

PHOTOCHEMISTRY OF METAL–METAL BONDED COMPLEXES

III *. MLCT PHOTOLYSIS OF $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ ($\text{M}, \text{M}' = \text{Mn}, \text{Re}$) IN 2-Me-THF AND THF AT 293 K; EVIDENCE OF PHOTOCATALYTIC FORMATION OF $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(\text{P}(\text{n-Bu})_3)]^+ [\text{M}(\text{CO})_5]^-$ UPON PHOTOLYSIS IN THE PRESENCE OF $\text{P}(\text{n-Bu})_3$

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Summary

Complexes of the type $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ ($\text{M}, \text{M}' = \text{Mn}, \text{Re}$) were photolyzed in 2-Me-THF at 293 K in the absence and presence of PR_3 by irradiation in the low energy $\text{M}' \rightarrow \alpha\text{-diimine}$ charge transfer band. In most cases the primary photoprocess appeared to be homolysis of the ($\text{M}-\text{M}'$) metal–metal bond. In the absence of PR_3 the radicals formed react with each other to give $\text{M}_2(\text{CO})_{10}$ and $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})_2$. It is shown that the stabilities of these $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})_2$ complexes depend on the $\alpha\text{-diimine}$ ligand used.

In the presence of PR_3 various reactions are observed, depending on the complex and the PR_3 ligand used. Thus, photolysis of $(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$ in the presence of PPh_3 or $\text{P}(\text{n-Bu})_3$ gives $\text{Mn}_2(\text{CO})_{10}$ and a reaction product of $\text{Re}_2(\text{CO})_6(\alpha\text{-diimine})_2$. However, $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ in the presence of PPh_3 gives $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ instead of $\text{Mn}_2(\text{CO})_{10}$. A remarkable reaction is observed when a $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ complex is photolyzed in the presence of the basic phosphine $\text{P}(\text{n-Bu})_3$, the ionic compound $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(\text{P}(\text{n-Bu})_3)]^+ [\text{Mn}(\text{CO})_5]^-$ being formed as the result of electron transfer from the radical $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(\text{P}(\text{n-Bu})_3)$ to $\text{Mn}(\text{CO})_5$ and $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$. This reaction is a photocatalyzed chain reaction with $\phi \approx 10$.

All these reactions involve initial homolysis of the metal–metal bond. Only in the case of $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{R-DAB})$ in the presence of PR_3 was a carbonyl group of the $\text{Mn}(\text{CO})_3(\text{R-DAB})$ fragment photosubstituted. The mechanisms of the reactions are discussed.

* For part I and II see refs. 20 and 21.

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Introduction

Low valence transition metal α -diimine complexes are highly coloured due to the presence of low energy metal to ligand charge transfer (MLCT) transitions. The chemistry [1], spectroscopy [2–10] and photochemistry [11–21] of these complexes has been studied in detail. We have extended our photochemical investigations in this field to complexes of the type $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ ($\text{M}, \text{M}' = \text{Mn}, \text{Re}$) which possess, in addition of a $\text{M}'\text{LCT}$ band, a $(\text{M}-\text{M}')$ metal-metal bond. The assignment of the lowest energy absorption band of these complexes to a $\text{M}' \rightarrow \alpha$ -diimine charge transfer transition was based on their Resonance Raman (RR) spectra [10].

The MLCT photochemistry of these complexes was previously studied in 2-Me-THF at $T \leq 230$ K [20] and in inert gas matrices and PVC films [21]. From these studies two different kinds of photochemical reactions were apparent. At $T \geq 200$ K in 2-Me-THF the metal-metal bond is broken homolytically for most complexes; a similar reaction was observed by Morse and Wrighton [18] for $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{phen})$, $(\text{CO})_5\text{ReRe}(\text{CO})_3(\text{phen})$ and $(\text{CO})_5\text{ReRe}(\text{CO})_3(\text{biquin})$ (biquin = 2,2'-biquinoline) in $\text{CH}_2\text{Cl}_2/\text{CCl}_4$. At lower temperatures ($T < 200$ K) in 2-Me-THF photosubstitution of CO is the main reaction [20]. This photoproduct is however, unstable at higher temperatures, and disproportionates to give $[\text{M}'(\text{CO})_3(\alpha\text{-diimine})(2\text{-Me-THF})]^+ [\text{M}(\text{CO})_5]^-$. The photochemical reactions at low temperatures gave a good insight in the primary photoprocesses of these complexes, and this information can be used to explain the more complicated photochemical reactions which take place at room temperature in the presence of nucleophilic ligands such as PR_3 .

In this article we present the results of a room temperature study in 2-Me-THF. It will be shown that the photochemical reactions which take place under these

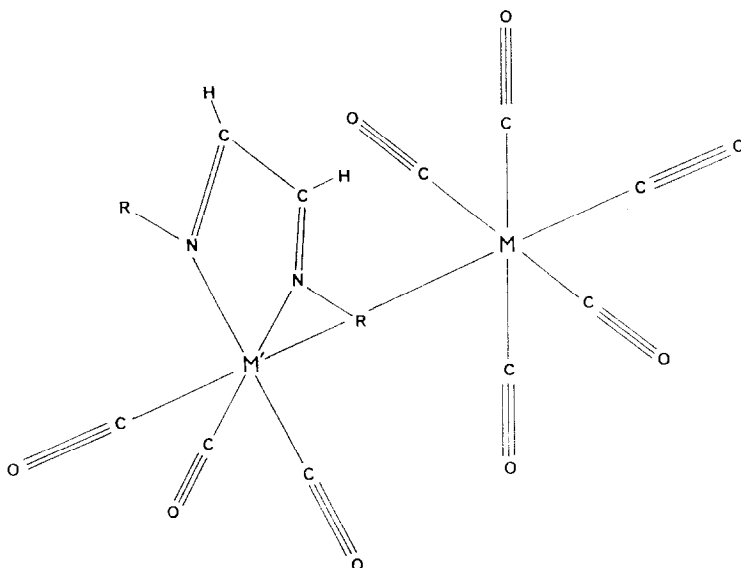


Fig. 1. Structure of $(\text{CO})_5\text{MM}'(\text{CO})_3(\text{R-DAB})$ ($\text{M}, \text{M}' = \text{Mn}, \text{Re}$).

conditions involve the same primary photoprocesses as occur at lower temperatures.

The α -diimine ligands used are 2,2'-bipyridine (bipy), 4,4'-dimethyl-2,2'-bipyridine (bipy'), 1,10-phenanthroline (phen), and 1,4-diaza-1,3-butadiene [= R-DAB; RN=CHCH=NR with R = *p*-tolyl (*p*-Tol) or iso-propyl (i-Pr)]. The structure of the complexes is shown in Fig. 1.

Experimental

The ligands [22] and binuclear metal carbonyl complexes [7,23] were synthesized by published methods.

All spectroscopic samples were dissolved in freshly distilled and deoxygenated 2-Me-THF or THF and made up by standard inert gas techniques. Special care was taken to exclude all light during manipulations of the samples. Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 spectrophotometer, IR spectra on a Nicolet 7199B FT-IR interferometer with a liquid nitrogen cooled Hg, Cd, Te-detector (32 scans, resolution 0.5 cm^{-1}), ^1H NMR spectra on a Varian T60 spectrometer, and ^{31}P NMR spectra on a Varian XL-100-15 spectrometer.

The light source for the photolysis experiments was a Coherent CR 8 Ar ion laser or a filtered medium pressure Hg-lamp. The laser power was 30–50 mW (1 mW for quantum yield measurements) and the laser beam was defocused before entering the sample. Photosubstitutional quantum yields were obtained from the electronic absorption spectral changes upon irradiation of a 2-Me-THF solution (2.5 cm^3 , ca. $10^{-4}\text{ mol dm}^{-3}$) in a quartz cell ($40 \times 10 \times 10\text{ mm}$). The photon flux was calculated from the laser power, which was measured by a Coherent model 201 power meter (first the laser power was measured, and then a 1% filter was placed into the laser beam to give a stable laser power of about 1 mW). Before calculation of the quantum yields, corrections were applied for reflections of the light within the cell, for transmission of the laser beam, and for absorption by the photo-product. The equipment was tested by ferrioxalate actinometry [24].

Preparation of $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$

$\text{Mn}(\text{CO})_3(\text{bipy}')\text{Br}$ was reduced by $\text{NaK}_{2.8}$ in freshly distilled and deoxygenated THF. The reduction was followed by IR spectroscopy and took about 4 h. The $\text{Na}^+ [\text{Mn}(\text{CO})_3(\text{bipy}')(\text{THF})]^-$ thus obtained was allowed to react with $\text{Mn}(\text{CO})_3(\text{bipy}')\text{Br}$ in THF. During the reaction the CO bands of $\text{Mn}(\text{CO})_3(\text{bipy}')\text{Br}$ and $[\text{Mn}(\text{CO})_3(\text{bipy}')(\text{THF})]^-$ disappeared and new bands were formed at 1976m, 1931s, 1880m and 1860m cm^{-1} . Attempts to isolate the photo-product failed. However, these CO stretching frequencies are the same as those found after photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$ in 2-Me-THF or THF (see Results and discussion section), and are therefore assigned to $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$. The failure to isolate $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$ from the product mixture is probably due to the equilibrium between $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$ and two $\text{Mn}(\text{CO})_3(\text{bipy}')$ radicals, as discussed later.

Photochemical preparation of $[\text{Mn}(\text{CO})_3(\text{bipy}')(\text{P}(\text{n-Bu})_3)]^+ [\text{Mn}(\text{CO})_5]^-$

$(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$ (0.58 mmol) and $\text{P}(\text{n-Bu})_3$ (0.42 μl) were dissolved in freshly distilled and deoxygenated THF (100 ml). The solution was irradiated with the green line of an Ar ion laser ($\lambda\ 514.5\text{ nm}$, $P\ 150\text{ mW}$) under nitrogen. To avoid possible photodecomposition of the photo-product the irradiation was performed in

a flow cell (thickness ca. 2 mm). The time required for quantitative conversion was 4 h. The resulting photo-product was examined by IR spectroscopy. The solution was evaporated to dryness and the excess of $P(n-Bu)_3$ was distilled in vacuo at room temperature. Attempts to crystallize the formed green oily substance failed.

Spectroscopic properties of $[Mn(CO)_3(bipy')(P(n-Bu)_3)]^+ [Mn(CO)_5]^-$. A ^{31}P signal due to complexed $P(n-Bu)_3$ was observed at 23.5 ppm in $CDCl_3$ with H_3PO_4 as external standard. Broad 1H NMR signals were observed at 2.73 for the $bipy'-CH_3$ protons, at 7.75 for the $bipy'-H_\beta$ protons, at 8.54 for the $bipy'-H_\delta$ protons and at 9.12 ppm for the $bipy'-H_\alpha$ protons. Furthermore, multiplets between 0.90 and 3.75 ppm due to complexed $P(n-Bu)_3$ were observed. IR CO stretching frequencies: 2032m, 1954m and 1929m cm^{-1} for $[Mn(CO)_3(bipy')(P(n-Bu)_3)]^+$ and 1898m, 1866s and 1854sh cm^{-1} for $[Mn(CO)_5]^-$, measured in 2-Me-THF.

Photochemical preparation of $(CO)_5ReMn(CO)_2(p-Tol-DAB)(PPh_3)$

$(CO)_5MnRe(CO)_3(p-Tol-DAB)$ (0.43 mmol) was dissolved in freshly distilled and deoxygenated THF (150 ml). An excess of PPh_3 was added and the solution was irradiated with the green line of an Ar ion laser (λ 514.5 nm, P 200 mW) under nitrogen. To avoid possible photodecomposition of the photo-product the irradiation was performed in a flow cell (thickness ca. 2 mm). The time required for almost quantitative conversion was about 4 h. The resulting mixture was examined by IR spectroscopy and the solution was then evaporated to dryness and chromatographed on Silicagel 60 (activated by heating at 150°C in vacuo) with n-hexane/THF as eluent (gradient elution). The product fraction was evaporated to dryness.

Spectroscopic properties of $(CO)_5ReMn(CO)_3(p-Tol-DAB)(PPh_3)$. A ^{31}P signal at 71 ppm (with H_3PO_4 as external standard) was observed in $CDCl_3$. A singlet 1H NMR signal was observed at 1.99 ppm for the tolyl- CH_3 protons, an AB pattern at 6.36, 6.44, 6.58 and 6.66 ppm for the tolyl-H protons, a multiplet at 6.96 ppm for PPh_3 protons and a singlet at 7.58 ppm for the imine protons. IR CO stretching frequencies: 2091m, 2022sh, 1995s, 1955m, 1890m and 1840m cm^{-1} , measured in 2-Me-THF.

Preparation of $[Mn(CO)_3(bipy')(THF)]^+ (OTF)^-$

$[Mn(CO)_3(bipy')(THF)]^+ (OTF)^-$ ($OTF = CF_3SO_3$) was prepared by treatment of $Mn(CO)_3(bipy')Br$ with $Ag(OTF)$ in THF; the $AgBr$ rapidly precipitated out. CO stretching frequencies: 2037, 1940 and 1931 cm^{-1} measured in THF.

Results and discussion

The complexes were photolyzed in 2-Me-THF at 293 K both in the absence and presence of PR_3 ($R = n$ -butyl (n-Bu), phenyl (Ph) or cyclo-hexyl (c-Hex)). The photoprocesses taking place for the various complexes are summarized in the Conclusion and they will now be discussed in relationship to the photolysis reactions observed at lower temperatures in 2-Me-THF [20].

Photolysis in the absence of PR_3

In the absence of a substituting ligand such as PR_3 all the $(CO)_5MnMn(CO)_3(\alpha$ -diimine) complexes give $Mn_2(CO)_{10}$ and $Mn_2(CO)_6(\alpha$ -diimine) $_2$ upon irradiation in the MLCT band. These photoproducts are the result of a homolytic splitting of the

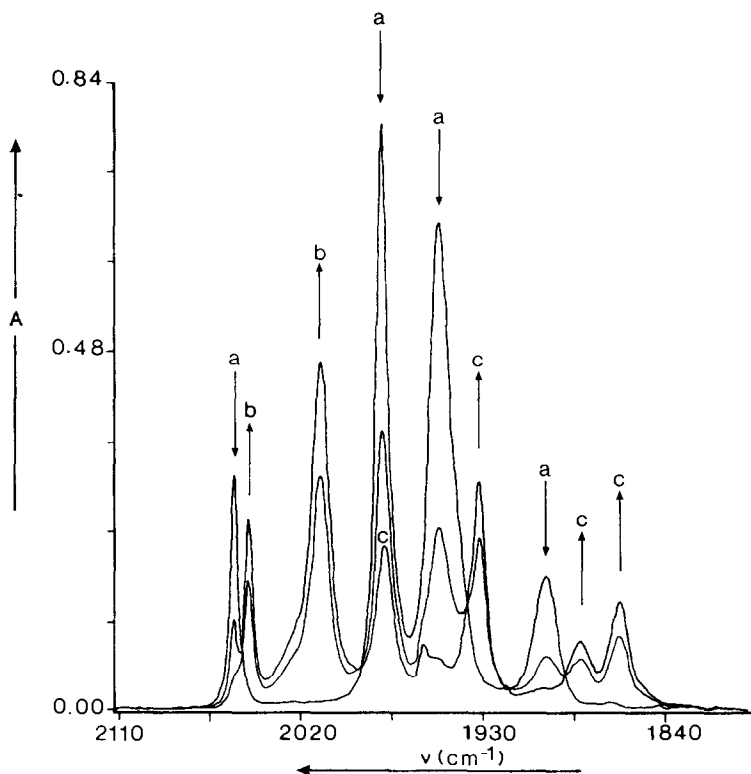


Fig. 2. IR spectral changes upon photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$ with λ 500 nm in 2-Me-THF. **a** = $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$; **b** = $\text{Mn}_2(\text{CO})_{10}$; **c** = $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$.

metal—metal bond. The $\text{Mn}(\text{CO})_5$ radicals formed react with each other to give the complex $\text{Mn}_2(\text{CO})_{10}$, which can easily be identified by its CO frequencies at 2045, 2009 and 1977 cm^{-1} [25]. The $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})$ radicals react to give $\text{Mn}_2(\text{CO})_6(\alpha\text{-diimine})_2$. The thermal stabilities of these complexes strongly depend on the α -diimine ligand. In the case of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$ a stable complex $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$ is formed at 293 K, and this is discussed in some detail below.

$(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$

The IR spectral changes in the CO stretching region upon photolysis of this complex in 2-Me-THF at 293 K with λ 514.5 nm are shown in Fig. 2, and the changes in the electronic absorption spectrum are shown in Fig. 3. The presence of several isosbestic points in both spectra indicates that a well-defined clean reaction takes place. Apart from the three CO vibrations at 2045, 2009 and 1977 cm^{-1} belonging to $\text{Mn}_2(\text{CO})_{10}$ [25], four bands appear at 1778, 1632, 1582 and 1563 cm^{-1} , respectively. In the absorption spectrum the MLCT band shifts from 540 to 850 nm. The $\sigma_b \rightarrow \sigma^*$ transition of the parent compound at 370 nm disappears, and the corresponding transition of $\text{Mn}_2(\text{CO})_{10}$ appears at 350 nm [25]. Less intense bands are observed at 400, 500 and 670 nm when the photolysis is complete.

The complex $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$ could not be isolated from the solution in the presence of $\text{Mn}_2(\text{CO})_{10}$. When the solution was kept in the dark these photo-products reverted to the parent compound.

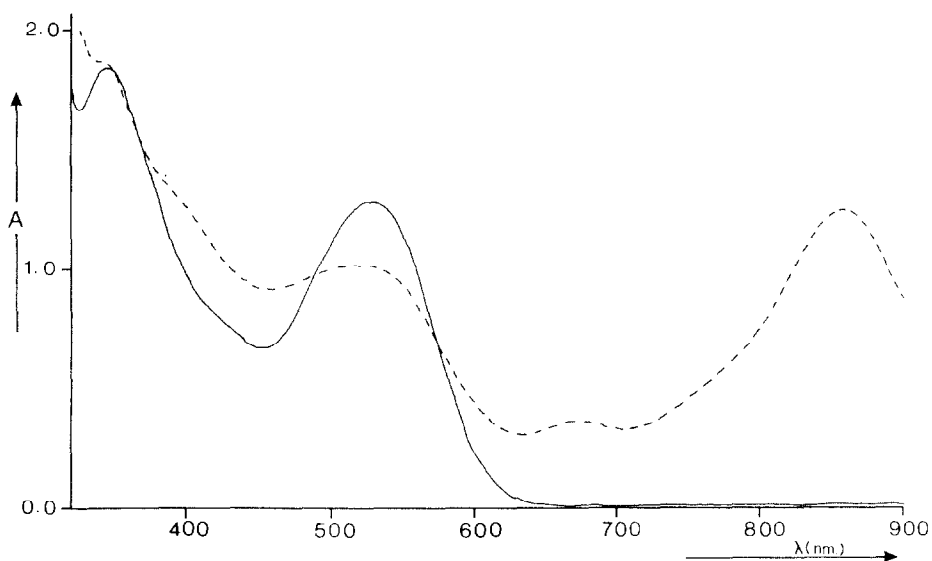


Fig. 3. Electronic absorption spectra of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$ (—) $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$ (-----) obtained before and after photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$ with λ 514.5 nm in 2-Me-THF.

Photolysis in a non-solvating solvent such as toluene resulted in the formation of $\text{Mn}_2(\text{CO})_{10}$ and decomposition products. Apparently, $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$ is partly split into $\text{Mn}(\text{CO})_3(\text{bipy}')$ radicals, which are stabilized by 2-Me-THF (or THF) but decompose in non-solvating solvents. We confirmed the presence of such radicals with ESR spectroscopy after the photolysis reaction of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{i-Pr-DAB})$ in 2-Me-THF at 230 K [20]. The reverse reaction to re-form the parent compound must be caused by attack of the $\text{Mn}(\text{CO})_3(\text{bipy}')$ radical at $\text{Mn}_2(\text{CO})_{10}$.

Because of the failure to isolate $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$ from the reaction mixture, we tried to prepare this complex by another procedure. A solution of $\text{Mn}(\text{CO})_3(\text{bipy}')\text{Br}$ in THF was allowed to react with $\text{Na}^+ [\text{Mn}(\text{CO})_3(\text{bipy}')(\text{THF})]^-$. However, although the formation of $\text{Mn}_2(\text{CO})_{10}$ was prevented, $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$ could still not be isolated from the solution. On the other hand, both the IR and electronic absorption spectra of the reaction mixture correspond to those of the photo-product described above. On the basis of this close resemblance we assign the IR bands at 1978, 1932, 1882 and 1863 cm^{-1} and the MLCT band at 850 nm to $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$. The shift to lower frequencies of the CO vibrations and the MLCT transition relative to those of the parent compound is consistent with the replacement of an electron-withdrawing $\text{Mn}(\text{CO})_5$ group by an electron-releasing $\text{Mn}(\text{CO})_3(\text{bipy}')$ fragment.

Photolysis of the corresponding complex $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{phen})$ results in the formation of $\text{Mn}_2(\text{CO})_6(\text{phen})_2$, with nearly the same CO stretching frequencies as the bipy' complex. We previously showed that photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{i-Pr-DAB})$ in 2-Me-THF at 230 K results in the formation of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_6(\text{i-Pr-DAB})_2$ [20]. In the latter complex the CO vibrations are shifted to higher frequency with respect to those for the bipy' complex because of the better π -acceptor ability of the R-DAB ligand. However, $\text{Mn}_2(\text{CO})_6(\text{i-Pr-DAB})_2$ proved to be unstable upon warming up to room temperature; a new product is then formed,

with CO frequencies at 2025, 1983 and 1920 cm^{-1} . The same frequencies are directly observed when the photolysis is performed at room temperature.

With the exception of $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{R-DAB})$ and $(\text{CO})_5\text{ReRe}(\text{CO})_3(\text{R-DAB})$ all complexes show this homolytic splitting of the metal–metal bond upon photolysis at 293 K, as evidenced by the formation of $\text{M}_2(\text{CO})_{10}$. The only difference is in the stability of the $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})_2$ complexes. Thus, in contrast to their Mn analogues, no stable $\text{Re}_2(\text{CO})_6(\alpha\text{-diimine})_2$ compounds could be detected in solution. They all decompose at 293 K like $\text{Mn}_2(\text{CO})_6(\text{i-Pr-DAB})_2$, to give a product which still contains one α -diimine ligand and presumably has the composition $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})(2\text{-Me-THF})_2$. The presence of one α -diimine ligand in these complexes is evident from the dependence of the CO-frequencies on the α -diimine ligand. When the photolysis is performed in the presence of PPh_3 (vide infra), the two 2-Me-THF molecules are replaced by PPh_3 , and this results in a small shift of the CO vibrations to higher frequencies.

Upon photolysis of $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{R-DAB})$ and $(\text{CO})_5\text{ReRe}(\text{CO})_3(\text{R-DAB})$ no homolytic splitting of the metal–metal bond takes place, since no $\text{Re}_2(\text{CO})_{10}$ is formed. The reactions of these complexes are still under study in our laboratory.

Photolysis in the presence of PR_3

When the complexes are photolyzed in the presence of PR_3 the radicals formed by the homolysis of the metal–metal bond may react with PR_3 before they react with each other. Moreover, photoproducts such as $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})_2$ may not be stable at room temperature and react to give $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})(\text{PR}_3)_2$. A variety of photo-products is formed, depending on the complex and the phosphine ligand. However, nearly all the photo-products result from the same primary photoprocess, viz. homolysis of the metal–metal bond. Only in the case of $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{R-DAB})$ was photosubstitution of CO observed (vide infra).

$(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$

Irradiation of these complexes in the presence of PR_3 ($\text{R} = \text{Ph}$ or $n\text{-Bu}$) results in the formation of a complex with CO stretching frequencies similar to those observed for $\text{Re}_2(\text{CO})_6(\alpha\text{-diimine})(2\text{-Me-THF})_2$. They are therefore assigned to the corresponding complex $\text{Re}_2(\text{CO})_6(\alpha\text{-diimine})(\text{PR}_3)_2$ (see Table 2) formed by the reaction of PR_3 with $\text{Re}_2(\text{CO})_6(\alpha\text{-diimine})_2$.

Other vibration bands are observed at 2045, 2009 and 1977 cm^{-1} for the photolysis of $(\text{CO})_5\text{MnRe}(\text{CO})_3(\text{i-Pr-DAB})$ in the presence of PPh_3 . These bands belong to $\text{Mn}_2(\text{CO})_{10}$. When however $\text{P}(n\text{-Bu})_3$ is used instead of PPh_3 a band is observed at 1943 cm^{-1} which is characteristic of $\text{Mn}_2(\text{CO})_8(\text{P}(n\text{-Bu})_3)_2$ [26]. There will always be a competition between the formation of $\text{Mn}_2(\text{CO})_{10}$ and the reaction of the $\text{Mn}(\text{CO})_5$ radical with PR_3 to $\text{Mn}(\text{CO})_4(\text{PR}_3)$. Apparently, the former reaction is favoured in the case of PPh_3 and the latter for $\text{P}(n\text{-Bu})_3$.

On the other hand, photolysis of the corresponding complexes $(\text{CO})_5\text{MnRe}(\text{CO})_3(\text{phen})$, $(\text{CO})_5\text{MnRe}(\text{CO})_3(p\text{-Tol-DAB})$ and $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ in the presence of PPh_3 results in the formation of $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ instead of $\text{Mn}_2(\text{CO})_{10}$ when the photon flux is sufficiently low (vide infra). Thus formation of $\text{Mn}_2(\text{CO})_{10}$ in the case of $(\text{CO})_5\text{MnRe}(\text{CO})_3(\text{i-Pr-DAB})$ cannot be the result of just a combination of two $\text{Mn}(\text{CO})_5$ radicals, since the same reaction should have occurred for $(\text{CO})_5\text{MnRe}(\text{CO})_3(\text{phen})$, $(\text{CO})_5\text{MnRe}(\text{CO})_3(p\text{-Tol-DAB})$ and

TABLE 1

IR CO STRETCHING FREQUENCIES (cm^{-1}) OF SOME $\text{Mn}_2(\text{CO})_6(\alpha\text{-diimine})_2$, $\text{M}_2(\text{CO})_6(\alpha\text{-diimine})(2\text{-Me-THF})_2$ AND $\text{M}_2(\text{CO})_6(\alpha\text{-diimine})(\text{PR}_3)_2$ ($\text{M} = \text{Mn, Re}$; $\text{R} = \text{Ph, n-Bu}$) COMPLEXES OBTAINED AFTER PHOTOLYSIS IN 2-Me-THF AT 293 K

Compound	CO-stretching frequencies			
$\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$	1979s	1932s	1882w	1863m
$\text{Mn}_2(\text{CO})_6(\text{phen})_2$	1982s	1943m	1890w	1869w
$\text{Mn}_2(\text{CO})_6(\text{i-Pr-DAB})_2^a$	2006m	1946s	1898w	1888w
$\text{Mn}_2(\text{CO})_6(\text{i-Pr-DAB})(2\text{-Me-THF})_2$		2025s	1938m	1920m
$\text{Mn}_2(\text{CO})_6(p\text{-Tol-PyCa})(2\text{-Me-THF})_2^b$		2027s	1944m	1917m
$\text{Mn}_2(\text{CO})_6(p\text{-Tol-PyCa})(\text{PPh}_3)_2^b$		2026m	1931m	1915m
$\text{Mn}_2(\text{CO})_6(p\text{-Tol-DAB})(\text{PPh}_3)_2$		2017m	1936w	1906w
$\text{Re}_2(\text{CO})_6(\text{i-Pr-DAB})(2\text{-Me-THF})_2$		2022m		1900s
$\text{Re}_2(\text{CO})_6(\text{i-Pr-DAB})(\text{PPh}_3)_2$		2009m	1911m	1883m
$\text{Re}_2(\text{CO})_6(\text{i-Pr-DAB})(\text{P}(\text{n-Bu})_3)_2$		2006m	1905m	1880m
$\text{Re}_2(\text{CO})_6(p\text{-Tol-DAB})(2\text{-Me-THF})_2$		2014m		1899s
$\text{Re}_2(\text{CO})_6(p\text{-Tol-DAB})(\text{PPh}_3)_2$		2017m	1923m	1899m
$\text{Re}_2(\text{CO})_6(p\text{-Tol-DAB})(\text{P}(\text{n-Bu})_3)_2$		2013m	1918m	1893m

^a Measured at 233 K, values according to ref. 20. ^b PyCa = pyridine-2-carbaldehyde-imine.

$(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$. We therefore suggest that $\text{Mn}_2(\text{CO})_{10}$ is formed by attack of the $\text{Mn}(\text{CO})_5$ radicals on the parent compound $(\text{CO})_5\text{MnRe}(\text{CO})_3(\text{i-Pr-DAB})$ to yield $\text{Mn}_2(\text{CO})_{10}$ and the $\text{Re}(\text{CO})_3(\text{i-Pr-DAB})$ radical. This reaction, which does not occur for $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$, is apparently faster than the reaction of $\text{Mn}(\text{CO})_5$ with PPh_3 since no $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ is formed.

$(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$

Photolysis of these complexes leads to the formation of various photo-products depending on the PR_3 ligands used. When the complexes are irradiated in the presence of PPh_3 homolytic splitting of the metal-metal bond occurs and $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$ is formed, with a CO vibration at 1956 cm^{-1} [26]. Under certain conditions, however, $\text{Mn}_2(\text{CO})_{10}$ can be formed instead of $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$. The latter photo-product is formed when the complex is irradiated with visible light with a normal low photon flux (medium pressure Hg-lamp, 500 nm filter). However, when an argon ion laser is used with a much higher photon flux ($\lambda\ 514.5\text{ nm}$, $P\ 20\text{ mW}$) $\text{Mn}_2(\text{CO})_{10}$ is also formed. Such a photon flux dependence has been observed before, e.g. by Stiegman and Tyler [27,28]. When the complex is irradiated with light of low intensity the concentration of $\text{Mn}(\text{CO})_5$ radicals formed will be small compared with that of PPh_3 and reaction with PPh_3 will then be favoured over formation of $\text{Mn}_2(\text{CO})_{10}$. At a higher photon flux the concentration of $\text{Mn}(\text{CO})_5$ radicals is larger, and this promotes the formation of $\text{Mn}_2(\text{CO})_{10}$.

The photo-products formed from the other radical $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})$ are not as well-defined as in the case of $(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$. The main product is $\text{Mn}_2(\text{CO})_6(\alpha\text{-diimine})(\text{PPh}_3)_2$, the CO frequencies of which are shown in Table 2.

When the photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ takes place in the presence of $\text{P}(\text{n-Bu})_3$ neither $\text{Mn}_2(\text{CO})_{10}$ nor $\text{Mn}_2(\text{CO})_8(\text{P}(\text{n-Bu})_3)_2$ is observed. Instead, $[\text{Mn}(\text{CO})_5]^-$ is formed, as is evident from the CO vibrations at 1898, 1866 and 1854 cm^{-1} [29]. Following these observations the photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$

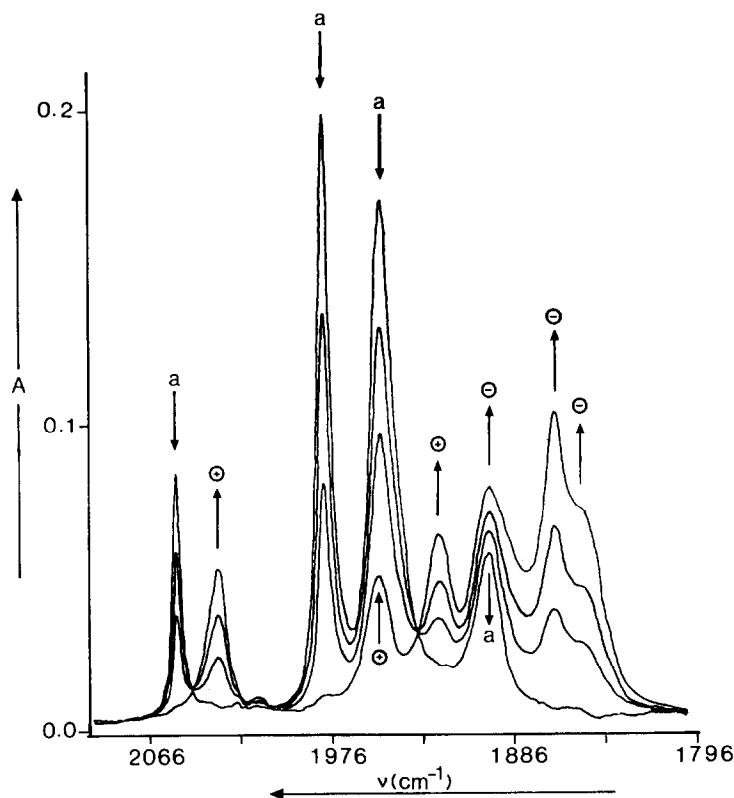


Fig. 4. IR spectral changes upon photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$ with λ 500 nm, in 2-Me-THF in the presence of $\text{P}(\text{n-Bu})_3$. a = $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$; \ominus = $[\text{Mn}(\text{CO})_5]^-$; \oplus = $[\text{Mn}(\text{CO})_3(\text{bipy}')(\text{P}(\text{n-Bu})_3)]^+$.

in the presence of $\text{P}(\text{n-Bu})_3$ was studied in detail. The IR spectral changes during this reaction are shown in Fig. 4. Apart from the bands belonging to $[\text{Mn}(\text{CO})_5]^-$ (indicated with \ominus in Fig. 4) three bands of a cation appear at 2032, 1953 and 1930 cm^{-1} .

In order to characterize this cation the ionic compound was isolated as an oil by performing the photochemical reaction on a preparative scale (see the Experimental section). The ^1H NMR spectrum shows the presence of the $\text{P}(\text{n-Bu})_3$ and bipy' ligand in 1/1 ratio. The ^{31}P NMR spectrum shows one signal at 762 Hz belonging to coordinated $\text{P}(\text{n-Bu})_3$. On the basis of these NMR and IR data the ionic compound is suggested to be $[\text{Mn}(\text{CO})_3(\text{bipy}')(\text{P}(\text{n-Bu})_3)]^+ [\text{Mn}(\text{CO})_5]^-$. The appearance of three CO bands for the cation indicates that it still contains the three CO groups of the $\text{Mn}(\text{CO})_3(\text{bipy}')$ radical.

Compared to that of the parent compound, the MLCT band (measured in THF) is shifted from 540 to 507 nm due to the increase of positive charge at Mn. Further evidence for the formation of this cation comes from a comparison of its CO frequencies with those of $[\text{Mn}(\text{CO})_3(\text{bipy}')(\text{THF})]^+ (\text{OTF})^-$ ($\text{OTF} = \text{CF}_3\text{SO}_3$). This compound, which was prepared by the reaction of $\text{Mn}(\text{CO})_3(\text{bipy}')\text{Br}$ with $\text{Ag}(\text{OTF})$ has CO vibrations at 2037, 1940 and 1931 cm^{-1} (in THF) close to the frequencies of $[\text{Mn}(\text{CO})_3(\text{bipy}')(\text{P}(\text{n-Bu})_3)]^+$.

Upon prolonged irradiation new CO bands show up at 1927 and 1859 cm^{-1} , the latter being partly obscured by a band from $[\text{Mn}(\text{CO})_5]^-$. These bands increase in intensity at the expense of those belonging to $[\text{Mn}(\text{CO})_3(\text{bipy}')(\text{P}(\text{n-Bu})_3)]^+$. Since the anion $[\text{Mn}(\text{CO})_5]^-$ is not affected during this reaction it seems that a carbonyl ligand of the cation is photosubstituted by $\text{P}(\text{n-Bu})_3$. The cation does, indeed, absorb at the wavelength of irradiation (514.5 nm). The formation of this photosubstitution product $[\text{Mn}(\text{CO})_2(\text{bipy}')(\text{P}(\text{n-Bu})_3)_2]^+$ is in accordance with the observation that much less of it is formed when the concentration of $\text{P}(\text{n-Bu})_3$ is lowered. Thus almost no reaction takes place when only one equivalent of $\text{P}(\text{n-Bu})_3$ is added to the solution of the parent compound $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$. Photolysis of other $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ complexes also results in the formation of $[\text{Mn}(\text{CO})_5]^-$. However, these reactions are less clean, presumably because the cations formed decompose to some extent. Photolysis of $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{phen})$ in the presence of $\text{P}(\text{n-Bu})_3$ also gives a ionic complex, whereas in the case of $(\text{CO})_5\text{ReRe}(\text{CO})_3(\text{phen})$ the $[\text{Re}(\text{CO})_5]^-$ ion is only observed as a side product, the main reaction being still unclear. The CO stretching frequencies of several ionic complexes formed are listed in Table 2.

The question remains of the mechanism through which the ionic compounds are formed. The first significant observation is the very high quantum yield for these reactions. Using a minimal laser power of about 1.1 mW (λ 514.4 nm) complete conversion of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$ into $[\text{Mn}(\text{CO})_3(\text{bipy}')\text{P}(\text{n-Bu})_3]^+$ $[\text{Mn}(\text{CO})_5]^-$ was accomplished after 20 s irradiation. Although an accurate quantum yield could not be determined because of the high reaction rate, a rough estimate could be made; complete conversion with a quantum yield of 1 would have taken place after about 200 s of irradiation and so the estimated quantum yield is 10. Such a high quantum yield points to a chain reaction.

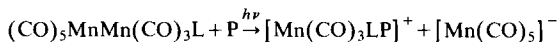
By analogy with the mechanisms of the photo-disproportionation of $\text{Mn}_2(\text{CO})_{10}$ in *N*-donor solvents [30] and of $(\eta^5\text{-CH}_3\text{-C}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_6$ in the presence of phosphines [31,32], the following chain mechanism is proposed for the disproportionation of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$ in 2-Me-THF in the presence of $\text{P}(\text{n-Bu})_3$ (see Scheme 1). The initiation reaction is the homolysis of the metal-metal bond, just as in the absence of $\text{P}(\text{n-Bu})_3$ (vide supra). The propagation steps (reactions 2–4) start from the radical $\text{Mn}(\text{CO})_3(\text{bipy}')$. This intermediate readily takes up $\text{P}(\text{n-Bu})_3$ to give the species $\text{Mn}(\text{CO})_3(\text{bipy}')(\text{P}(\text{n-Bu})_3)$, which plays the key role in the disproportionation reaction. Such intermediates are assumed to play an im-

TABLE 2
IR CO STRETCHING FREQUENCIES (cm^{-1}) OF SOME $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(\text{P}(\text{n-Bu})_3)]^+$ AND $[\text{Mn}(\text{CO})_2(\alpha\text{-diimine})(\text{P}(\text{n-Bu})_3)_2]^+$ CATIONS MEASURED IN 2-Me-THF

Cation	CO-stretching frequency		
$[\text{Mn}(\text{CO})_3(\text{bipy}')(\text{P}(\text{n-Bu})_3)]^+$	2032	1953	1930
$[\text{Mn}(\text{CO})_2(\text{bipy}')(\text{P}(\text{n-Bu})_3)_2]^+$		1927	1859
$[\text{Mn}(\text{CO})_3(\text{i-Pr-DAB})(\text{P}(\text{n-Bu})_3)]^+$	2026	1941	1875
$[\text{Mn}(\text{CO})_2(\text{i-Pr-DAB})(\text{P}(\text{n-Bu})_3)_2]^+$		1890	1848
$[\text{Mn}(\text{CO})_2(\textit{p-Tol-PyCa})(\text{P}(\text{n-Bu})_3)_2]^+{}^a$		1935	1868

^a PyCa = pyridine-2-carbaldehyde-imine.

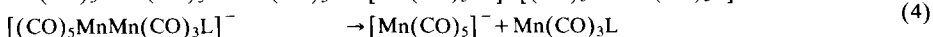
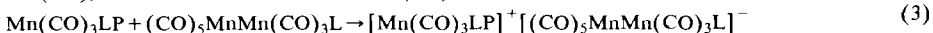
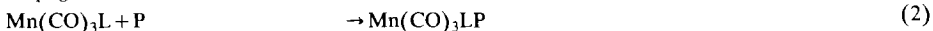
Reaction:



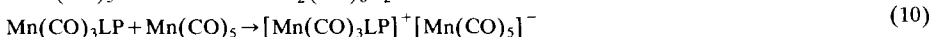
Initiation:



Propagation:



Termination:



SCHEME 1. Radical chain mechanism for the photodisproportionation of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ in the presence of $\text{P}(\text{n-Bu})_3$; $\text{L} = \alpha\text{-diimine}$ and $\text{P} = \text{P}(\text{n-Bu})_3$.

portant part in the photo-disproportionation reactions of $\text{Mn}_2(\text{CO})_{10}$ [30] and $(\eta^5\text{-CH}_3\text{-C}_5\text{H}_4)_2\text{Mo}_2(\text{CO})_6$ [31,32]. Thus, Stiegman and Tyler proposed that the photodisproportionation of $\text{Mn}_2(\text{CO})_{10}$ in *N*-donor solvents takes place by electron transfer from the 19-electron intermediate $\text{Mn}(\text{CO})_3\text{N}_3$ to $\text{Mn}_2(\text{CO})_{10}$ [30]. This mechanism differs from that suggested by McCullen and Brown [33] according to which electron transfer takes place from the 17-electron species $\text{Mn}(\text{CO})_3\text{N}_2$. Support for the mechanism of Stiegman and Tyler comes from the photodisproportionation of $(\text{CO})_5\text{MMn}(\text{CO})_3(\alpha\text{-diimine})$ ($\text{M} = \text{Mn}, \text{Re}$) at $T \leq 200$ K in 2-Me-THF [20]. We have shown that these complexes only disproportionate after photo-substitution of one CO group of the $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})$ moiety by 2-Me-THF. These photo-products $(\text{CO})_5\text{MMn}(\text{CO})_2(\alpha\text{-diimine})(2\text{-Me-THF})$ disproportionate upon raising the temperature due to intramolecular transfer and this shows that the intramolecular electron transfer or heterolytic splitting of the metal–metal bond only takes place when one of the metal fragments contains three basic groups, just as in the case of $\text{Mn}(\text{CO})_3\text{N}_3$.

Electron transfer will take place from $\text{Mn}(\text{CO})_3(\text{bipy}')\text{P}(\text{n-Bu})_3$ to $\text{Mn}(\text{CO})_5$ (reaction 10) and to the parent compound $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')$ (reaction 3). The first reaction is a terminating step, whereas the latter leads to the formation of the unstable anion $[(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bipy}')^-]$, which decomposes into $[\text{Mn}(\text{CO})_5]^-$ and $\text{Mn}(\text{CO})_3(\text{bipy}')$ (reaction 4). The latter radical is responsible for the chain reaction. The main products of this reaction are $[\text{Mn}(\text{CO})_3(\text{bipy}')(\text{P}(\text{n-Bu})_3)]^+$ and $[\text{Mn}(\text{CO})_5]^-$, and these ions are in fact the only products observed in the reaction mixture.

Of the termination steps, reactions 5 and 7 will be unfavourable with respect to 6 and 8 since the $\text{Mn}(\text{CO})_5$ radicals produced by the homolysis of the metal–metal bond in $(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$ readily react with $\text{P}(\text{n-Bu})_3$ to give

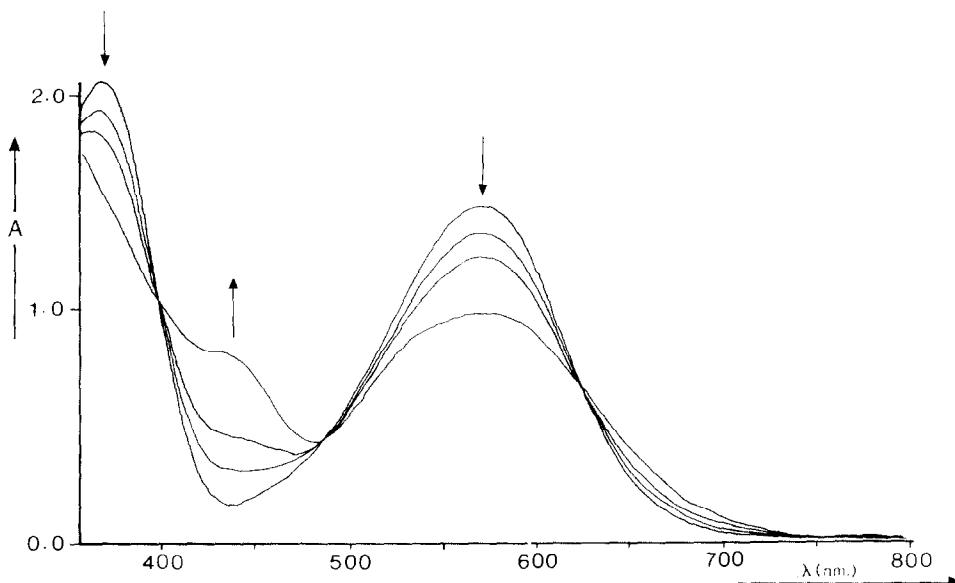


Fig. 5. Electronic absorption spectral changes of a 2-Me-THF solution of $(\text{CO})_5\text{ReMn}(\text{CO})_3(p\text{-Tol-DAB})$ containing a 200-fold excess of $\text{P}(c\text{-Hex})_3$, during photolysis with λ 514.5 nm.

$\text{Mn}_2(\text{CO})_8(\text{P}(n\text{-Bu})_3)_2$ (vide supra). Although this latter complex was not observed in this work its main CO band at 1945 cm^{-1} could have been hidden under the 1953 cm^{-1} band of the cation.

$(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{R-DAB})$

Until recently the primary photo-process in all the reactions was the homolytic splitting of the metal-metal bond. However, in recent studies [20,21] we have shown that these complexes can also undergo photosubstitution of CO of the $\text{Mn}(\text{CO})_3(\alpha\text{-diimine})$ moiety. At room temperature this latter reaction is only observed for $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{R-DAB})$ in the presence of PR_3 ($\text{R} = \text{Ph}, n\text{-Bu}$ or $c\text{-Hex}$). Figure 5 shows the changes in the absorption spectrum upon irradiation with λ 514.5 nm of $(\text{CO})_5\text{ReMn}(\text{CO})_3(i\text{-Pr-DAB})$ in the presence of $\text{P}(c\text{-Hex})_3$, while Fig. 6 shows the changes in the CO stretching region upon photolysis (λ 500 nm) of $(\text{CO})_5\text{ReMn}(\text{CO})_3(p\text{-Tol-DAB})$ in the presence of PPh_3 .

Both spectra show good isosbestic points. Because of photosubstitution of the electron-withdrawing CO group by the basic phosphine, both the MLCT band and the CO vibrations shift to lower energy. One of the photo-products, $(\text{CO})_5\text{ReMn}(\text{CO})_2(p\text{-Tol-DAB})(\text{PPh}_3)$ was isolated by performing the photolysis on a larger scale. The CO frequencies of several of these $(\text{CO})_5\text{ReMn}(\text{CO})_2(\text{R-DAB})(\text{PR}_3)$ complexes are listed in Table 3.

The same photosubstitution reaction has been observed in 2-Me-THF at 133 K for the complexes $(\text{CO})_5\text{MMn}(\text{CO})_3(\alpha\text{-diimine})$ ($\text{M} = \text{Mn}, \text{Re}$) [20]. It led to the formation of $(\text{CO})_5\text{MMn}(\text{CO})_2(\alpha\text{-diimine})(2\text{-Me-THF})$, which were shown to be intermediates in the formation of the ionic compounds $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(2\text{-Me-THF})]^+ [\text{Mn}(\text{CO})_5]^-$.

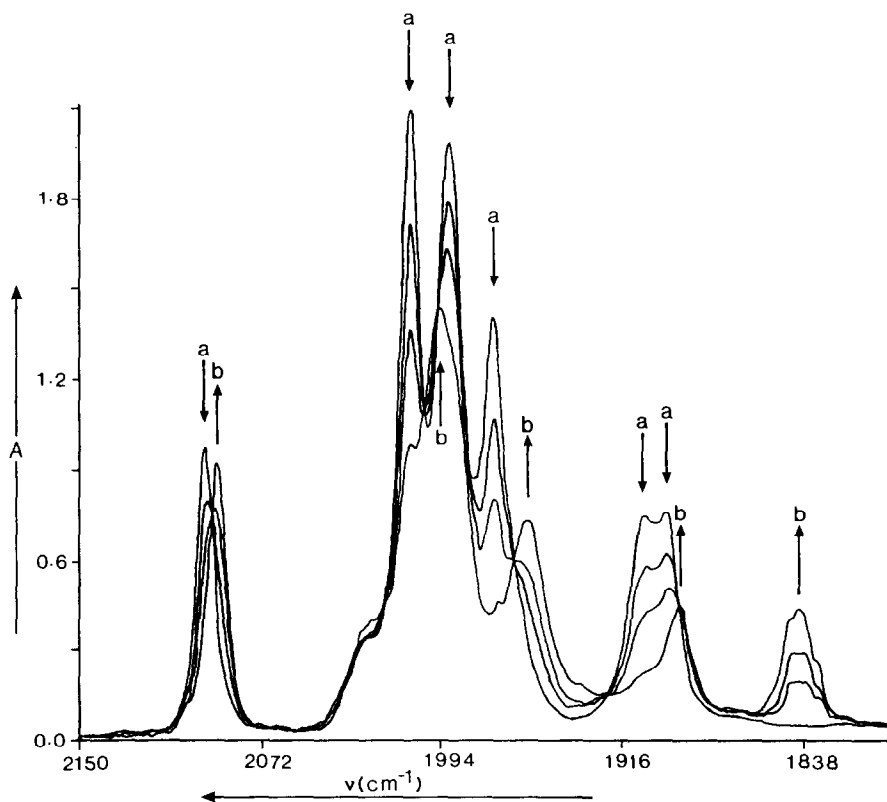


Fig. 6. IR spectral changes upon photolysis of $(\text{CO})_5\text{ReMn}(\text{CO})_3(p\text{-Tol-DAB})$ with λ 500 nm in 2-Me-THF in the presence of PPh_3 . **a** = $(\text{CO})_5\text{ReMn}(\text{CO})_3(p\text{-Tol-DAB})$; **b** = $(\text{CO})_5\text{ReMn}(\text{CO})_2(p\text{-Tol-DAB})(\text{PPh}_3)$.

The mechanism of this photosubstitution reaction is suggested to be similar to that proposed for the photosubstitution of CO by PR_3 in $\text{Fe}(\text{CO})_3(\text{R-DAB})$ [12]. Both types of complexes $\text{Fe}(\text{CO})_3(\text{R-DAB})$ [5] and $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{R-DAB})$ [10] show very weak Resonance Raman effects upon excitation in the MLCT band, which means that no bonds of the complexes are severely affected in the MLCT state and thus that this state is not photoactive. However, rather high quantum

TABLE 3

IR CO-STRETCHING FREQUENCIES (cm^{-1}) OF SOME $(\text{CO})_5\text{ReMn}(\text{CO})_2(\text{R-DAB})(\text{L})$ ($\text{R} = i\text{-Pr}$, $p\text{-Tol}$; $\text{L} = \text{PPh}_3$, $\text{P}(\text{n-Bu})_3$, CO) COMPLEXES MEASURED IN 2-Me-THF AT 293 K

Compound	CO stretching frequencies						
$(\text{CO})_5\text{ReMn}(\text{CO})_3(i\text{-Pr-DAB})$	2088m	2018w	1987s	1970m	1903w	1890w	
$(\text{CO})_5\text{ReMn}(\text{CO})_2(i\text{-Pr-DAB})(\text{PPh}_3)$	2084m	2023w	1990s	1952m	1884w	1829w	
$(\text{CO})_5\text{ReMn}(\text{CO})_2(i\text{-Pr-DAB})(\text{P}(\text{n-Bu})_3)$	2081m	2025w	1986s	1949m	1881m	1826m	
$(\text{CO})_5\text{ReMn}(\text{CO})_3(p\text{-Tol-DAB})$	2096m	2025sh	2007vs	1990vs	1971s	1905m	1897m
$(\text{CO})_5\text{ReMn}(\text{CO})_2(p\text{-Tol-DAB})(\text{PPh}_3)$	2091s	2022sh	1995vs	1955s	1890m	1840m	
$(\text{CO})_5\text{ReMn}(\text{CO})_2(p\text{-Tol-DAB})(\text{P}(\text{n-Bu})_3)$	2089s	2019w	2005s	1984vs	1954m	1886m	1835m

yields are found for the photosubstitution of CO by PR_3 in both $\text{Fe}(\text{CO})_3(\text{R-DAB})$ ($\phi \approx 0.25$) [12] and $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{i-Pr-DAB})$ (ϕ 0.89 for PPh_3 and ϕ 0.60 for $\text{P}(\text{c-Hex})_3$, respectively). In order to account for these high quantum yields in the light of the photoinactivity of the MLCT states, a strong coupling model was proposed [12,34] according to which excited state energy is converted into vibrational motions of the complex. As a result a metal–nitrogen bond can be broken, a PR_3 ligand attacks the open site, CO is released, and the metal–nitrogen chelate bond is re-formed. Although this breaking of a metal–nitrogen bond could not be proved for $\text{Fe}(\text{CO})_3(\text{R-DAB})$ there is supporting evidence for this mechanism from the photolysis of $(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$ in 2-Me-THF at 133 K [20] and in a PVC film at 193 K [21]. For these complexes the primary photo-product appeared to be $(\text{CO})_5\text{MnRe}(\text{CO})_3(\sigma\text{-N-}\alpha\text{-diimine})$, a complex in which the α -diimine ligand is $\sigma\text{-N}$ monodentately coordinated to Re. The difference in quantum yield between the photosubstitution of CO in $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{i-Pr-DAB})$ by PPh_3 (ϕ 0.89) and $\text{P}(\text{c-Hex})_3$ (ϕ 0.60) arises from the difference in cone angle between these two phosphines (145 and 170°, respectively [35]).

The question remains why photosubstitution of CO is preferred here above the homolytic splitting of the metal–metal bond. As stated in the Introduction, a photochemical reaction can occur from the ${}^3\sigma_{\text{b}}\pi^*$ or ${}^3d_{\pi}\pi^*$ state. The homolysis of the metal–metal bond will occur from the ${}^3\sigma_{\text{b}}\pi^*$ state, since in this state the metal–metal bond is weakened. On the other hand, photosubstitution of CO is the result of the conversion of the electronic energy of the photoinactive ${}^3d_{\pi}\pi^*$ state into vibrational energy. There is no reason why the ${}^3\sigma_{\text{b}}\pi^*$ state should be photoactive for all the complexes except $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{R-DAB})$. A more probable explanation for the unusual behaviour of this complex is a change in the relative energies of the ${}^3\sigma_{\text{b}}\pi^*$ and ${}^3d_{\pi}\pi^*$ states. The ${}^3d_{\pi}\pi^*$ state of this complex is suggested to be so low in energy with respect to ${}^3\sigma_{\text{b}}\pi^*$ that only a reaction from this ${}^3d_{\pi}\pi^*$ can occur. That this behaviour is not primarily influenced by the PR_3 ligand can be seen from the observation that even in the absence of PR_3 no homolysis of the metal–metal bond takes place.

Conclusions

In this article it is shown that photolysis of $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ in 2-Me-THF at 293 K in the absence of a substituting ligand can lead to different reactions for the various complexes. However, for most complexes the primary step is homolytic splitting of the metal–metal bond which results in the formation of $\text{M}_2(\text{CO})_{10}$ and $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})_2$. In most cases this latter compound was unstable, and decomposed into $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})(2\text{-Me-THF})_2$. Only $\text{Mn}_2(\text{CO})_6(\text{bipy}')_2$ and $\text{Mn}_2(\text{CO})_6(\text{phen})_2$ were stable.

The photolysis experiments were also performed in the presence of PPh_3 and $\text{P}(\text{n-Bu})_3$. Thus photolysis of $(\text{CO})_5\text{MnM}'(\text{CO})_3(\alpha\text{-diimine})$ ($\text{M}' = \text{Mn, Re}$) in the presence of PPh_3 gave $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})(\text{PPh}_3)_2$ instead of $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})_2$ or $\text{M}'_2(\text{CO})_6(\alpha\text{-diimine})(2\text{-Me-THF})_2$. When $\text{P}(\text{n-Bu})_3$ was present a photocatalytic disproportionation was observed, to give $[\text{Mn}(\text{CO})_3(\alpha\text{-diimine})(\text{P}(\text{n-Bu})_3)]^+ [\text{Mn}(\text{CO})_5]^-$, for the photolysis of all the $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ complexes and of $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{phen})$. This disproportionation was not observed for $(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$, and instead $\text{Re}_2(\text{CO})_6(\alpha\text{-diimine})(\text{P}(\text{n-Bu})_3)$ was found as a photoproduct.

An exceptional photochemical reaction was observed for $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{R-DAB})$. The metal-metal bond is not broken with these complexes, but instead CO substitution takes place when photolysis is performed in the presence of PPh_3 or $\text{P}(\text{n-Bu})_3$.

The photolysis reactions of $(\text{CO})_5\text{ReRe}(\text{CO})_3(\alpha\text{-diimine})$ are more complicated, and are still under study.

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