF Photochemistry of d^6 *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ (DTO = dithiooxamide)

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Abstract

The complex *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ (Cycl-DTO = *N,N'*-dimethylpiperazine-2,3-dithione) shows a wavelength dependent photochemistry which is seldom observed for transition metal complexes having the lowest MLCT state.

The reaction from the lowest $\text{Re} \rightarrow \text{DTO}$ MLCT state is substitution of Br^- . This reaction proceeds via an associative mechanism since it has a low, concentration dependent, quantum yield and only takes place for not too bulky, highly nucleophilic phosphine ligands such as $\text{P}(\text{nBu})_3$. The photoproduct **A** of the reaction with $\text{P}(\text{nBu})_3$ isomerizes thermally to **B**, which complex can in turn be reconverted into **A** by irradiation with visible light. **A** and **B** are assigned to *mer*- and *fac*- $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+\text{Br}^-$, respectively. This assignment is supported by ^{31}P NMR data and by the IR and UV-Vis spectra of **A** and **B** when compared with those of the separately prepared isomers of the corresponding complex $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+[\text{OTf}]^-$.

Irradiation of the parent compound with 366 nm light into the 370 nm band gives rise to efficient loss of CO. This reaction is proposed to occur from the lowest ^3LF state in agreement with similar results reported for $\text{Re}(\text{CO})_5\text{Br}$.

Introduction

Many coordination and organometallic complexes are photolabile since their lowest excited states are reactive metal-centred states [1]. Quantum yields for ligand loss are often high ($\phi > 0.1$ mol/einstein). When the lowest excited state has instead a metal to ligand charge transfer (MLCT) character, the complex is normally fairly photostable. Thus, complexes such as $\text{Ru}(\text{bpy})_3^{2+}$ and $\text{Re}(\text{CO})_3(\text{bpy})\text{Cl}$, having their MLCT band at lower energy than the LF transitions, only photoreact at higher temperatures by thermal population of a reactive ^3LF state [2, 3]. The

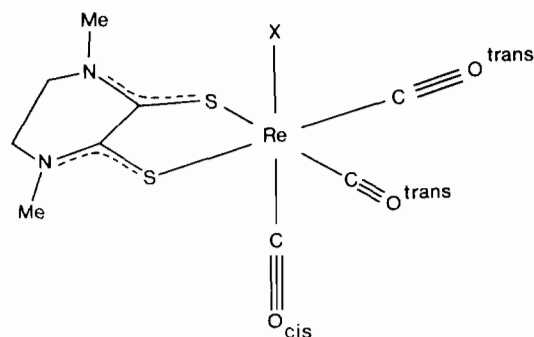


Fig. 1. Structure of *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{X}$ (DTO = dithiooxamide; X = halide).

MLCT states themselves are normally not reactive, although a few exceptions have recently been reported [4–12]. One of these exceptions concerns the complexes $\text{W}(\text{CO})_4(\alpha\text{-diimine})$ which undergo MLCT photochemistry upon irradiation into their lowest-energy absorption band [4–7]. The quantum yields of photosubstitution of CO by PR_3 appeared to be low ($\phi = 10^{-4}$ – 10^{-5} mol/einstein) and the reactions were found to be associative.

In this article we report the results of a study on the complex *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ (Cycl-DTO = *N,N'*-dimethylpiperazine-2,3-dithione), which showed both LF and MLCT photochemistry. The structural, theoretical and spectroscopic properties of this complex have recently been described [13]. The coordinated ligand consists of two thioamide groups, having a dihedral angle of 18° (Fig. 1). Because of this small angle the π^* orbitals of these groups strongly overlap giving rise to an intense MLCT band at *c.* 500 nm. The photochemistry of this complex has been studied both by irradiating into this MLCT band and into the second band at 370 nm, giving rise to different reactions.

Experimental

Materials and Preparations

The dithiooxamide ligand [14, 15] and the *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ complex [13] were prepared

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according to literature procedures. All spectroscopic solutions, prepared by standard inert-gas techniques, were made in solvents which were distilled several times from sodium and deoxygenated before use. All ^{31}P NMR data are given relative to H_3PO_4 .

Photochemical Preparation of $\text{Re}(\text{CO})_2(\text{Cycl-DTO})\text{-}(\text{PR}_3)\text{Br}$ ($R = \text{cHex}, \text{nBu}$) and $[\text{Re}(\text{CO})_2(\text{Cycl-DTO})\text{-}(\text{P}(\text{nBu})_3)_2]^+\text{Br}^-$

fac- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ (0.19 mmol) and PR_3 ($R = \text{cHex}$, 0.4 mmol; $R = \text{nBu}$, 0.19 mmol) were dissolved in 70 ml of freshly distilled and deoxygenated THF and irradiated for 8 days ($R = \text{cHex}$) with a medium pressure Hg lamp (filtered, $\lambda > 313$ nm) or 17 h ($R = \text{nBu}$) with $\lambda = 350$ nm (Rayonet, photochemical reactor, type RPR-208). The reaction was followed by IR spectroscopy. After evaporation, the residue was purified by column chromatography (silica gel 60; eluent n-hexane: THF = 1:4). The air-stable blue products were isolated and identified by IR, ^1H and ^{31}P NMR.

$\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{cHex})_3)\text{Br}$: IR (in THF, cm^{-1}) $\nu(\text{CO})$ 1918, 1841; ^1H NMR (in CDCl_3 , 293 K, TMS internal, δ ppm) 3.7–3.5 (m, 10H), 2.5–1.3 (m, 33H); ^{31}P NMR (in CDCl_3 , 293 K, δ ppm) 17.92 (s).

$[\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)_2]^+\text{Br}^-$: IR (in THF, cm^{-1}) $\nu(\text{CO})$ 1922, 1842; ^1H NMR (in CDCl_3 , 293 K, TMS internal, δ ppm) 3.7–3.5 (m, 10H) 1.8–0.9 (m, 27H); ^{31}P NMR (in CDCl_3 , 293 K, δ ppm) –6.65 (s).

When the above photochemical reaction between *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ and $\text{P}(\text{nBu})_3$ in THF was performed with a fourfold excess of the phosphine ligand, $[\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)_2]^+\text{Br}^-$ was formed instead (15 h with $\lambda = 350$ nm, Rayonet). After completion of this reaction the solution was evaporated to dryness and the residue was purified by column chromatography using a silica gel 60/n-pentane column with a length of 5 cm. Gradient elution was applied (n-pentane \rightarrow THF \rightarrow ethanol) and after elution with THF:ethanol = 85:15 a blue

product fraction was obtained which was evaporated to dryness. Attempts to crystallize the blue oily substance failed. IR (in THF, cm^{-1}) $\nu(\text{CO})$ 1929, 1865.

Spectroscopy and Photochemistry

Absorption spectra were measured on a Perkin-Elmer Lambda 5 spectrophotometer, IR spectra on a Nicolet 7199B FTIR spectrometer with a liquid-nitrogen-cooled MCT detector (32 scans, resolution 1.0 cm^{-1}), ^1H and ^{31}P NMR spectra on a Bruker AC 100 apparatus.

A filtered medium pressure Hg lamp and an SP Model 171 Ar^+ laser were used as light sources for the photochemical reactions.

Results and Discussion

Table 1 presents the IR (CO-stretching region) and UV–Vis spectral data of the photoproducts formed.

MLCT Photochemistry

Irradiation of a THF solution of *fac*- $\text{Re}(\text{CO})_3\text{-}(\text{Cycl-DTO})\text{Br}$ with the 514.5 nm laser line in the presence of PR_3 only gave rise to a photoreaction when the phosphine was basic and not too bulky. Thus, no reaction was observed with $\text{P}(\text{cHex})_3$ and $\text{P}(\text{OMe})_3$ but the complex did react with $\text{P}(\text{nBu})_3$. The low efficiency of the reaction increased with increasing concentration of the phosphine. Unfortunately, no reliable quantum yields could be determined because of secondary photochemical and thermal reactions. The low quantum yield (estimated value 10^{-4} – 10^{-5} mol/einstein) and its dependence on the concentration, size and nucleophilic character of the PR_3 ligand, point to an associative mechanism, just as in the case of the corresponding photochemistry of $\text{W}(\text{CO})_4(\alpha\text{-diimine})$ complexes [5, 7].

TABLE 1. IR and UV–Vis spectral data

Complex	IR $\nu(\text{CO})^{\text{THF}}$ (cm^{-1})	UV–Vis λ_{max} (MLCT) $^{\text{THF}}$ (nm)
<i>fac</i> - $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$	2020, 1930, 1898	374, 517
$[\text{Re}(\text{CO})_3(\text{Cycl-DTO})]^+\text{[OTf]}^-$	2028, 1929, 1913	458
<i>mer</i> - $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+\text{Br}^-$ (isomer A)	2012, 1917, 1891	380sh, 486
<i>fac</i> - $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+\text{Br}^-$ (isomer B)	2026, 1938, 1921	469
<i>mer</i> - $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+\text{[OTf]}^-$	2012, 1917, 1891	380sh, 484
<i>fac</i> - $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+\text{[OTf]}^-$	2026, 1938, 1921	469
$\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{cHex})_3)\text{Br}$	1918, 1841	623
$\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{OMe})_3)\text{Br}$	1942, 1865	580
$\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)\text{Br}$	1922, 1843	608
$[\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)_2]^+\text{Br}^-$	1929, 1865	576

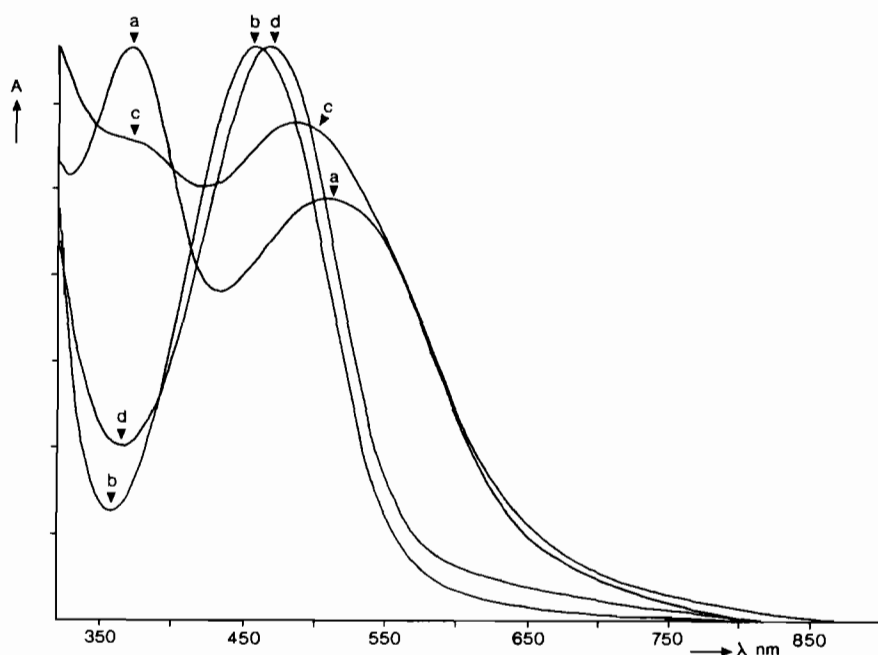


Fig. 2. Electronic absorption spectra at 293 K in THF of (a) *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$; (b) $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})]^+[\text{OTF}]^-$; (c) *mer*- $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+\text{Br}^-$ (isomer A); (d) *fac*- $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+\text{Br}^-$ (isomer B).

During the reaction three new CO vibrations showed up at 2012, 1917 and 1891 cm^{-1} , obviously belonging to another tricarbonyl species (product A). The absorption spectrum of A still contained an intense MLCT band at 486 nm (see Fig. 2), which implies that the DTO ligand was still present in the photoproduct.

A slowly converted thermally into another tricarbonyl species (product B), having its CO-stretching vibrations at somewhat higher frequencies and the MLCT band at 469 nm (Table 1). However, when the solution of B in THF was once more irradiated with the 514.5 nm line, this complex reacted back to give A.

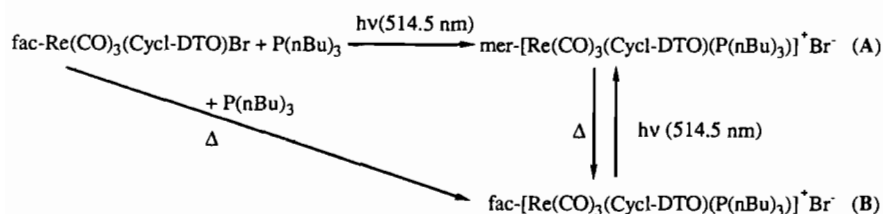
These observations indicate that A and B are isomers of the same complex. In order to assign these isomers the effect of substitution of Br^- in *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ by $\text{P}(\text{nBu})_3$ was studied. For this purpose $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})]^+[\text{OTF}]^-$ ($\text{OTF}^- = \textit{ortho}$ -trifluoromethanesulfonate) was prepared by adding an equimolar amount of AgOTF to a THF solution of *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$. After filtration $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})]^+[\text{OTF}]^-$ was obtained in the filtrate. Addition of excess $\text{P}(\text{nBu})_3$ under exclusion of light then gave rise to the formation of $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+[\text{OTF}]^-$ in 100% yield. The CO-stretching frequencies, ^{31}P NMR shift and UV-Vis data of this product were nearly the same as those of B. Apparently, the only difference between the two complexes are the counterions, being OTF^- and Br^- , respectively. It is therefore not surprising that irradiation of this OTF^- complex

with visible light caused an almost complete conversion into a species having similar CO-stretching frequencies and UV-Vis data as A.

From the above results it is concluded that A and B represent two isomeric forms of the complex $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+\text{Br}^-$. Unfortunately, no single crystals of these isomers could be obtained and the IR and UV-Vis spectra did not give much information about the conformation of the isomers. The NMR spectra showed, however, that the coordinated $\text{P}(\text{nBu})_3$ ligand had its ^{31}P NMR signal at -9.90 ppm in B and at -17.4 ppm in A (both in CDCl_3). Comparing these ^{31}P NMR shifts with that of free $\text{P}(\text{nBu})_3$ (-30.6 ppm) it follows that $\text{P}(\text{nBu})_3$ is more loosely bound in A. From this result it is concluded that A represents the *mer*-conformation of $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+\text{Br}^-$, in which the $\text{P}(\text{nBu})_3$ ligand is coordinated to the metal in the equatorial plane opposite to the DTO ligand, thereby exerting a strong *trans*-effect. The thermodynamically more stable complex B is assigned accordingly to the *fac*-conformation.

Thus, irradiation of *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ into its low-energy MLCT band gives rise to replacement of Br^- by $\text{P}(\text{nBu})_3$ with a concomitant change of structure from *fac* to *mer* (product A). This photochemical reaction is then followed by a thermal isomerization of A to B as shown schematically in Scheme 1.

Scheme 1 also shows that B can be prepared thermally out of *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$. A similar associative mechanism as observed for the



Scheme 1.

photoreaction of the parent compound was found for the photoisomerization of **B** into **A**. No reaction occurred in a non-coordinating solvent such as CH_2Cl_2 when no extra $\text{P}(\text{nBu})_3$ was added to the solution. In the presence of $\text{P}(\text{nBu})_3$ the reaction proceeded with increasing quantum yield when the concentration of the phosphine ligand was increased. Again, these quantum yields could not be determined quantitatively because of the photochemical and thermal instability of **A**. In a coordinating solvent such as THF, the photoisomerization proceeded both in the absence and presence of $\text{P}(\text{nBu})_3$. This means that this reaction only takes place when a seven coordinated intermediate can be formed, e.g. by coordination of $\text{P}(\text{nBu})_3$ or THF to the metal in the MLCT excited state of the complex. As reported before for the corresponding $\text{W}(\text{CO})_4(\alpha\text{-diimine})$ complexes [5, 7] such an intermediate will only be formed when the substituting ligand is not too bulky and acts as a strong nucleophile. This also explains why the photoreaction of the parent compound did not take place for $\text{P}(\text{cHex})_3$ and $\text{P}(\text{OMe})_3$.

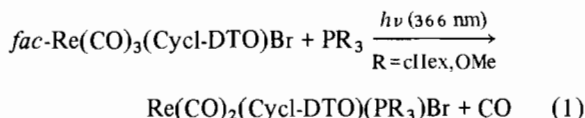
The question remains how this photochemical behaviour of $\text{fac-Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ can be explained in view of the fact that such a low-energy Br^- loss reaction is normally not observed for this type of $\text{Re}(\text{CO})_3\text{LBr}$ complex. A recent LCAO-X α -MO study on the model complex $\text{fac-Re}(\text{CO})_3(\text{H}_2\text{-DTO})\text{Br}$ has shown that backdonation from the metal fragment to the lowest π^* orbital of the $\text{H}_2\text{-DTO}$ ligand essentially occurs from an orbital with substantial Br-4p (69%) and hardly any Re-d (8%) character [13]. No less than 0.212 e appeared to be donated from the halide orbital to $\text{DTO-}\pi^*$. Experimental evidence for this interaction was provided by the crystal structure of $\text{fac-Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$, which showed a bending of the DTO ligand in the direction of the Re-Br bond. According to these calculations the LUMO of $\text{fac-Re}(\text{CO})_3(\text{H}_2\text{-DTO})\text{Br}$ appeared to be mainly $\text{DTO-}\pi^*$ in character and DTO-Br^- anti-bonding. As a result the Re-Br^- bond will also be weakened in the lowest MLCT states of these complexes giving rise to the observed Br^- loss reaction.

LF Photochemistry

The complex $\text{fac-Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ has, apart from the MLCT band at 500 nm, a second absorption

band at about 370 nm, which has been assigned to a second $\text{Re} \rightarrow \text{DTO}$ MLCT band on the basis of its intensity, solvatochromic behaviour and the results of MO calculations [13]. LF transitions are expected in the same spectral region but these are normally much weaker and will therefore easily escape detection. Since the LF states are, however, much more reactive than the MLCT states, reactions will preferably occur from the former states.

Contrary to the above results obtained by excitation with 514.5 nm, irradiation with 366 nm of a medium pressure Hg-lamp into the 370 nm band caused an efficient photochemical reaction for all phosphines, including $\text{P}(\text{cHex})_3$ and $\text{P}(\text{OMe})_3$. For these latter ligands the photoreaction was, however, more simple than for $\text{P}(\text{nBu})_3$ since they only showed the appearance of two new CO-stretching vibrations of a dicarbonyl species (Table 1) and a red shift of the MLCT band (Fig. 3 for $\text{P}(\text{cHex})_3$). These results point to a photosubstitution of an electron-withdrawing carbonyl ligand by the phosphine according to reaction (1).



In the case of $\text{P}(\text{nBu})_3$, irradiation with 366 nm caused the appearance of several new CO bands, from which two (at 2012 and 1917 cm^{-1} , respectively) (Fig. 4) disappeared after prolonged irradiation.

These two bands, together with one at *c.* 1890 cm^{-1} , which was partly obscured by the bands of the parent compound, belong to the previously assigned isomer **A** (denoted as 2 in Fig. 4). Apart from this, three new bands showed up at 1928 (broad), 1865 and 1843 cm^{-1} , respectively, which will be shown to belong to two different dicarbonyl photoproducts (denoted as 3 and 4 in Fig. 4). When this reaction was performed at 263 K, isomer **A** was not formed anymore (just as upon irradiation with 514.5 nm at this temperature) and only two new IR bands showed up at 1922 and 1843 cm^{-1} , respectively. In accordance with the photoproduct of reaction (1) for $\text{R} = \text{cHex}$ (Table 1) these bands are assigned to the photosubstitution product $\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)\text{Br}$ indicated as product

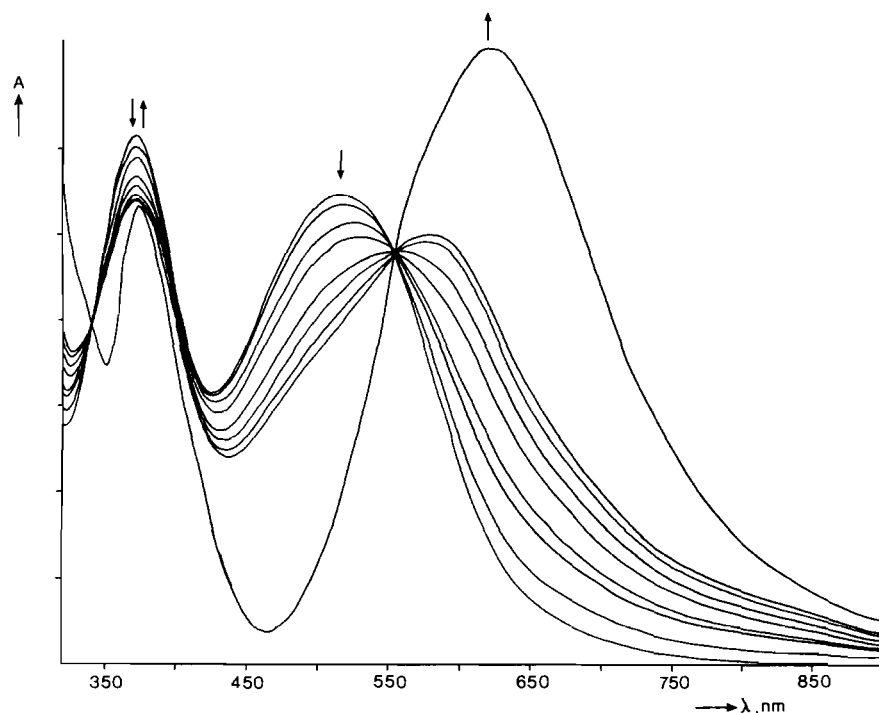


Fig. 3. UV-Vis spectral changes accompanying the photochemical reaction of *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ with $\text{P}(\text{cHex})_3$ upon irradiation with 366 nm in THF at 293 K.

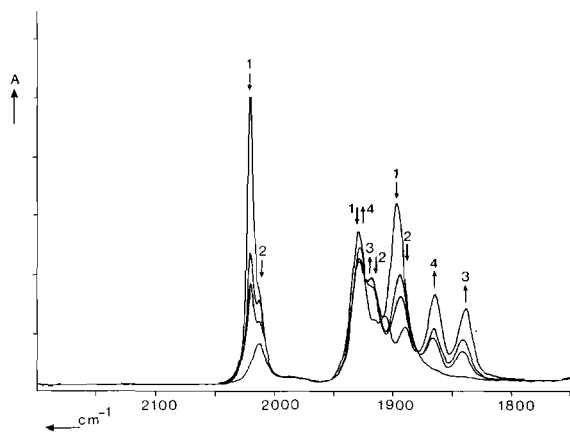
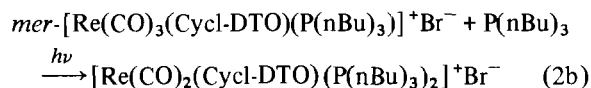
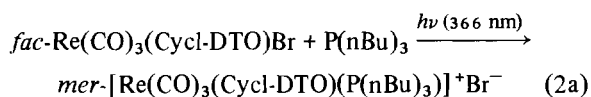


Fig. 4. Infrared spectral changes during the photolysis of $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$ with $\text{P}(\text{nBu})_3$ with 366 nm in THF at 293 K. (1) *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$; (2) *mer*- $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)]^+\text{Br}^-$ (isomer A); (3) $\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)\text{Br}$; (4) $[\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)_2]^+\text{Br}^-$.

3 in Fig. 4. The CO-stretching frequencies of the remaining photoproduct 4 were established at 1929 and 1865 cm^{-1} by subtracting from the final spectrum of Fig. 4 the spectra of 2 and 3. From the observation that the IR bands of 4 showed up concomitant with the decrease of the bands belonging to A (2) it is concluded that 4 is the photoproduct of A. Product 4 is therefore assigned as $[\text{Re}(\text{CO})_2-$

$(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)_2]^+\text{Br}^-$. This assignment is further corroborated by the 366 nm irradiation of the *in situ* prepared product A via the $[\text{Re}(\text{CO})_3(\text{Cycl-DTO})]^+[\text{OTF}]^-$ route as described in the previous section. New bands then showed up at 1931 and 1865 cm^{-1} , obviously belonging to the dicarbonyl product $[\text{Re}(\text{CO})_2(\text{Cycl-DTO})(\text{P}(\text{nBu})_3)_2]^+[\text{OTF}]^-$. Thus, in the case of $\text{P}(\text{nBu})_3$ the following reactions occurred apart from reaction (1).



Irradiation of B with 366 nm only gave rise to photoisomerization to A and the CO-loss product was only formed out of this latter isomer. This difference in photochemical behaviour between the isomers A and B is remarkable. We have recently observed a similar effect upon UV irradiation of the *syn*- and *anti*-isomers of $(\text{CO})_5\text{W}=\text{C}(\text{OMe})\text{Ph}$ which have close-lying LF and MLCT states [16]. The *anti*-isomer then gave rise to photoisomerization, the *syn*-isomer showed release of CO. Most probably,

the reactive LF and MLCT states shift with respect to each other upon going from one isomer to the other. Both dicarbonyl complexes 3 and 4 of Fig. 4 have been made on a preparative scale and identified (see 'Experimental').

A similar CO-loss reaction as observed for the DTO complex was reported for $\text{Re}(\text{CO})_5\text{Br}$ upon 366 nm irradiation [17, 18]. Both reactions will occur from the lowest ^3LF state.

Conclusions

In conclusion it can be said that the complex under study, *fac*- $\text{Re}(\text{CO})_3(\text{Cycl-DTO})\text{Br}$, is rather special in showing two different photochemical reactions depending on the wavelength of irradiation. Excitation into the low-energy MLCT band caused the photosubstitution of Br^- by a nucleophile with low quantum yield. The reaction proceeds via an associative mechanism. In contrast to this, efficient dissociative loss of CO occurs from the lowest ^3LF state upon irradiation with 366 nm light.

References

- G. L. Geoffroy and M. S. Wrighton, *Organometallic Photochemistry*, Academic Press, New York, 1979.
- K. Kalyanasundaran, *Coord. Chem. Rev.*, **46** (1982) 159.
- T. J. Meyer, *Pure Appl. Chem.*, **58** (1986) 1193.
- R. W. Balk, Th. L. Snoeck, D. J. Stufkens and A. Oskam, *Inorg. Chem.*, **19** (1980) 3015.
- H. K. Van Dijk, P. C. Servaas, D. J. Stufkens and A. Oskam, *Inorg. Chim. Acta.*, **104** (1985) 179.
- P. C. Servaas, H. K. van Dijk, Th. L. Snoeck, D. J. Stufkens and A. Oskam, *Inorg. Chem.*, **24** (1985) 4494.
- S. Wieland and R. van Eldik, *J. Chem. Soc., Chem. Commun.*, (1989) 367.
- D. J. Stufkens, *Coord. Chem. Rev.*, in press.
- H. K. van Dijk, D. J. Stufkens and A. Oskam, *J. Am. Chem. Soc.*, **111** (1989) 541.
- M. W. Kokkes, D. J. Stufkens and A. Oskam, *J. Chem. Soc., Dalton Trans.*, (1984) 1005.
- P. C. Servaas, D. J. Stufkens and A. Oskam, *Inorg. Chem.*, **28** (1989) 1774.
- P. C. Servaas, D. J. Stufkens and A. Oskam, *Inorg. Chem.*, **28** (1989) 1780.
- P. C. Servaas, D. J. Stufkens, A. Oskam, P. Vernooijs, E. J. Baerends, D. J. A. De Ridder and C. H. Stam, *Inorg. Chem.*, **28** (1989) 4104.
- R. Isaksson, T. Liljefors and J. Sandström, *J. Chem. Res. M.* (1981) 664.
- R. N. Hurd, G. De La Mater, G. C. McElheny, R. J. Turner and V. H. Wallingford, *J. Org. Chem.*, **26** (1961) 3980.
- P. C. Servaas, D. J. Stufkens and A. Oskam, *J. Organomet. Chem.*, in press.
- M. S. Wrighton, D. L. Morse, H. B. Gray and D. K. Ottesen, *J. Am. Chem. Soc.*, **98** (1976) 1111.
- D. R. Tyler and D. P. Petrylak, *Inorg. Chim. Acta*, **53** (1981) L185.