

Table III. ^{13}C and ^{15}N NMR Data^a for Three Isotopic Forms of $[\text{Fe}(\text{CN})_5\text{NO}_2]^{4-}$

$[\text{Fe}(^{13}\text{CN})_5(^{15}\text{NO}_2)]^{4-}$ (8)			
$\delta(^{13}\text{C}_{\text{ax}})$	+174.0 (p × d)	$^2J(^{13}\text{C}_{\text{ax}}\text{Fe}^{13}\text{C}_{\text{eq}})$	9.1
$\delta(^{13}\text{C}_{\text{eq}})$	+176.7 (d × d)	$^2J(^{13}\text{C}_{\text{ax}}\text{Fe}^{15}\text{N})$	5.4
$\delta(^{15}\text{N})$	+174.4 (d × p)	$^2J(^{13}\text{C}_{\text{eq}}\text{Fe}^{15}\text{N})$	1.9
$[\text{Fe}(^{13}\text{CN}_{\text{ax}})(^{12}\text{CN}_{\text{eq}})(^{13}\text{CN}_{\text{eq}})_3(^{15}\text{NO}_2)]^{4-}$ (9)			
$\delta(^{13}\text{C}_{\text{ax}})$	+174.2 (q × d)	$^2J(^{13}\text{C}_{\text{ax}}\text{Fe}^{13}\text{C}_{\text{eq}})$	9.1
$\delta(^{13}\text{C}_{\text{eq}})$	b	$^2J(^{13}\text{C}_{\text{ax}}\text{Fe}^{15}\text{N})$	5.4
$\delta(^{15}\text{N})$	b	$^2J(^{13}\text{C}_{\text{eq}}\text{Fe}^{15}\text{N})$	b
$[\text{Fe}(^{12}\text{CN}_{\text{ax}})(^{13}\text{CN}_{\text{eq}})_4(^{15}\text{NO}_2)]^{4-}$ (10)			
$\delta(^{13}\text{C}_{\text{eq}})$	+176.7 (d)	$^2J(^{13}\text{C}_{\text{eq}}\text{Fe}^{15}\text{N})$	1.9
$\delta(^{15}\text{N})$	b		

^aSee footnote a, Table II. ^bNot observed; see text.

$(\text{CN})_5(^{15}\text{NO}_2)]^{4-}$ to grow in intensity at the expense of the spectrum of $[\text{Fe}(\text{CN})_5(^{15}\text{NO})]^{2-}$. It has previously been demonstrated^{19,20} that the nitroprusside ion reacts with hydroxide to yield $[\text{Fe}(\text{CN})_5\text{NO}_2]^{4-}$. Hence, we have detected, by the combined use of ^{13}C and ^{15}N NMR spectroscopy, two routes for the conversion of $[\text{Fe}(\text{CN})_5(\text{NO})]^{2-}$ into $[\text{Fe}(\text{CN})_5(\text{NO}_2)]^{4-}$, both by addition of hydroxide and by direct exchange with nitrite via 7. The essential difference between these routes is that addition of hydroxide causes no exchange of the nitrogen bound to iron, whereas attack by nitrite via 7 can cause isotopic exchange of nitrogen. An attempt to observe the reverse of the hydroxide reaction, by addition of acid, was inconclusive, as any change was accompanied by extensive decomposition. When aqueous sodium hydroxide was added to $[\text{Fe}(\text{CN})_5(^{14}\text{NO})]^{2-}$ in the absence of added nitrite, the ^{13}C spectrum of nitroprusside was very rapidly replaced by that of $[\text{Fe}(\text{CN})_5(^{14}\text{NO}_2)]^{4-}$ accompanied by the weak spectrum of a second pentacyanoiron(II) complex characterized by $\delta(^{13}\text{C}_{\text{ax}})$ 177.2, $\delta(^{13}\text{C}_{\text{eq}})$ 172.8, and $^2J(^{13}\text{C}_{\text{ax}}\text{Fe}^{13}\text{C}_{\text{eq}}) = 9$ Hz. This second species was not identified, but it may have been $[\text{Fe}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$.

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In all samples of $[\text{Fe}(\text{CN})_5\text{NO}]^{2-}$, no matter how carefully handled, we detected the slow emergence of a minor resonance, a singlet at +177.9 ppm. This may have been due to the primary photoproduct^{21,22} $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{2-}$, in which the kinetic lability of the aqua ligand in the d^5 complex allows scrambling, possibly via a pseudorotation process, of the axial and equatorial ligands in the intermediate $[\text{Fe}(\text{CN})_5]^{2-}$. Alternatively this singlet could be due to $[\text{Fe}(\text{CN})_6]^{4-}$, whose reported²³ chemical shift is +177.2 ppm, since free cyanide, as from the photoproduct $[\text{Fe}(\text{CN})_5\text{H}_2\text{O}]^{2-}$, is known²⁴ to react with nitroprusside, yielding $[\text{Fe}(\text{CN})_6]^{4-}$.

These spectroscopic observations on nitroprusside and certain of its derivatives show that, by use of double labeling with ^{13}C and ^{15}N , it is possible to obtain a ready distinction between the several species in solution, on the basis of their characteristic chemical shifts and coupling constants. This will prove of value for the identification, in solution, of the inorganic products resulting from the reactions of the nitroprusside ion with nucleophiles^{25,26} and in studies of the physiological action of nitroprusside.²⁷

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Registry No. $\text{Fe}_4\text{S}_3(\text{NO})_7^-$, 97210-39-4; $\text{Fe}_4\text{Se}_3(\text{NO})_7^-$, 97210-40-7; $\text{Fe}_2(\text{SMe})_2(\text{NO})_4$, 79408-10-9; $\text{Fe}_2(\text{S-}i\text{-Pr})_2(\text{NO})_4$, 96613-18-2; $\text{Fe}(\text{CN})_5(\text{NO})^{2-}$, 15078-28-1; $\text{Fe}(\text{CN})_5(\text{NO}_2)^{4-}$, 15003-01-7; $\text{Fe}_2\text{S}_4(\text{NO})_4$, 53276-80-5; $\text{Fe}_4\text{Se}_4(\text{NO})_4$, 81366-92-9; $\text{Fe}_2(\text{SMe})_2(^{15}\text{NO})_4$, 97234-18-9; $\text{Fe}_2(\text{S-}i\text{-Pr})_2(^{15}\text{NO})_4$, 97234-19-0; $\text{Na}_4[\text{Fe}(^{13}\text{CN})_6]$, 97210-41-8; $\text{Na}_2[\text{Fe}(^{13}\text{CN})_5\text{NO}]$, 94792-79-7; $\text{Na}_2[\text{Fe}(^{13}\text{CN})_5(^{15}\text{NO})]$, 97210-42-9.

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Photochemistry of Metal-Metal-Bonded Complexes. 1. MLCT Photolysis of $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ (M, M' = Mn, Re) in 2-MeTHF between 133 and 230 K

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The photolysis in 2-MeTHF is reported for several complexes $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ (M, M' = Mn, Re) at temperatures varying from 133 to 230 K. Above 200 K homolysis of the metal-metal bond occurs for the complexes with M = Mn and M' = Mn, Re. At temperatures below 200 K the main reaction products are $[\text{M}(\text{CO})_5]^-$ and $[\text{M}'(\text{CO})_3(\alpha\text{-diimine})(2\text{-MeTHF})]^+$ if M = Mn, Re and M' = Mn. Although these 2-MeTHF-coordinated cations reacted back with $[\text{M}(\text{CO})_5]^-$ to the parent compound upon raising the temperature, several P(*n*-Bu)₃-substituted complexes $[\text{M}(\text{CO})_5]^-[\text{M}'(\text{CO})_3(\alpha\text{-diimine})(\text{P}(\text{n-Bu})_3)]^+$ could be isolated. It appeared that the ions were not formed by direct heterolysis of the metal-metal bond but instead by thermal disproportionation of a photosubstituted product $(\text{CO})_5\text{MM}'(\text{CO})_2(\alpha\text{-diimine})(2\text{-Me-THF})$. Several P(*n*-Bu)₃-substituted complexes $(\text{CO})_5\text{MM}'(\text{CO})_2(\alpha\text{-diimine})(\text{P}(\text{n-Bu})_3)$ could be identified for M = Re, M' = Mn. Contrary to the complexes with M = Mn, Re and M' = Mn, the corresponding $(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$ ones did not show photosubstitution of CO but instead breaking of a metal-nitrogen bond upon photolysis at 133 K. It is proposed that this bond breaking is the primary photoprocess at lower temperatures and that it is followed by release of CO in the case of M' = Mn. An energy vs. distortion diagram is presented according to which the homolytic splitting of the metal-metal bond and the breaking of the metal-nitrogen bond occur from two different close-lying excited states, $^3\sigma_g\pi^*$ and $^3d_x\pi^*$, respectively.

Introduction

In this paper we report the photolysis in 2-MeTHF between 133 and 230 K of the metal-metal-bonded complexes $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ [M, M' = Mn, Re except M = M'

= Re; $\alpha\text{-diimine}$ = 1,10-phenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridine (bpy'), pyridine-2-carbaldehyde *p*-tolylimine (*p*-Tol-PyCa) or 1,4-diaza-1,3-butadiene (R-DAB, RN=CH-CH=NR).¹ The complexes, having the structure shown in Figure

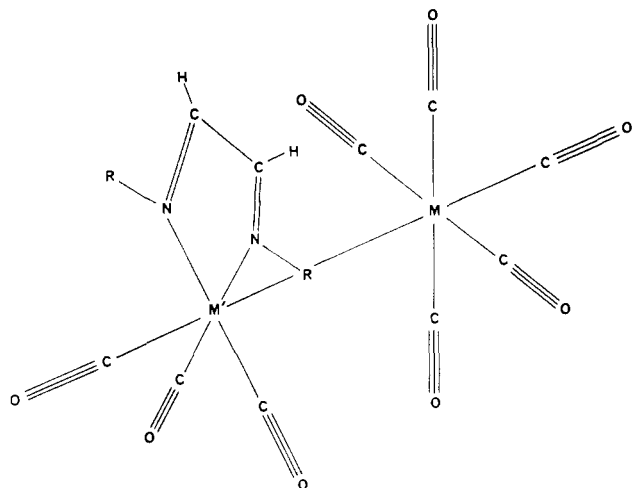


Figure 1. Structure of $(\text{CO})_5\text{MM}'(\text{CO})_3(\text{R-DAB})$ ($\text{M}, \text{M}' = \text{Mn}, \text{Re}$).

1, are derived from $\text{Mn}_2(\text{CO})_{10}$ by substitution of two CO groups at one metal center by an α -diimine ligand. The photochemistry of these complexes is of interest in two respects. Up to now, $\text{Mn}_2(\text{CO})_{10}$ has been the cornerstone example for the photochemical investigations of metal–metal-bonded carbonyls. Both homolytic splitting of the metal–metal bond² and release of CO ^{3,4} have been observed for this complex. Moreover, upon photolysis in the presence of excess pyridine or amine ($=\text{N}$), disproportionation has been observed.^{5,6} For this latter reaction two different mechanisms have been proposed. According to McCullen and Brown,⁶ homolytic splitting of the Mn–Mn bond is followed by decomposition of $\cdot\text{Mn}(\text{CO})_5$ radicals into $\cdot\text{Mn}(\text{CO})_3\text{N}_2$. These latter 17-electron radicals then transfer an electron to $\text{Mn}_2(\text{CO})_{10}$ with formation of $\cdot\text{Mn}(\text{CO})_5$ and $\text{Mn}[(\text{CO})_5]^-$.

Quite recently however, Stiegman and Tyler⁷ have proposed another mechanism according to which electron transfer to $\text{Mn}_2(\text{CO})_{10}$ takes place from the 19-electron radical $\cdot\text{Mn}(\text{CO})_3\text{N}_3$. Now, if the first mechanism is correct, we may also expect a heterolytic splitting of the Mn–Mn bond for $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$, which also contain two N-donor atoms at one of the metal fragments.

A second important aspect of these complexes is the assignment of their lowest energy absorption band at about 550 nm (Figure 2). Wrighton et al. observed a homolytic splitting of the metal–metal bond 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) upon irradiation into this band.⁸ Because of this they assigned this band to a charge-transfer transition from the

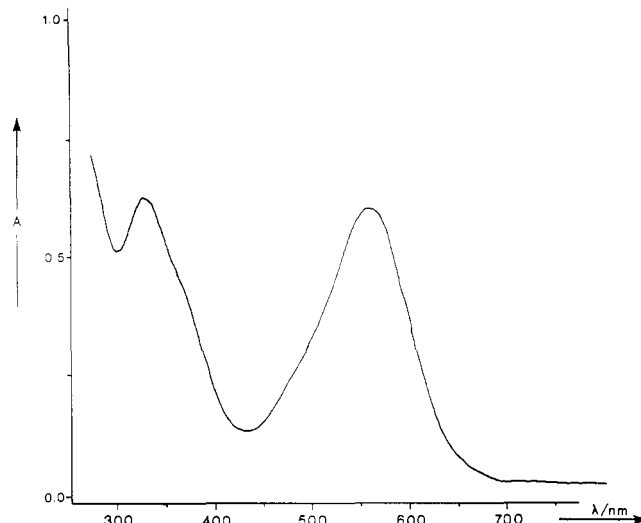


Figure 2. Electronic absorption spectrum of $(\text{CO})_5\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$ measured in *n*-pentane.

metal–metal-bonding orbital (σ_b) to the lowest π^* orbital of the α -diimine ligand. The metal–metal bond will then be weakened in the excited state and this will cause the splitting of this bond. This assignment is however questionable for the following reasons. First of all, the σ_b and π^* orbitals will hardly overlap and a transition between them can not account for the high intensity ($\epsilon_{\text{max}} \approx 9500$) of the absorption band. Second, if the metal–metal bond is weakened during the electronic transition, a strong resonance Raman (RR) effect should occur for $\nu(\text{M-M})$, the metal–metal stretching mode, upon excitation into this band. However, these RR spectra only show a weak RR effect for this vibration not exceeding that of the metal–ligand stretching modes.⁹ In fact, these RR spectra are closely similar to those of the corresponding mononuclear d^6 complexes $\text{M}(\text{CO})_4(\alpha\text{-diimine})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$)¹⁰ and the d^8 complexes $\text{M}(\text{CO})_3(\alpha\text{-diimine})$ ($\text{M} = \text{Fe}, \text{Ru}$),^{11,12} all containing a low-energy metal (d_π) $\rightarrow \alpha$ -diimine (π^*) charge-transfer (MLCT) transition. In agreement with these latter complexes, we assign the corresponding absorption band of these $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ complexes to a $\text{M}'(d_\pi) \rightarrow \alpha\text{-diimine}(\pi^*)$ MLCT transition.⁹ The $\text{M}'(d_\pi)$ orbital is not directly involved in the metal–metal bond but is responsible for the $\text{M}'\text{-}\alpha\text{-diimine} \pi$ back-bonding in the complex. In this article the photolysis of several of these $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ complexes in 2-MeTHF is reported and discussed in view of this new assignment for the absorption band. The photolysis has been studied at temperatures ranging from $T = 133$ K, below which temperature 2-MeTHF solidifies to a glass, up to $T = 230$ K. At still higher temperatures several photoproducts and radicals formed decompose rather rapidly, giving rise to side reactions, which will be discussed in more detail in a forthcoming paper.¹³

Experimental Section

The ligands¹⁴ and binuclear metal carbonyl complexes^{8,15} were synthesized according to published methods. $[\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})\text{Br}(\text{THF})]^+[\text{OTf}]^-$ was prepared by reaction of $\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})\text{Br}$

- (1) Most 1,4-diaza-1,3-butadienes have the general formula $\text{RN}=\text{C}(\text{R}')-\text{C}(\text{R}'')=\text{NR}$, an important subgroup of this class being $\text{RN}=\text{CH}-\text{CH}=\text{NR}$ (R-DAB(H, H)). For economy of space, if the R grouping is specifically stated, then the form R(substituent)-DAB is used, and this implies proton substitution at the α -diimine carbon atoms; e.g., *i*-PrN=CH–CH=N-*i*-Pr becomes *i*-Pr-DAB. Abbreviations for the R groups in R-DAB and PR_3 used are *i*-Pr = isopropyl, *t*-Bu = *tert*-butyl, *n*-Bu = *n*-butyl, Ph = phenyl, *p*-Tol = *p*-tolyl; van Koten, G.; Vrieze, K. *Adv. Organomet. Chem.* **1982**, *21*, 153.
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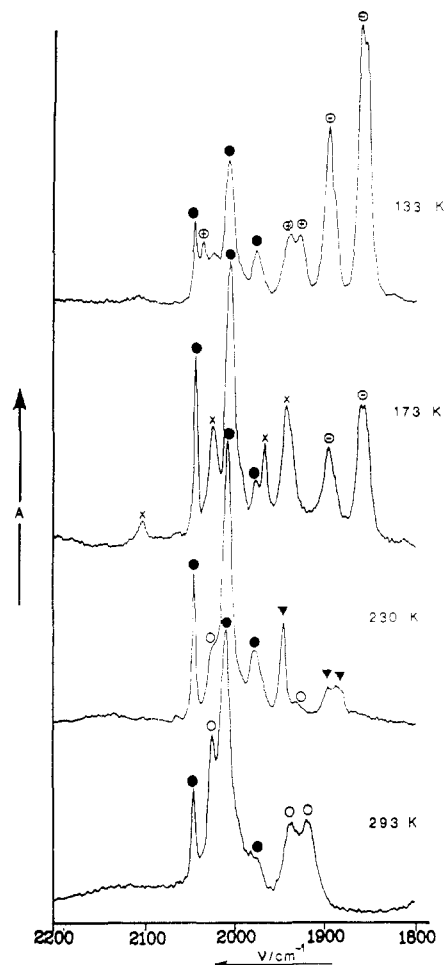


Figure 3. IR CO stretching modes of the products formed upon photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$ in 2-MeTHF with $\lambda = 514.5\text{-nm}$ radiation at different temperatures: (●) $\text{Mn}_2(\text{CO})_{10}$; (▼) $\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})_2$; (○) $(\text{CO})_3(2\text{-MeTHF})_2\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$; (×) $\text{Mn}_2(\text{CO})_9(2\text{-MeTHF})$; (⊖) $[\text{Mn}(\text{CO})_5]^-$; (⊕) $[\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})(2\text{-MeTHF})]^+$.

and $\text{Ag}(\text{OTf})$ in THF. The formed AgBr precipitated readily.

All spectroscopic samples were dissolved in freshly distilled and deoxygenated 2-MeTHF and prepared with standard inert-gas techniques. Special care was taken to exclude all light during manipulations of the samples. Electronic absorption spectra were measured on Cary 14 or Perkin-Elmer Lambda 5 spectrophotometers, IR spectra on a Nicolet 7199 B FT-IR interferometer with a liquid-nitrogen-cooled Hg, Cd, Te detector (32 scans, resolution = 0.5 cm^{-1}), and ESR spectra on a Bruker ER 200D-MR X-band spectrophotometer. Coupling constants were obtained by a computer simulation.

As light source for the photolysis experiments a Coherent CR 8 Ar⁺ ion laser was used. The laser power was 30–50 mW, and the laser beam was defocused before entering the sample.

Results and Discussion

A. Photolysis at $T \geq 200\text{ K}$. Figure 3 shows the CO stretching vibrations of the products formed when $(\text{CO})_5\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$ is photolyzed at different temperatures in 2-MeTHF with the $\lambda = 514.5\text{-nm}$ line of the argon ion laser. These bands have been obtained by subtracting from the spectra the bands of the solvent and the parent compound. At $T = 230\text{ K}$, $\text{Mn}_2(\text{CO})_{10}$ is formed with CO stretching modes at 2045, 2009, and 1977 cm^{-1} ¹⁶ (Figure 3b). The changes of the electronic absorption spectrum accompanying this reaction are shown in Figure 4. Photolysis causes a shift of the metal-metal-bonding (σ_b) → metal-metal-antibonding (σ^*) transition from 340 to 350 nm due to formation of $\text{Mn}_2(\text{CO})_{10}$.¹⁶ At the same time, the MLCT band at 550 nm shifts to 745 nm. The formation of $\text{Mn}_2(\text{CO})_{10}$ is the

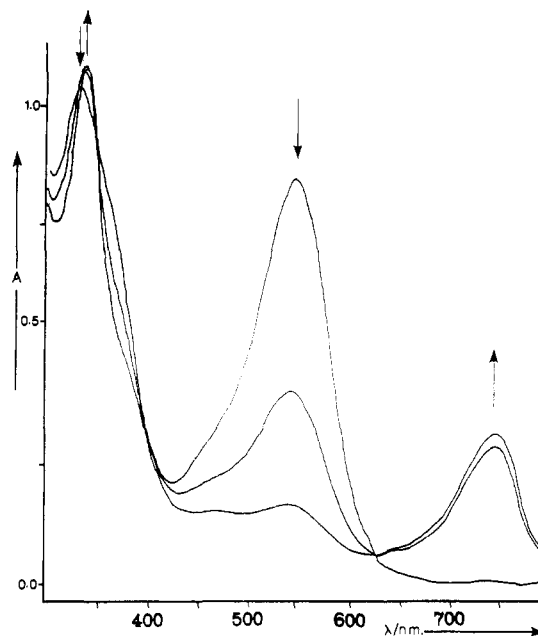


Figure 4. Electronic absorption spectral changes of a 2-MeTHF solution of $(\text{CO})_5\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$ upon photolysis with $\lambda = 514.5\text{-nm}$ radiation at 230 K.

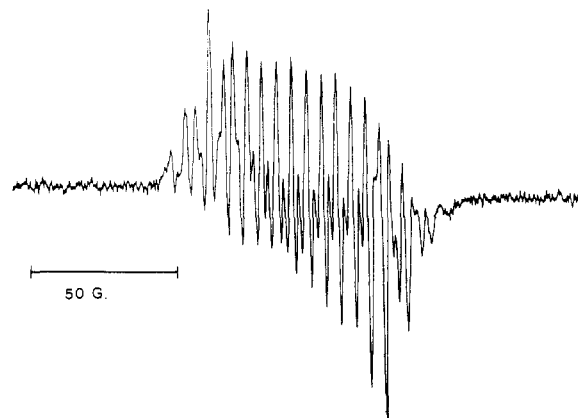
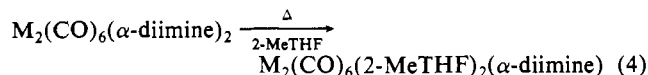
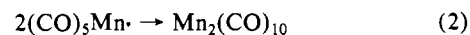
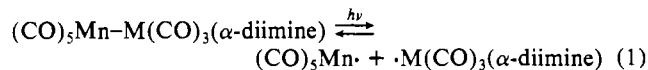


Figure 5. ESR spectrum obtained after photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$ in 2-MeTHF at 230 K. Photolysis was performed by a medium-pressure Hg-lamp using a glass filter. The coupling constants are $A_{\text{Mn}} = 9.53\text{ G}$, $A_{\text{N}} = 7.40\text{ G}$, and $A_{\text{H}} = 4.75\text{ G}$. The g factor is 2.011.

result of a homolytic splitting of the metal-metal bond (Scheme I). Apparently, the $\cdot\text{Mn}(\text{CO})_5$ radicals combine to give $\text{Mn}_2(\text{CO})_{10}$.

Scheme I



$(\text{CO})_{10}$. At the same time $\cdot\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})$ radicals are formed that could be identified, presumably as 18-electron radicals $\cdot\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})(2\text{-MeTHF})$, by ESR (Figure 5). The A values, derived from this ESR spectrum, $A_{\text{Mn}} = 9.53\text{ G}$, $A_{\text{N}} = 7.40\text{ G}$, and $A_{\text{H}} = 4.75\text{ G}$ indicate a large delocalization of the electron over the DAB ligand.¹⁸ The same spectrum was obtained by Alberti and Hudson upon photolysis of $\text{Mn}_2(\text{CO})_{10}$ in the presence of $i\text{-Pr-DAB}$.¹⁷ The $\cdot\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})$ radicals will

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Table I. IR CO Stretching Frequencies (cm^{-1}) of $\text{Mn}_2(\text{CO})_6(\alpha\text{-diimine})_2$ and $\text{M}_2(\text{CO})_6(\alpha\text{-diimine})(2\text{-MeTHF})_2$ ($\text{M} = \text{Mn, Re}$) Complexes Obtained after Photolysis in 2-MeTHF at $T \geq 200$ K

compd	temp	CO stretching freq ^a				
$\text{Mn}_2(\text{CO})_6(\text{bpy}')_2$	293	1979 (s)	1932 (s)	1882 (w)	1863 (m)	
$\text{Mn}_2(\text{CO})_6(\text{phen})_2$	293	1982 (s)	1943 (m)	1890 (w)	1869 (w)	
$\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})_2$	230	2006 (m)	1946 (s)	1898 (w)	1888 (w)	
$\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})(2\text{-MeTHF})_2$	293	2035 (s)	1938 (m)		1920 (m)	
$\text{Mn}_2(\text{CO})_6(p\text{-Tol-PyCa})(2\text{-MeTHF})_2$	293	2027 (s)	1944 (m)		1917 (m)	
$\text{Re}_2(\text{CO})_6(p\text{-Tol-DAB})(2\text{-MeTHF})_2$	293	2014 (m)	1899 (s)			

^as = strong, m = medium, w = weak.

combine to give $(i\text{-Pr-DAB})(\text{CO})_3\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$, a binuclear metal–metal-bonded complex with a DAB ligand at each metal fragment. Such complexes have been observed before as thermally unstable side products of the reaction between $[\text{Mn}(\text{CO})_5]^-$ and $\text{Mn}(\text{CO})_3\text{X}(\text{R-DAB})$ ($\text{X} = \text{Cl, Br, I}$).⁸ The MLCT band at 745 nm and the three CO vibrations at 1946, 1898, and 1888 cm^{-1} are assigned to this $\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})_2$ complex. A fourth CO vibration of this complex was found at 2006 cm^{-1} after subtraction of the $\text{Mn}_2(\text{CO})_{10}$ vibrations from the spectrum in figure 3b. The shift of the MLCT band from 550 to 745 nm on going from $(\text{CO})_5\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$ to $\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})_2$ agrees with the difference in electron-withdrawing power between the $\text{Mn}(\text{CO})_5$ and $\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})$ fragments. The thermal instability of this $\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})_2$ complex is evident from the disappearance of the 745-nm band upon raising the temperature to $T = 293$ K and from the shift of the CO stretching vibrations to 2025, 1938, and 1920 cm^{-1} . These latter vibrations are also found when the photolysis takes place at $T = 293$ K (Figure 3a). The shift of the CO stretching modes to higher frequencies is in accordance with a substitution of an $i\text{-Pr-DAB}$ ligand by the less electron-donating 2-MeTHF molecules with formation of $(2\text{-MeTHF})_2(\text{CO})_3\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$.¹³ Due to this thermal instability the $\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})_2$ complex could not be isolated. In contrast with this, the corresponding photoproduct of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bpy}')$, $\text{Mn}_2(\text{CO})_6(\text{bpy}')_2$, appeared to be stable at room temperature. The CO vibrations of this latter complex, which has been described before by Morse and Wrighton,⁸ are shifted to lower frequency with respect to those of the $i\text{-Pr-DAB}$ complex (Table I) due to the lower π -acceptor ability of the bpy' ligand. The reason for the difference in thermal stability will be discussed in a forthcoming paper.¹³ Homolytic splitting of the metal–metal bond is observed for all $(\text{CO})_5\text{MnM}(\text{CO})_3(\alpha\text{-diimine})$ ($\text{M} = \text{Mn, Re}$) complexes at $T \geq 200$ K. The CO frequencies of several $\text{Mn}_2(\text{CO})_6(\alpha\text{-diimine})_2$ and $\text{M}_2(\text{CO})_6(\alpha\text{-diimine})(2\text{-MeTHF})_2$ photoproducts are collected in Table I.

On the basis of these results the mechanism shown in Scheme I is proposed for the photolysis of the $(\text{CO})_5\text{MnM}(\text{CO})_3(\alpha\text{-diimine})$ complexes in 2-MeTHF at $T \geq 200$ K. $\cdot\text{M}(\text{CO})_3(i\text{-Pr-DAB})(2\text{-MeTHF})$ radicals have been identified by ESR for both $\text{M} = \text{Mn}$ and $\text{M} = \text{Re}$. These ESR signals could be observed for a long time after the photolysis had taken place, which means that the $\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})_2$ complexes are partially dissociated into their radicals. The same holds for the $\text{Mn}_2(\text{CO})_6(\text{bpy}')_2$ complex, which reacts back in the dark to $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bpy}')$ in the presence of $\text{Mn}_2(\text{CO})_{10}$. This reaction can only proceed via a radical mechanism.

B. Photolysis at $T < 200$ K. Irradiation of $(\text{CO})_5\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$ at temperatures below 130 K, at which temperature 2-MeTHF solidifies to a glass, did not cause a photochemical reaction. However, upon photolysis at temperatures above 130 K and below 200 K, new bands appear in the CO stretching region at the expense of those belonging to $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})_2$.

From these, the bands at 1884, 1861, and 1857 cm^{-1} (indicated by \ominus in Figure 3c,d) belong to $[\text{Mn}(\text{CO})_5]^-$.¹⁶ The bands at 2043, 1939 and 1928 cm^{-1} are assigned to the solvated cation $[\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})(2\text{-Me-THF})]^+$ and indicated by \oplus in Figure 3d. This assignment is based on the close similarity between these bands and those of the cation of $[\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})-$

$(\text{THF})]^+[\text{OTF}]^-$, which has been prepared separately and has the CO stretching frequencies 2037 and 1937 cm^{-1} .

Upon photolysis of other $(\text{CO})_5\text{MMn}(\text{CO})_3(\alpha\text{-diimine})$ ($\text{M} = \text{Mn, Re}$) complexes, problems can arise with respect to the detection of the frequencies of the cation. They are rather weak and often obscured by the bands of other photoproducts, especially when at lower temperatures photosubstitution of a CO ligand by 2-MeTHF takes place (see below). Comparing the CO frequencies of the photoproducts obtained at 173 and 133 K (Figure 3c,d), we note an increase of the amount of $[\text{Mn}(\text{CO})_5]^-$ and $[\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})(2\text{-MeTHF})]^+$ in the latter case at the expense of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})_2$. Besides, bands show up at 2102, 2025, 1969, and 1945 cm^{-1} (indicated by \times in Figure 3c) in the 173 K spectrum, which are not observed upon photolysis at 230 K and which are very weak in the 133 K spectrum. These bands apparently belong to a complex that is only formed when $\text{Mn}_2(\text{CO})_{10}$ is a major photoproduct and that is unstable at higher temperatures. Indeed, these bands disappear from the spectrum when the solution is raised in temperature after irradiation at 173 K. We therefore assign these bands to the complex $\text{Mn}_2(\text{CO})_9(2\text{-MeTHF})$, and this assignment is strongly supported by a comparison of these frequencies with those of $\text{Mn}_2(\text{CO})_9\text{L}$ ($\text{L} = \text{amine, imine}$). For instance, $\text{Mn}_2(\text{CO})_9(\text{benzotrile})$ has its CO vibrations at 2095, 2027, 2006, 1995, 1967, and 1949 cm^{-1} .¹⁹ The two bands around 2000 cm^{-1} will be obscured here by the strong band of $\text{Mn}_2(\text{CO})_{10}$. $\text{Mn}_2(\text{CO})_9(2\text{-MeTHF})$ will be formed by reaction of $\cdot\text{Mn}(\text{CO})_5$ with its decomposition product $\cdot\text{Mn}(\text{CO})_4(2\text{-MeTHF})$. Raising the temperature causes substitution of 2-MeTHF by CO from the solution. Upon photolysis at temperatures below 173 K, much less $\cdot\text{Mn}(\text{CO})_5$ is formed, and the amounts, of both $\text{Mn}_2(\text{CO})_{10}$ and $\text{Mn}_2(\text{CO})_9(2\text{-MeTHF})$ are then drastically reduced.

The ions formed upon photolysis at $T < 200$ K are not stable at higher temperatures. When the temperature is raised, they react back to the parent compound since 2-MeTHF then loses its coordinating properties. However, if $\text{P}(n\text{-Bu})_3$ is added to a solution of the ions, $[\text{Mn}(\text{CO})_3(i\text{-Pr-DAB})(\text{P}(n\text{-Bu})_3)]^+[\text{Mn}(\text{CO})_5]^-$ is formed, which is a stable compound at room temperature (see below).

On the basis of these results, one might conclude that photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$ leads to both homolytic and heterolytic splitting of the metal–metal bond, depending on the temperature of the 2-MeTHF solution. However, if we photolyze instead the corresponding complexes $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{phen})$ and $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bpy}')$ at 133 K neither $\text{Mn}_2(\text{CO})_{10}$ nor $[\text{Mn}(\text{CO})_5]^-$ is formed. Instead a photosubstitution product is formed, which will now be discussed in more detail.

Photosubstitution of CO by 2-MeTHF Before the Disproportionation Reaction Takes Place. Figure 6 shows the IR spectral changes in the CO stretching region upon photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{phen})$ at 133 K with the $\lambda = 514.5\text{-nm}$ line of an argon ion laser. In contrast to the photolysis of the corresponding $i\text{-Pr-DAB}$ complex only a small amount of $[\text{Mn}(\text{CO})_5]^-$ is formed (indicated by \ominus). Instead, free CO shows up upon photolysis ($\nu = 2132$ cm^{-1} , see insert). Furthermore, all CO vibrations shift to lower frequency (Table II), which points to a photosubstitution of CO by the electron-donating ligand 2-

Table II. IR CO Stretching Frequencies (cm^{-1}) of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\alpha\text{-diimine})$ and $(\text{CO})_5\text{ReMn}(\text{CO})_3(\alpha\text{-diimine})$ and of Their 2-MeTHF and $\text{P}(n\text{-Bu})_3$ Substitution Products Measured in 2-MeTHF at $T < 200$ K

compd	temp, K	CO stretching freq ^b							
$(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bpy}')$	133	2053 (m)	1978 (s)	1953 (s)				1893 (m)	
$(\text{CO})_5\text{MnMn}(\text{CO})_2(\text{bpy}')\text{-}(2\text{-MeTHF})$	133	2039 (m)	1962 (w)	1939 (vs)	1922 (m)		1875 (m)	1816 (m)	
$(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{phen})$	133	2054 (m)	1960 (vs)	1952 (s)				1897 (m)	
$(\text{CO})_5\text{MnMn}(\text{CO})_2(\text{phen})\text{-}(2\text{-MeTHF})$	133	2039 (m)	1964 (w)	1940 (vs)	1924 (m)		1877 (m)	1820 (m)	
$(\text{CO})_5\text{MnMn}(\text{CO})_2(\text{phen})\text{-}(\text{P}(n\text{-Bu})_3)$	133	2034 (m)	1961 (w)	1939 (vs)	1928 (sh)		1890 (m)	1834 (m)	
$(\text{CO})_5\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$	133	2063 (m)	1998 (w)	1978 (vs)	1973 (m)	1955 (sh)		1897 (m)	
$(\text{CO})_5\text{MnMn}(\text{CO})_2(i\text{-Pr-DAB})\text{-}(2\text{-MeTHF})^a$	133	2047 (m)		1961 (vs)	1933 (s)		1883 (m)	1824 (m)	
$(\text{CO})_5\text{MnMn}(\text{CO})_3(p\text{-Tol-DAB})$	133	2069 (m)	2008 (w)	1989 (vs)	1980 (vs)	1965 (w)		1905 (m)	
$(\text{CO})_5\text{MnMn}(\text{CO})_3(p\text{-Tol-PyCa})$	133	2059 (m)	1986 (w)	1977 (vs)	1964 (m)	1952 (m)	1943 (m)	1896 (m)	
$(\text{CO})_5\text{MnMn}(\text{CO})_2(p\text{-Tol-PyCa})\text{-}(2\text{-MeTHF})^a$	133	2043 (m)	1980 (w)	1954 (s)	1940 (vs)	1926 (m)	1880 (m)	1823 (m)	
$(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{phen})$	133	2075 (m)	2000 (w)	1975 (vs)	1961 (m)	1948 (w)		1884 (m)	
$(\text{CO})_5\text{ReMn}(\text{CO})_2(\text{phen})\text{-}(2\text{-MeTHF})$	133	2061 (m)	1979 (w)	1955 (vs)	1925 (m)	1853 (m)		1807 (m)	
$(\text{CO})_5\text{ReMn}(\text{CO})_2(\text{phen})\text{-}(\text{P}(n\text{-Bu})_3)$	173	2058 (m)		1957 (vs)	1932 (m)	1880 (m)		1825 (m)	
$(\text{CO})_5\text{ReMn}(\text{CO})_3(i\text{-Pr-DAB})$	133	2089 (m)	2017 (w)	1986 (vs)	1963 (s)	1891 (m)		1881	
$(\text{CO})_5\text{ReMn}(\text{CO})_2(i\text{-Pr-DAB})\text{-}(2\text{-MeTHF})$	133	2078 (m)	2008 (w)	1978 (vs)	1939 (m)	1874 (m)		1813	
$(\text{CO})_5\text{ReMn}(\text{CO})_2(i\text{-Pr-DAB})\text{-}(\text{P}(n\text{-Bu})_3)$	173	2077 (m)	2006 (w)	1980 (vs)	1944 (m)	1878 (m)		1822	
$(\text{CO})_5\text{ReMn}(\text{CO})_3(p\text{-Tol-DAB})$	143	2097 (m)	2029 (w)	2006 (vs)	1989 (s)	1967 (s)		1899 (s)	
$(\text{CO})_5\text{ReMn}(\text{CO})_2(p\text{-Tol-DAB})\text{-}(2\text{-MeTHF})$	143	2090 (m)		2002 (vs)	1983 (m)	1945 (m)	1885 (m)	1825 (m)	

^aSpectra obtained by difference spectroscopy. ^bvs = very strong, s = strong, m = medium, w = weak, sh = shoulder.

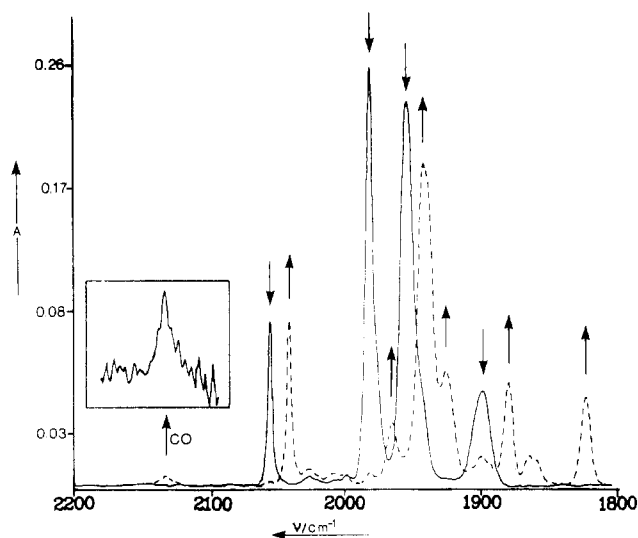


Figure 6. IR spectral changes upon photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{phen})$ with $\lambda = 514.5\text{-nm}$ radiation in 2-MeTHF at 133 K.

MeTHF. This photoproduct could not be isolated and identified since it disproportionates upon raising the temperature. A similar disproportionation reaction was observed for the phosphine-substituted product, which was formed by reaction of the phosphine with the 2-MeTHF-substituted complex (see below). However, the corresponding photoproducts $(\text{CO})_5\text{ReMn}(\text{CO})_2(\text{R-DAB})\text{-}(\text{PR}'_3)$ ($\text{R} = i\text{-Pr}, p\text{-Tol}$; $\text{R}' = \text{Ph}, n\text{-Bu}$) did not disproportionate and could be isolated and identified.¹³ In these latter complexes a CO ligand of the $\text{Mn}(\text{CO})_3(\text{R-DAB})$ moiety of the complex appeared to be substituted by PR'_3 . Table II shows the CO stretching frequencies of several $(\text{CO})_5\text{MMn}(\text{CO})_3(\alpha\text{-diimine})$ ($\text{M} = \text{Mn}, \text{Re}$) complexes and their 2-MeTHF and $\text{P}(n\text{-Bu})_3$ derivatives. From a comparison of these data, it is evident that 2-MeTHF and $\text{P}(n\text{-Bu})_3$ have substituted the same CO ligand

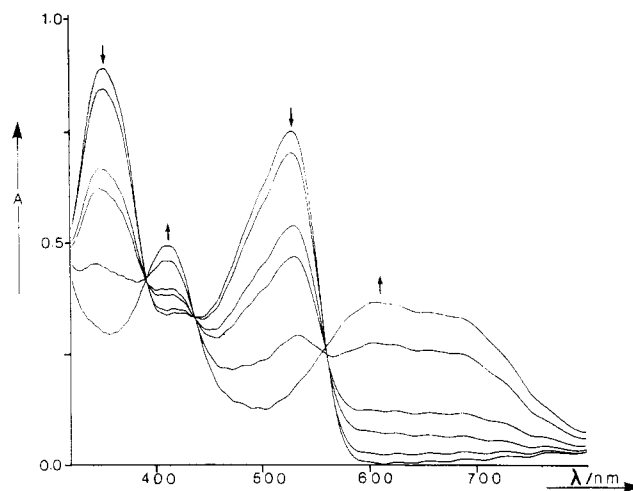


Figure 7. Electronic absorption spectral changes upon photolysis of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{phen})$ with $\lambda = 514.5\text{-nm}$ radiation in 2-MeTHF at 133 K.

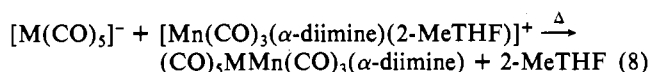
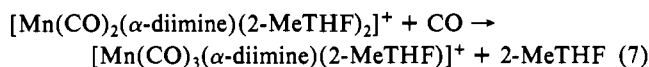
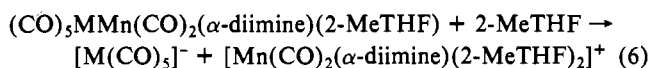
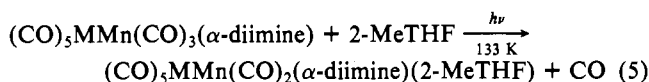
of the complex. Figure 7 shows the changes in the absorption spectrum accompanying the photosubstitution reaction of $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{phen})$ in 2-MeTHF at 133 K. The MLCT band at 520 nm disappears, and a new broad band shows up between 580 and 700 nm. This shift of the MLCT band to lower energy is in agreement with the photosubstitution of a CO group of the $\text{Mn}(\text{CO})_3(\text{phen})$ moiety by the electron-donating ligand 2-MeTHF.

When the temperature is raised from 133 to 203 K, the CO frequencies of the substituted complex disappear and the bands at 1890 and 1865 cm^{-1} belonging to $[\text{Mn}(\text{CO})_5]^-$ show up in the spectrum. The CO vibrations of the cation formed by this heterolytic splitting of the metal-metal bond could not be identified with certainty, probably due to coincidence of its weak bands with other ones. This cation may have the composition $[\text{Mn}(\text{CO})_2\text{-}$

(phen)(2-MeTHF)₂]⁺ or [Mn(CO)₃(phen)(2-MeTHF)]⁺ depending on the kind of reaction taking place after the heterolysis (with 2-MeTHF or with CO). Up to now only the second type of cation could be identified with certainty for any of these complexes (see e.g. Figure 3d). All (CO)₅MMn(CO)₃(α-diimine) (M = Mn, Re) complexes more or less react in the same way although the thermal stability of the photosubstitution products (CO)₅MMn(CO)₂(α-diimine)(2-MeTHF) strongly depends on the metal and the α-diimine ligand. Thus, for the complex (CO)₅ReMn(CO)₃(*p*-Tol-DAB), the CO frequencies of this intermediate could only be observed by careful subtracting of the frequencies of the parent compound and ions (Figure 8). The spectrum of the intermediate (Figure 8b) has the same CO pattern as the spectrum of the photoproduct (CO)₅MnMn(CO)₂(phen)(2-MeTHF) shown in Figure 6. Just as in the case of (CO)₅MnMn(CO)₃(phen), raising the temperature as well as a further irradiation results in an increase of the CO bands of [Re(CO)₅]⁻. The disproportionation upon further irradiation is certainly due to local heating by the laser beam since the photosubstitution product itself hardly absorbs at 514.5 nm.

On the basis of these results we propose the following mechanism for the disproportionation reaction (M = Mn, Re):

Scheme II



When (CO)₅MnMn(CO)₃(phen) is photolyzed in 2-MeTHF at 133 K in the presence of P(*n*-Bu)₃, first of all reaction 5 takes place. However, when the temperature of the solution is raised to 173 K, the coordinated 2-MeTHF is replaced by P(*n*-Bu)₃. The changes in the CO stretching region during this reaction are shown in Figure 9a. The bands at 1877 and 1822 cm⁻¹ belonging to the Mn(CO)₂(phen)(2-MeTHF) moiety shift slightly to higher frequency, whereas the other bands hardly change. This shift to higher frequency means that P(*n*-Bu)₃ is a less basic ligand in these complexes than 2-MeTHF. The same effect has been found for the complexes Ph₃SnMn(CO)₂(α-diimine)(L) (L = P(*n*-Bu)₃, 2-MeTHF).²⁰ The difference in electron-donating character of these ligands is also reflected in the stability of their substitution products. Whereas the 2-MeTHF complex already disproportionates at 200 K, heterolytic splitting of the P(*n*-Bu)₃ complex only occurs at room temperature. The CO frequencies of the ions formed during the latter reaction are shown in Figure 9b.

Photolysis of (CO)₅MnRe(CO)₃(α-diimine) in 2-MeTHF at 133 K. The (CO)₅MnRe(CO)₃(α-diimine) complexes show another photochemical reaction in 2-MeTHF at 133 K than the (CO)₅MMn(CO)₃(α-diimine) (M = Mn, Re) ones discussed before. For two of these complexes, (CO)₅MnRe(CO)₃(*i*-Pr-DAB) and (CO)₅MnRe(CO)₃(phen) the photolysis has been studied. The changes in the CO stretching region for the photolysis of (CO)₅MnRe(CO)₃(*i*-Pr-DAB) with λ = 514.4-nm radiation are shown in Figure 10. During the photolysis of this complex the MLCT band at about 500 nm disappears and no new band shows up in the visible region. When the temperature is raised to 203 K, the MLCT band returns. A similar reversible behavior is observed in the IR spectrum upon raising the temperature. During the photolysis some [Mn(CO)₅]⁻ is formed. Furthermore, a small amount of Mn₂(CO)₁₀ is formed due to some homolytic splitting. However, contrary to the photolysis of the (CO)₅MMn(CO)₃(α-diimine) complexes at 133 K, no free CO

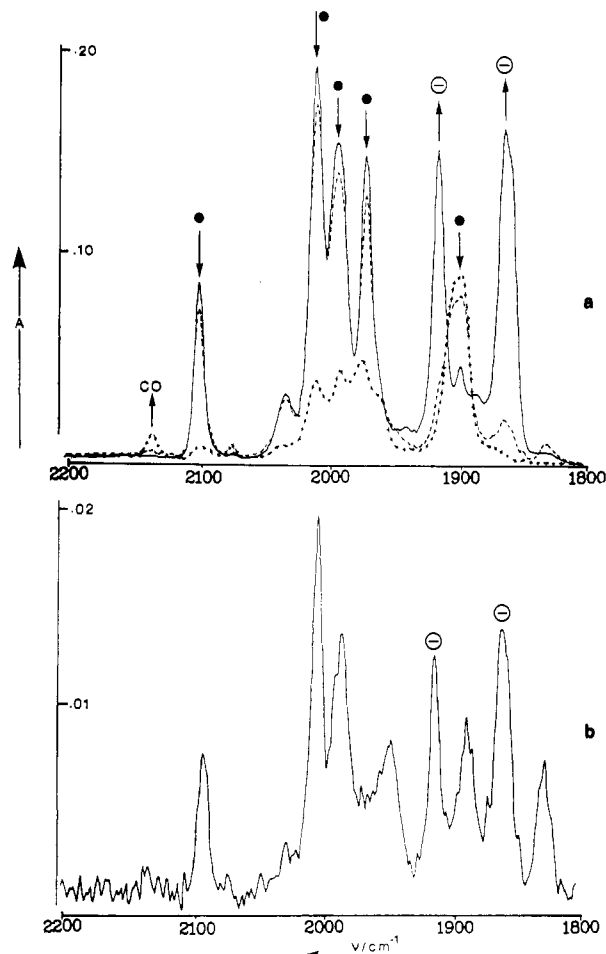


Figure 8. (a) IR spectral changes upon photolysis of (CO)₅ReMn(CO)₃(*p*-Tol-DAB) with λ = 514.5-nm radiation in 2-MeTHF at 143 K: (●) (CO)₅ReMn(CO)₃(*p*-Tol-DAB); (⊖) [Re(CO)₅]⁻; (—) *t* = 0; (---) *t* = 3 s; (++++) *t* = 5 min. (b) Spectrum of the intermediate, obtained by subtracting the spectrum of the parent compound from the spectrum taken after 3 s of photolysis (the dotted line in Figure 8a). Only a small amount of [Re(CO)₅]⁻ is formed in this short time.

is observed and the CO vibrations of the main photoproduct at 2032, 2003, 1917, 1883, and 1871 cm⁻¹ do not agree with those of the photosubstitution products found for the former complexes. A similar reaction is observed upon photolysis of (CO)₅MnRe(CO)₃(phen) although a larger amount of ions are formed here than in the case of the *i*-Pr-DAB complex. Raising the temperature to 173 K also results in back-reaction of the new photoproduct to the parent compound. At that temperature the ions are still present in the solution, and by subtraction of the CO frequencies of the parent compound and [Mn(CO)₅]⁻ from the spectrum, the CO frequencies of the [Re(CO)₃(phen)(2-MeTHF)]⁺ cation (2044 and 1921 cm⁻¹) could be obtained. The CO frequencies of the main photoproduct of the phen complex are found at 2037, 2028, 1937, 1917, and 1898 cm⁻¹. They are shifted to higher frequency with respect to the same photoproduct of the corresponding *i*-Pr-DAB complex. Increasing the energy of the radiation source favors the formation of the ions at the expense of the new photoproduct.

The disappearance of the MLCT band cannot be the result of complete loss of the α-diimine ligand from the complex since different CO frequencies are found for the photoproduct in the case of the R-DAB and phen complex. It rather points to a change of bonding mode of the α-diimine ligand. Although many of such bonding modes have been found for these ligands, viz. σ (2e) monodentate, σ,σ (4e) chelate, σ,σ' (4e) bridging, η²,η² (4e) chelate, σ,σ,η² (6e), and σ,σ,η²,η² (8e),²¹ only a few of them are

(20) Andréa, R. R.; Stufkens, D. J.; Oskam, A., submitted for publication.

(21) A recent review dealing with the chemistry of α-diimine ligands is: Vrieze, K.; van Koten, G. *Adv. Organomet. Chem.* **1982**, *21*, 153.

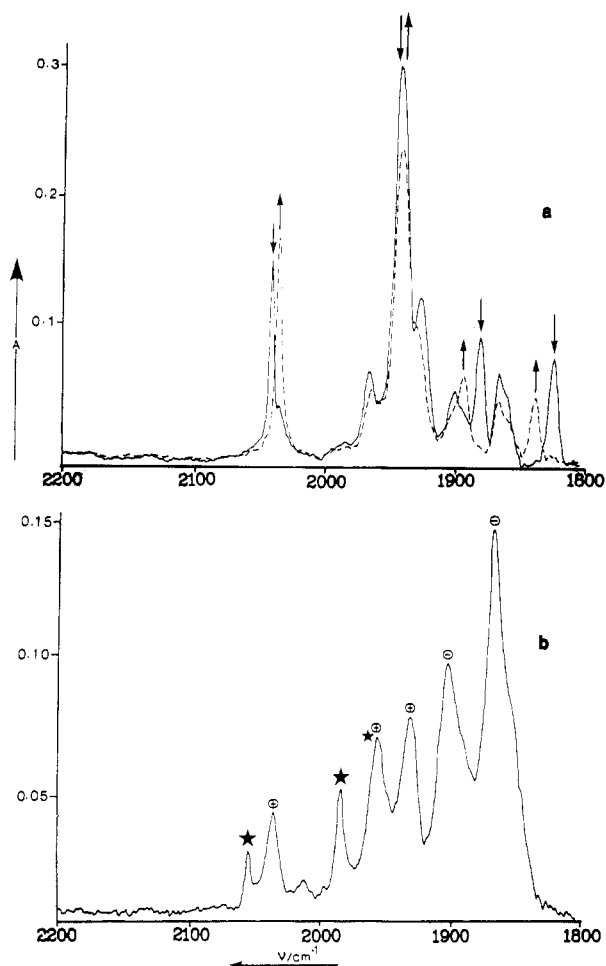


Figure 9. (a) IR spectral changes of the carbonyl stretching modes of $(\text{CO})_5\text{MnMn}(\text{CO})_2(\text{phen})(2\text{-MeTHF})$ in 2-MeTHF upon raising the temperature from 133 to 174 K in the presence of $\text{P}(n\text{-Bu})_3$. (b) IR CO stretching frequencies of $[\text{Mn}(\text{CO})_3(\text{phen})(\text{P}(n\text{-Bu})_3)]^+[\text{Mn}(\text{CO})_5]^-$ obtained after raising the temperature from 173 to 293 K: (\oplus) $[\text{Mn}(\text{CO})_3(\text{phen})(\text{P}(n\text{-Bu})_3)]^+$; (\ominus) $[\text{Mn}(\text{CO})_5]^-$; (\star) $(\text{CO})_5\text{MnMn}(\text{CO})_2(\text{phen})$.

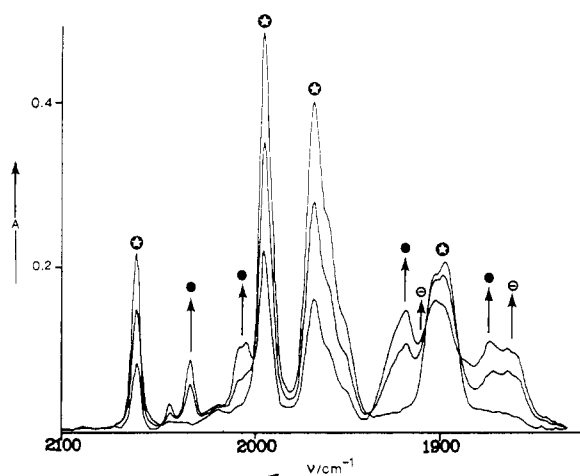


Figure 10. IR spectral changes of the carbonyl stretching modes of $(\text{CO})_5\text{MnRe}(\text{CO})_3(i\text{-Pr-DAB})$ upon photolysis with $\lambda = 514.5\text{-nm}$ radiation in 2-MeTHF at 133 K: (\star) $(\text{CO})_5\text{MnRe}(\text{CO})_3(i\text{-Pr-DAB})$; (\oplus) $[\text{Mn}(\text{CO})_5]^-$; (\bullet) $(\text{CO})_5\text{MnRe}(\text{CO})_3(2\text{-MeTHF})(\sigma\text{-}i\text{-Pr-DAB})$.

possible for both the R-DAB and phen ligand. Thus, η^2 -type bonding via a π orbital has never been found for phen and this excludes η^2, η^2 -, σ, σ, η^2 -, and $\sigma, \sigma, \eta^2, \eta^2$ -type bonding. Besides, a changeover from σ, σ -chelate bonding in the parent compound into η^2, η^2 bonding in the photoproduct, which has for example been found for $\text{Fe}(\text{CO})_3(\text{R-DAB})$ complexes upon photolysis in rare-gas

matrices at 10 K,²²⁻²⁴ would have caused a shift of the CO vibrations to higher frequency. Furthermore, formation of a complex in which the ligand is σ, σ, η^2 - or $\sigma, \sigma, \eta^2, \eta^2$ -coordinated to both metals, would have been accompanied by release of CO. Such a changeover from σ, σ -chelate bonding into $\sigma, \sigma, \eta^2, \eta^2$ -coordination has been observed upon photolysis of $(\text{CO})_5\text{MnRe}(\text{CO})_3$ (σ, σ -R-DAB) in rare-gas matrices at 10 K.^{25,26} However, CO is released then, and the frequencies of the $(\text{CO})_3\text{MnRe}(\text{CO})_3$ ($\sigma, \sigma, \eta^2, \eta^2$ -R-DAB) complex formed do not agree with those of this photoproduct obtained upon photolysis in 2-MeTHF at 133 K. In view of this, only a changeover from σ, σ -chelate bonding in the parent compound into σ, σ -bridging or σ -monodentate bonding has to be taken into account. From these, only the σ -monodentate bonding is of interest here since the concentrations are too low to cause dimerization of the complex. Such a σ -monodentate-bonded α -diimine ligand occurs in, e.g., $\text{Cr}(\text{CO})_5(\text{R-DAB})$,²⁷ $\text{M}(\text{CO})_5(4,4'\text{-dialkyl-2,2'-bipyridine})$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$),²⁸ and $\text{MCl}_2(\text{PPh}_3)(t\text{-Bu-DAB})$ ($\text{M} = \text{Pd}, \text{Pt}$).²⁹ It has also been postulated as an intermediate in several thermal³⁰ and photochemical reactions^{23,31,32} of α -diimine complexes. Thus, irradiation of $\text{Fe}(\text{CO})_3(\text{R-DAB})$ complexes in solution at room temperature in the presence of a nucleophile results in photosubstitution of one or two carbonyls via an intermediate in which the R-DAB ligand is σ -monodentate bound.²³

The shift of the CO vibrations to lower frequency with respect to the parent compound is due to coordination of the basic 2-MeTHF ligand at the open site of the $\text{Re}(\text{CO})_3(\sigma\text{-}\alpha\text{-diimine})$ moiety of the complex.

Up to now σ -monodentate bonding has not been observed for phen. It could therefore be argued that different photoproducts are formed for the *i*-Pr-DAB and phen complexes, e.g. formation of a σ -monodentate-bonded *i*-Pr-DAB ligand and complete loss of the ligand in the case of phen, yielding $(\text{CO})_5\text{MnRe}(\text{CO})_3(2\text{-MeTHF})_2$. This explanation is however unlikely for the following reasons. First of all, the photoproducts of the R-DAB and phen complexes show the same intensity pattern in the CO stretching region with the bands at 1917 and 1937 cm^{-1} for the R-DAB and phen complexes, respectively, being the strongest in both cases. This indicates that the same kind of photoproduct is formed for both complexes. Secondly, we performed the photolysis experiment for $(\text{CO})_5\text{MnRe}(\text{CO})_3(\text{phen})$ at 133 K in the presence of $\text{P}(n\text{-Bu})_3$. This resulted in formation of the same photoproduct as observed upon photolysis in the absence of $\text{P}(n\text{-Bu})_3$. Raising the temperature to 173 K resulted in a back-reaction of the photoproduct to the parent compound, and no side products due to a reaction with $\text{P}(n\text{-Bu})_3$ were observed. Now, if the photoproduct were $(\text{CO})_5\text{MnRe}(\text{CO})_3(2\text{-MeTHF})_2$ not only would a back-reaction to the parent compound be expected but also a reaction with $\text{P}(n\text{-Bu})_3$, yielding $(\text{CO})_5\text{MnRe}(\text{CO})_3(\text{P}(n\text{-Bu})_3)_2$. The absence of this latter complex is a strong argument that the photoproduct is $(\text{CO})_5\text{MnRe}(\text{CO})_3(\sigma\text{-phen})(2\text{-MeTHF})$ and not $(\text{CO})_5\text{MnRe}(\text{CO})_3(2\text{-MeTHF})_2$.

The same photoproduct with similar, although much broader, CO frequencies is formed upon photolysis of $(\text{CO})_5\text{MnRe}$

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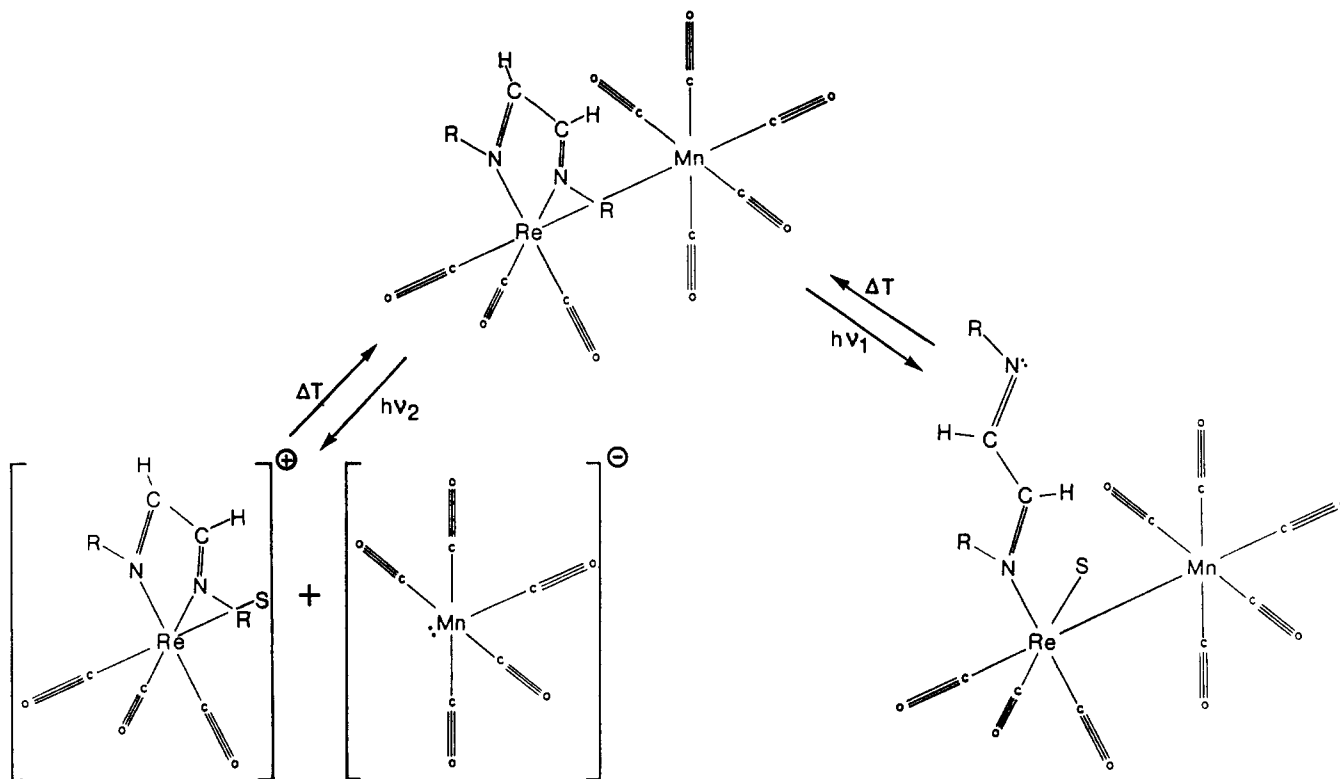


Figure 11. Photolysis of $(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$ in 2-MeTHF (S) at $T \leq 173$ K. Formation of the ions is favored when $\nu_2 > \nu_1$.

$(\text{CO})_3(i\text{-Pr-DAB})$ in a PVC film at 198 K with $\lambda = 514.5\text{-nm}$ radiation.²⁵ Since the PVC film is cast from THF, the solvent molecules, still present in the film, stabilize the photoproduct by coordination to the open site of the $\text{Re}(\text{CO})_3(\sigma\text{-}i\text{-Pr-DAB})$ moiety of the complex. The same reversible behavior as found in 2-MeTHF is observed in PVC films. When the temperature is raised to room temperature, THF loses its coordinating properties and the parent compound is re-formed. The photolysis of the $(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$ complexes is shown schematically in Figure 11.

C. The Photochemical Mechanism. It has been stated (in the Introduction) that the low-energy absorption band of these $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ complexes cannot be assigned to a transition from the metal–metal-bonding orbital (σ_b) to the lowest π^* level of the $\alpha\text{-diimine}$ ligand but instead can be assigned to a transition from a M' (d_π) orbital not involved in the metal–metal bond to π^* . This assignment was mainly based on the close similarity between the RR spectra of these complexes and those of the mononuclear $d^6 M(\text{CO})_4(\alpha\text{-diimine})$ ($M = \text{Cr}, \text{Mo}, \text{W}$)¹⁰ and $d^8 M'(\text{CO})_3(\alpha\text{-diimine})$ ($M' = \text{Fe}, \text{Ru}$)^{11,12} analogues. The electronic transition is therefore directed to the $^1d_\pi\pi^*$ state, and from this state intersystem crossing will occur to the $^3d_\pi\pi^*$ state, although in the case of $M' = \text{Re}$ the meaning of the spin character of these states is questionable. However, although the $^1d_\pi\pi^*$ state and not the $^1\sigma_b\pi^*$ state becomes occupied during the electronic transition, intersystem crossing may also occur to the $^3\sigma_b\pi^*$ state. This is shown schematically in the energy vs. distortion diagram of Figure 12. Up to now the relative energies of these triplet states are not known, and work is in progress to determine them.

From both triplet states a photochemical reaction can occur. The reaction from the $^3\sigma_b\pi^*$ state will certainly lead to cleavage of the metal–metal bond. Our results show that this splitting is homolytic and that it is the main reaction in 2-MeTHF at $T \geq 200$ K. Just as in the case of the corresponding $d^6 M(\text{CO})_4(\alpha\text{-diimine})$ ³³ and $d^8 M(\text{CO})_3(\alpha\text{-diimine})$ ²² complexes, photochemical reactions from the $^3\text{MLCT}$ ($^3d_\pi\pi^*$) state will lead to release of CO and this is in fact observed for several of the complexes under study in 2-MeTHF at 133 K.

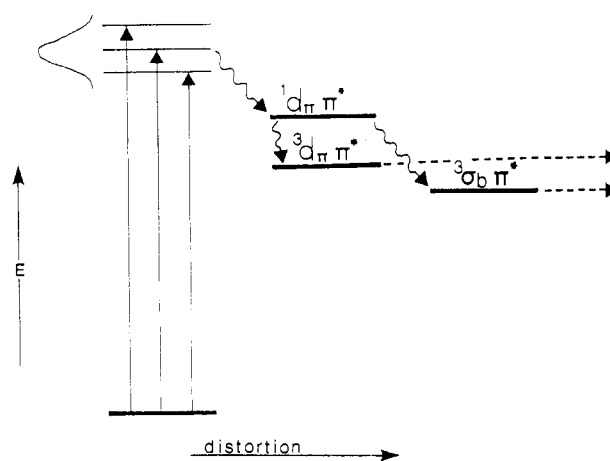


Figure 12. Energy vs. distortion diagram for $(\text{CO})_5\text{MM}'(\text{CO})_3(\alpha\text{-diimine})$ ($M, M' = \text{Mn}, \text{Re}$).

We therefore conclude that the high-temperature reaction (homolysis) occurs from the $^3\sigma_b\pi^*$ state and the low-temperature reaction (release of CO) from the $^3d_\pi\pi^*$ state. It is not yet clear whether this change of reaction is a mere temperature effect or that the increase of viscosity of the solvent plays an important role here. In the first case we deal with a $^3\sigma_b\pi^*$ state close in energy to the $^3d_\pi\pi^*$ state but only occupied at higher temperatures. This situation is similar to that observed for the complexes $[\text{Rh}(\text{NH}_3)_5(4\text{-R-py})]^{3+}$ ³⁴ and $M(\text{CO})_5(\text{L})$ ($\text{L} = 4\text{-R-py}$, pyridazine; $M = \text{Cr}, \text{W}$)³⁵ in which a ^3LF state is close in energy to a $^3\text{MLCT}$ state. It is, however, possible that the viscosity plays an important role here. This viscosity increases drastically upon cooling. The radicals formed by the homolytic splitting of the metal–metal bond cannot then diffuse through the solution, and they will react back to give the parent compound. As a result the quantum yield for the homolytic splitting decreases, which makes it possible to observe the much slower reaction from the $^3d_\pi\pi^*$ state, which is release of CO. CO can still diffuse through

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the solvent; it even diffuses in rare-gas matrices at 10 K.

The question remains as to what the mechanism is for the release of CO. In the case of the d^6 $M(\text{CO})_4(\alpha\text{-diimine})$ complexes, CO is released for complexes in which the $^3\text{MLCT}$ state is delocalized over the carbonyls in the cis position with respect to the $\alpha\text{-diimine}$ ligand.³³ As a result of this delocalization the metal-CO π back-bonding is weakened, and a CO ligand is released. This delocalization of the excited state over the cis carbonyls is reflected in a high relative intensity of $\nu_s(\text{CO})_{\text{cis}}$ in the RR spectra. In the case of the d^8 $M(\text{CO})_3(\alpha\text{-diimine})$ complexes the release of CO could not be explained with a delocalization of the $^3\text{MLCT}$ state over one or more carbonyl ligands. Instead a strong coupling model³⁶ was proposed in which the primary step in solution is the breaking of a metal-nitrogen bond with formation of an intermediate in which the $\alpha\text{-diimine}$ ligand is σ -monodentate bound.²³ A nucleophilic ligand then attacks the open site, CO is released and the σ,σ -coordination of the $\alpha\text{-diimine}$ ligand is restored again. Although the intermediate could not be identified in the case of the $M(\text{CO})_3(\alpha\text{-diimine})$ complexes, it has been observed for the $(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$ complexes. We propose the same mechanism for these complexes as for the d^8 $M(\text{CO})_3(\alpha\text{-diimine})$ ones, and this will also be the case for the corresponding $(\text{CO})_5\text{MMn}(\text{CO})_3(\alpha\text{-diimine})$ ($M = \text{Mn, Re}$) complexes in which CO is photosubstituted by 2-MeTHF. The difference in behavior between the two types of complexes is certainly due to the fact that the Re-CO bond is much stronger than the Mn-CO bond. As a result the reaction stops before CO is released in the case of the $(\text{CO})_5\text{MnRe}(\text{CO})_3(\alpha\text{-diimine})$ complexes. When these latter complexes are irradiated with higher energy ($\lambda = 350$ nm), disproportionation into the ions is observed just as in the case of the $(\text{CO})_5\text{MMn}(\text{CO})_3(\alpha\text{-diimine})$ complexes (Figure 11). This wavelength dependence of the reaction is also in agreement with the results for the d^8 $M(\text{CO})_3(\alpha\text{-diimine})$ complexes.^{23,36}

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There is a close relationship between this photochemistry and the mechanisms proposed by McCullen and Brown⁶ and Stiegman and Tyler⁷ for the disproportionation reaction of $\text{Mn}_2(\text{CO})_{10}$ in pyridine. McCullen and Brown proposed a mechanism in which electron transfer takes place from a 17-electron $\cdot\text{Mn}(\text{CO})_3\text{N}_2$ radical to $\text{Mn}_2(\text{CO})_{10}$, whereas Stiegman and Tyler proposed electron transfer from a 19-electron radical with three basic groups, $\cdot\text{Mn}(\text{CO})_3\text{N}_3$. Our experiments show that heterolysis takes place for the $(\text{CO})_5\text{MMn}(\text{CO})_2(\alpha\text{-diimine})(2\text{-MeTHF})$ complexes with three basic donor atoms at one metal fragment and not for the corresponding parent compounds $(\text{CO})_5\text{MMn}(\text{CO})_3(\alpha\text{-diimine})$. This result is in agreement with the mechanism proposed by Stiegman and Tyler.

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Registry No. $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{bpy}')$, 97570-64-4; $(\text{CO})_5\text{MnMn}(\text{CO})_3(\text{phen})$, 60166-19-0; $(\text{CO})_5\text{MnMn}(\text{CO})_3(i\text{-Pr-DAB})$, 71603-98-0; $(\text{CO})_5\text{MnMn}(\text{CO})_3(p\text{-Tol-DAB})$, 71604-00-7; $(\text{CO})_5\text{MnMn}(\text{CO})_3(p\text{-Tol-PyCa})$, 97591-94-1; $(\text{CO})_5\text{ReMn}(\text{CO})_3(\text{phen})$, 61993-44-0; $(\text{CO})_5\text{ReMn}(\text{CO})_3(i\text{-Pr-DAB})$, 97570-65-5; $(\text{CO})_5\text{ReMn}(\text{CO})_3(p\text{-Tol-DAB})$, 97570-66-6; $(\text{CO})_5\text{MnMn}(\text{CO})_2(\text{bpy}')(2\text{-MeTHF})$, 97570-67-7; $(\text{CO})_5\text{MnMn}(\text{CO})_2(\text{phen})(2\text{-MeTHF})$, 97570-68-8; $(\text{CO})_5\text{MnMn}(\text{CO})_2(\text{phen})(P\text{-Bu})_3$, 97570-69-9; $(\text{CO})_5\text{MnMn}(\text{CO})_2(i\text{-Pr-DAB})(2\text{-MeTHF})$, 97570-70-2; $(\text{CO})_5\text{MnMn}(\text{CO})_2(p\text{-Tol-PyCa})(2\text{-MeTHF})$, 97591-95-2; $(\text{CO})_5\text{ReMn}(\text{CO})_2(\text{phen})(2\text{-MeTHF})$, 97570-71-3; $(\text{CO})_5\text{ReMn}(\text{CO})_2(\text{phen})(P(n\text{-Bu})_3)$, 97570-72-4; $(\text{CO})_5\text{ReMn}(\text{CO})_2(i\text{-Pr-DAB})(2\text{-MeTHF})$, 97570-73-5; $(\text{CO})_5\text{ReMn}(\text{CO})_2(i\text{-Pr-DAB})(P(n\text{-Bu})_3)$, 97570-74-6; $(\text{CO})_5\text{ReMn}(\text{CO})_2(p\text{-Tol-DAB})(2\text{-MeTHF})$, 97570-75-7; $\text{Mn}_2(\text{CO})_6(\text{bpy}')_2$, 97570-76-8; $\text{Mn}_2(\text{CO})_6(\text{phen})_2$, 97570-77-9; $\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})_2$, 90885-36-2; $\text{Mn}_2(\text{CO})_6(i\text{-Pr-DAB})(2\text{-MeTHF})_2$, 97570-78-0; $\text{Mn}_2(\text{CO})_6(p\text{-Tol-PyCa})(2\text{-MeTHF})_2$, 97570-79-1; $\text{Re}_2(\text{CO})_6(p\text{-Tol-DAB})(2\text{-MeTHF})_2$, 97570-80-4; $\text{Mn}_2(\text{CO})_{10}$, 10170-69-1.

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Characterization and Reaction Kinetics of Intermediates Produced in the Photolysis of $M(\text{CO})_6$ ($M = \text{Cr, Mo, W}$) Solutions Containing a 1,4-Diazabutadiene Ligand

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Electronic absorption data have been recorded on a microprocessor-controlled diode-array spectrophotometer at short time intervals following the photolysis of $M(\text{CO})_6$ ($M = \text{Cr, Mo, W}$) in benzene containing 1,4-di-*tert*-butyl-1,4-diazabutadiene (1,4-dab). These spectra illustrate rapid formation of a primary reaction intermediate that is assigned to be a solvent impurity species, $M(\text{CO})_5(\text{impurity})$. This species is then scavenged by ligand to form monodentate $M(\text{CO})_5(1,4\text{-dab})$. UV-visible difference spectra of these reaction intermediates are reported. Rates of formation of $M(\text{CO})_5(1,4\text{-dab})$ have been measured as a function of temperature and ligand concentration. The data imply that $M(\text{CO})_5(\text{impurity})$ is converted to $M(\text{CO})_5(1,4\text{-dab})$ via a dissociative mechanism. Monodentate $M(\text{CO})_5(1,4\text{-dab})$ subsequently extrudes CO by a relatively slow first-order kinetic process to form $M(\text{CO})_4(1,4\text{-dab})$. Rates of chelation for L (ligand) = 1,4-dab are compared with literature values for L = 1,10-phenanthroline and 2,2'-bipyridine and are discussed in terms of the stereochemistry of L when it is coordinated to a metal center in a monodentate fashion.

Introduction

Although a great deal is now known about ligand substitution chemistry of low-valent transition-metal centers, our knowledge of the identity, structure, and reactivity of their reaction intermediates is still very limited. This knowledge is important to a further development of organometallic chemistry. Information about the nature of ligand substitution events at low-valent transition-metal centers is useful in systematic organometallic

synthesis and in the design of homogeneous catalytic processes. In many of these processes unsaturated species are thought to be involved as reaction intermediates.¹ However, direct spectral evidence for these reaction intermediates and quantitative mea-

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