Organometallics 1994, *13*, 2641-2650

The Remarkable Photochemistry of *fac*-$XMn(CO)_3$(α-diimine) (X = Halide): Formation of $Mn_2(CO)_6(\alpha\text{-diimine})_2$ via the *mer* Isomer and Photocatalytic Substitution of X^- in the Presence of PR_3

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Received November 8, 1993[●]

This article describes the remarkable photochemistry of complexes *fac*-$XMn(CO)_3$(α-diimine) (X = Cl, Br, I) upon irradiation into their lowest-energy CT band. The primary photoprocess is loss of CO, as was established by flash photolysis and low-temperature IR spectroscopy. The CO-loss product reacted thermally and photochemically to give *mer*-$XMn(CO)_3$(α-diimine), which in turn transformed thermally into the *fac* isomer at temperatures above 213 K. Irradiation of *mer*-$XMn(CO)_3$(α-diimine) resulted in the formation of the 16-electron radical complexes $Mn^+(CO)_3(\alpha\text{-diimine}^{\bullet-})$, which were identified at room temperature by ESR spectroscopy and which dimerized to give $Mn_2(CO)_6(\alpha\text{-diimine})_2$ for α-diimine = bpy. At low temperatures these radical complexes formed rather stable adducts $Mn^+(CO)_3(\alpha\text{-diimine}^{\bullet-})(PR_3)$ with PR_3 (R = nBu, OMe). At room temperature these adducts initiated the catalytic substitution of X^- by PR_3 in the starting complex *fac*-$XMn(CO)_3$(α-diimine). The primary photoprocess of *fac*-$XMn(CO)_3$(α-diimine) (loss of CO) most likely occurs from the lowest LF state. Contrary to this, irradiation of *mer*-$XMn(CO)_3$(α-diimine) gives rise to homolysis of the Mn–X bond. This remarkable difference in photochemical behavior of the *fac* and *mer* isomers is discussed.

Introduction

Complexes containing an α-diimine ligand such as 2,2′-bipyridine (bpy) are characterized by intense absorption bands in the visible or near ultraviolet. For complexes of low valent transition metals these bands belong to metal to ligand charge transfer (MLCT) transitions to the lowest π^* orbital of the α-diimine ligand.[1] Such complexes have recently received wide interest, since they may act as efficient photosensitizers for intra- and intermolecular energy and electron transfer processes. Well-known examples are $Ru(bpy)_3^{2+}$ and its derivatives[2] and $[LRe(CO)_3(bpy)]^{0/+}$ (L = halide, organic donor/acceptor, nitrogen donor).[3] Only for a few complexes are the MLCT states themselves reactive, giving rise to cleavage of a metal–ligand bond. Examples are $M(CO)_4$(α-diimine) (M = Cr, Mo, W),[4] $M'(CO)_3$(α-diimine) (M′ = Fe, Ru),[5] and $Ni(CO)_2$(α-diimine).[6] For most complexes, however, the photolability, if any, is due to the presence of a reactive LF state close to the lowest MLCT state. The photosubstitution quantum yields of complexes such as $Ru(NH_3)_5(pyX)^{2+}$,[7] $CpRe(CO)_2(pyX)$,[8] $Fe(CN)_5(pyX)^{3-}$,[9] and $W(CO)_5(pyX)$[10] (see also Ford[11]) then depend on the energy gap between these states.

A deviating behavior has been observed for the complexes $L_nMM'(CO)_3$(α-diimine) (L_nM = $(CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, $Cp(CO)_2Fe$, Ph_3Sn; M′ = Mn,Re).[1d,12] In addition to loss of CO for the complexes with M′ = Mn, these

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[●] Abstract published in *Advance ACS Abstracts*, April 15, 1994.

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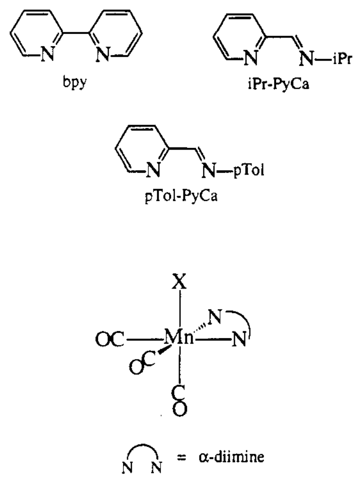

Figure 1. Structures of the α-diimine ligands and the general molecular geometry of the complexes *fac*-XMn(CO)$_3$(α-diimine).

compounds undergo homolysis of the metal–metal bond upon irradiation into their low-lying MLCT transitions. We have studied in detail the photochemistry of these systems and have recently observed similar homolysis reactions for the corresponding complexes *fac*-(R)Re(CO)$_3$(α-diimine) (R = Me, Et, benzyl).[13] The M′(CO)$_3$(α-diimine) radicals formed show interesting chemical and catalytic properties which have been studied in detail.[14] For M′ = Mn the radicals dimerize to give Mn$_2$(CO)$_6$(α-diimine)$_2$, while they initiate electron transfer chain reactions in the presence of a basic phosphine such as P(nBu)$_3$.

Quite recently, we have made the remarkable observation that the radical formation is not restricted to the above-mentioned complexes, but even occurs for the simple complexes *fac*-XMn(CO)$_3$(α-diimine) (X = halide). Irradiation of such a complex at room temperature gave rise to the formation of Mn$_2$(CO)$_6$(α-diimine)$_2$ via its *mer* isomeric form, according to reaction 1. In this article we

$$fac\text{-XMn(CO)}_3(\alpha\text{-diimine}) \xrightarrow{h\nu} mer\text{-XMn(CO)}_3(\alpha\text{-diimine}) \xrightarrow{h\nu} {}^1/_2\text{Mn}_2\text{(CO)}_6(\alpha\text{-diimine})_2 \quad (1)$$

present the results of a detailed investigation of the mechanism of this novel reaction and of the catalytic reactions of these *fac*-XMn(CO)$_3$(α-diimine) complexes in the presence of a phosphine ligand. The α-diimine ligands used in this study are 2,2′-bipyridine (bpy), pyridine-2-carbaldehyde *N*-isopropylimine (iPrPyCa) and pyridine-2-carbaldehyde *N*-*p*-tolylimine (pTolPyCa). The structures of these ligands and of the *fac*-XMn(CO)$_3$(α-diimine) complexes are schematically depicted in Figure 1.

Experimental Section

Materials and Preparations. All solvents were distilled from Na under a nitrogen atmosphere. P(nBu)$_3$ and P(OMe)$_3$ were distilled under vacuum from CaH$_2$. Bu$_4$NPF$_6$ was dried in vacuo overnight at 80 °C. AgOtf (Otf$^-$ = CF$_3$SO$_3^-$), bpy, and tBuNO were obtained commercially and used without further purification.

iPrPyCa and pTolPyCa were synthesized according to literature procedures.[15] The complexes *fac*-XMn(CO)$_3$(α-diimine) (X = Cl, Br, I; α-diimine = bpy, iPrPyCa, pTolPyCa) were prepared as previously described,[16] with the modification that the syntheses were performed by refluxing in hexane for 3 h under exclusion of light. The complexes were purified by column chromatography (Silica 60, activated by heating overnight under vacuum at 150 °C) in the dark with gradient elution of *n*-hexane–THF. The complexes Mn(CO)$_3$(α-diimine)$^+$Otf$^-$ were prepared as previously described[17] under exclusion of light. All spectroscopic samples were prepared by standard inert gas techniques.

Spectroscopic Measurements and Photochemistry. IR spectra were measured on a Nicolet 7199B FTIR interferometer provided with a liquid-nitrogen cooled MCT detector (32 scans, resolution 1.0 cm^{-1}). Electronic absorption spectra were recorded on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer, equipped with a 3600 data station. Low-temperature IR and UV/vis measurements were performed using an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 100 and AMX 300 spectrometers. ESR spectra were recorded on a Varian E6 spectrometer with 100-kHz modulation.

Transient absorption spectra were obtained using a Spectra Physics GCR-3 Nd:YAG laser as the excitation source. The 1064-nm fundamental yielded 5-ns pulses at a maximum of 10 pulses/s. The required 532-nm pulse was obtained by frequency doubling using KDP crystals. A right-angle optical system was used for the excitation-analyzing set up. A 450-W high pressure xenon lamp was used as the probe light. In order to enhance its brightness during the observation time gate of the detector, the xenon lamp was pulsed with a Müller Elektronik MSP 05 pulser. The probe light, after passing through the sample cell, was dispersed via a spectrograph (EG & G Model 1234) equipped with a 150 g/mm grating and a 250-μm slit, resulting in a 6-nm spectral resolution. The data collection system consisted of an EG & G Model 1460 OMA-III console provided with a 1302 fast pulser (gate width: 5 ns) and an EG & G Model 1421 gated diode array detector.

Spectroelectrochemical reductions were performed in situ in an IR spectroelectrochemical OTTLE (optically transparent thin layer electrochemical) cell,[18] equipped with a Pt-minigrid working electrode (32 wires/cm). For IR OTTLE measurements either NaCl or CaF$_2$ windows and for UV/vis OTTLE measurements CaF$_2$ or quartz windows were utilized. The working electrode surroundings were masked carefully to avoid the spectral beam passing through the nonelectrolyzed solution. Controlled-potential electrolyses within the OTTLE cell were carried out by using a PAR Model 174 potentiostat. For all spectroelectrochemical samples the concentrations of *fac*-XMn(CO)$_3$(α-diimine) and Bu$_4$NPF$_6$ were 10^{-2} and 3×10^{-1} M, respectively.

For irradiation of the spectroscopic samples use was made of a Spectra Physics 2025 Ar$^+$ laser, a tunable CR 490 dye laser with Rhodamine 6G as dye, an Oriel 100-W high pressure mercury lamp and a Philips HPK 125-W high pressure mercury lamp provided with the appropriate interference filter. For all photochemical samples the concentration of *fac*-XMn(CO)$_3$(α-diimine) was 10^{-2} M.

Force Field Calculations. Since all complexes contain carbonyl ligands which absorb very strongly in the infrared, structures may be analyzed using Cotton and Kraihanzel energy

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Table 1. CO-Stretching Frequencies and Maxima of the Low-Energy Absorption Bands of the Complexes *fac*-XMn(CO)$_3$(α-diimine) in THF at Room Temperature

complex	ν(CO) (cm^{-1})	λ_{max} (nm)
fac-ClMn(CO)$_3$(bpy)	2025 (s), 1936 (m), 1913 (m)	420, 360
fac-BrMn(CO)$_3$(bpy)	2023 (s), 1935 (m), 1914 (m)	430, 375
fac-IMn(CO)$_3$(bpy)	2019 (s), 1933 (m), 1916 (m)	445, 385
fac-BrMn(CO)$_3$(iPrPyCa)	2023 (s), 1935 (m), 1915 (m)	455, 360
fac-BrMn(CO)$_3$(pTolPyCa)	2025 (s), 1942 (m), 1917 (m)	475, 325

factored force fields.[19] This simply means that force fields were calculated only for the CO vibrations and all coupling was neglected, except that between CO ligands. Anharmonicity was also neglected. The force field determination has been further simplified by an elegant empirical method by Timney.[20] Timney's ligand effect constant method, as it has come to be known, allows us to predict force constants and corresponding CO vibrations using two general equations:

$$1.\ k_{\mathrm{CO}} = k_d + \sum \epsilon_{\mathrm{L}}^{\theta}$$

$$2.\ k_{12} = A - B[(k_1 + k_2)/2]$$

where k_d is the force constant of the fragment MCO and depends on the number, d, of electrons at the metal center. $\Sigma\epsilon_L^\theta$ are the ligand effect constants (LECs) which have been evaluated for numerous ligands in the main geometries: octahedral, tetrahedral, and trigonal bipyramidal. A and B are constants depending on the angle between the two interacting CO groups. All the LECs can be found in the original paper.

This method has proved invaluable in cases such as *fac*-BrMn(CO)$_3$(bpy), for which there are four force constants (k_{ax}, k_{eq}, k_{axeq}, and k_{eqeq}) but only three observed frequencies. Isotopic data are very difficult to obtain for these types of complexes since they are only soluble in polar solvents in which only broad peaks are seen, masking all possible ^{13}C and ^{18}O satellites.

Results and Discussion

Spectroscopic Properties. Table 1 presents the CO-stretching frequencies and the maxima of the low-energy absorption bands of the complexes which, according to previous X-ray structure determinations[21] and ^{1}H and ^{13}C NMR measurements,[16] exist in the facial isomeric form both in the solid and in solution. The three CO bands belong to the three IR active modes (2a′ + a″) of the complexes having C_s symmetry. The lowest-energy electronic absorption band of these complexes is intense and solvatochromic, and its position shifts to a longer wavelength when the π^* orbital decreases in energy going from bpy to RPyCa (R = iPr, pTol). These observations point to an assignment of this band to MLCT transitions, just as for other transition metal α-diimine complexes.[22,23] There is, however, evidence from MO calculations and resonance Raman (rR) spectra that the metal orbitals from which these MLCT transitions originate, strongly interact with the halide p$_\pi$ orbitals. Thus, MO calculations on *fac*-XMn(CO)$_3$(bpy) (X = Cl, I)[21d] and *fac*-BrRe(CO)$_3$(H$_2$DTO) (DTO = dithiooxamide)[24] have shown that the HOMO of these complexes has strong metal–halide antibonding character. Moreover, a recent rR study of *fac*-BrRe(CO)$_3$(pTolDAB) revealed that excitation into the lowest-energy absorption band of this complex is accompanied with a rather strong rR effect for ν(ReBr).[25]

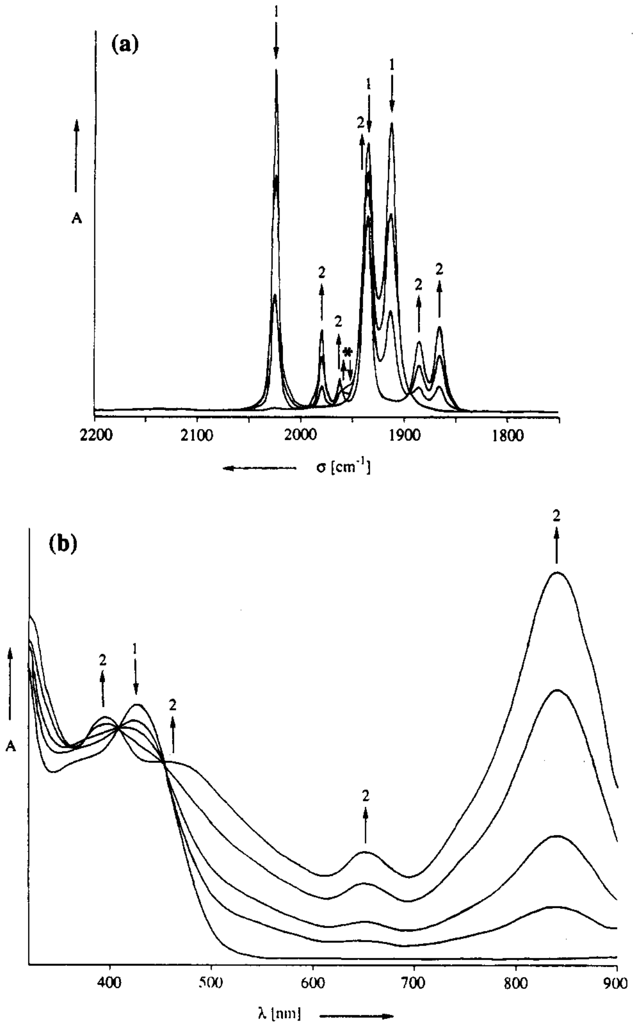

Figure 2. IR (CO-stretching region) (a) and UV/vis (b) spectral changes during the photochemical reaction of *fac*-BrMn(CO)$_3$(bpy) in THF at room temperature: 1 = *fac*-BrMn(CO)$_3$(bpy), 2 = Mn$_2$(CO)$_6$(bpy)$_2$, * = *mer*-BrMn(CO)$_3$(bpy).

Photolysis at Room Temperature. Irradiation of a solution of *fac*-XMn(CO)$_3$(bpy) (X = Cl, Br, I) in THF into the lowest-energy absorption band gave rise to the formation of a product with CO-stretching vibrations at 1980 (m), 1962 (w), 1936 (s), 1886 (m), and 1867 (m) cm^{-1} (Figure 2a) and UV/vis bands at 840, 755 (sh), 655, 460, and 400 nm (Figure 2b). On the basis of previous results[14a,17] these bands are assigned to the dimer Mn$_2$(CO)$_6$(bpy)$_2$. During this reaction an intermediate product was formed in a low concentration with CO-stretching vibrations at 2043 (vw), 1948 (s), and 1903 (m) cm^{-1} (Figure 3), and a lowest-energy absorption band at 510 nm (Figure 4). A similar intensity pattern of the ν(CO) IR bands has been reported for the complexes *mer-trans*-L$_2$XMn(CO)$_3$ (L = PR$_3$, AsR$_3$)[26a–d], *mer*-Mn(CO)$_3$L(PR$_3$)$^+$ClO$_4^-$ (L =

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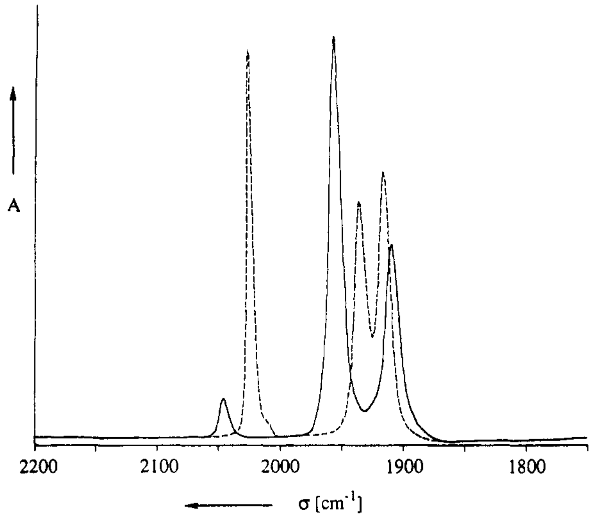

Figure 3. IR (CO-stretching region) spectra of *fac*- (- - -) and *mer*-BrMn(CO)$_3$(bpy) (—) in THF. (Since *mer*-BrMn(CO)$_3$(bpy) is an intermediate in the photochemical reaction, the spectrum could only be obtained by subtraction.)

Ph$_2$P(CH$_2$)$_n$PPh$_2$, n = 1 (dppm) or n = 2 (dppe)),[26e,f] and *mer*-XMn(CO)$_3$(dppm).[26g] A characteristic property of these complexes is the very low IR intensity of the highest frequency band. We therefore assign the CO bands at 2043 (vw), 1948 (s), and 1903 (m) cm^{-1} to *mer*-XMn(CO)$_3$(bpy). In order to confirm this assignment, force field calculations were carried out on the *mer*-BrMn(CO)$_3$(bpy) complex using the frequencies of the *fac* isomer as reference data. The empirical equations for *fac*-BrMn(CO)$_3$(bpy) are given below and are based on previous calculations on the Re analogue.[27]

$$k_{ax} = k_6 + 2\epsilon_{CO}{}^{cis} + 2\epsilon_{bpy}{}^{cis} + \epsilon_{Br}{}^{trans} = 1510\ \mathrm{N\ m^{-1}}$$

$$k_{eq} = k_6 + 2\epsilon_{CO}{}^{cis} + \epsilon_{bpy}{}^{cis} + \epsilon_{bpy}{}^{trans} + \epsilon_{Br}{}^{cis} = 1560\ \mathrm{N\ m^{-1}}$$

$$k_{axeq} = 206 - 0.0956[(k_{ax} + k_{eq})/2] = 50\ \mathrm{N\ m^{-1}}$$

$$k_{eqeq} = 206 - 0.0956(k_{eq}) = 55\ \mathrm{N\ m^{-1}}$$

The isomerization process should leave k_{eq} and k_{axeq} unchanged. So reevaluating k_{ax} and assuming that $k_{axax} \sim 2k_{axeq}$ yields a new force field, which agrees with the frequencies involved and produces normal coordinates which correspond to the intensity pattern of the observed CO-stretching vibrations.

$$k_{ax}' = k_6 + \epsilon_{CO}{}^{cis} + \epsilon_{CO}{}^{trans} + 2\epsilon_{bpy}{}^{cis} + \epsilon_{Br}{}^{cis} = 1562\ \mathrm{N\ m^{-1}}$$

The frequencies derived from these calculations perfectly match the experimental data (Table 2).

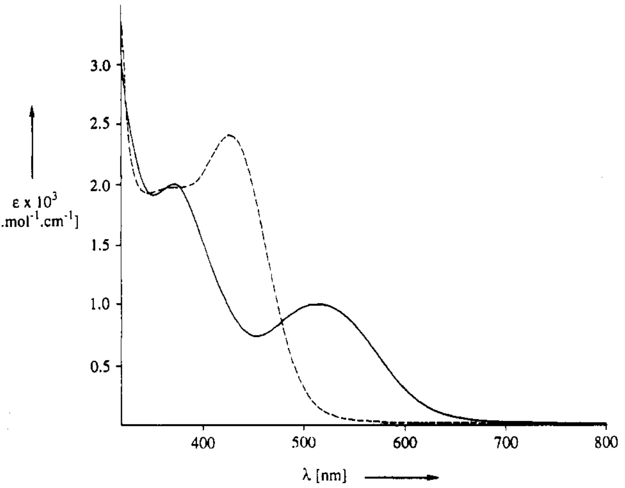

Figure 4. UV/vis spectra of *fac*- (- - -) and *mer*-BrMn(CO)$_3$(bpy) (—) in THF. (Since *mer*-BrMn(CO)$_3$(bpy) is an intermediate in the photochemical reaction, the spectrum could only be obtained by subtraction.)

Table 2. Observed and Calculated CO-Stretching Frequencies and Force Field of *fac*- and *mer*-BrMn(CO)$_3$(bpy)

isomer	ν(CO)$_{obs}$ (cm^{-1})	ν(CO)$_{calc}$ (cm^{-1})	symmetry	force field (N m^{-1})
fac	2023 (s)	2021	a′	k_{ax} = 1510
	1935 (m)	1930	a″	k_{eq} = 1560
	1914 (m)	1910	a′	k_{axeq} = 50
				k_{eqeq} = 55
mer	2043 (vw)	2046	a′	k_{ax} = 1562
	1948 (s)	1943	a′	k_{eq} = 1555
	1903 (m)	1903	a″	k_{axeq} = 45
				k_{axax} = 100

When the reaction was carried out in toluene the same products were formed. However, the starting complexes partly photodecomposed in this solvent and the overall yield of the reaction was therefore much lower.

The photochemical reaction of *fac*-BrMn(CO)$_3$(bpy) was also performed in THF-d_8 in an NMR tube and followed by NMR spectroscopy, in order to obtain ^{1}H data of *mer*-BrMn(CO)$_3$(bpy). The reaction was performed inside a Bruker CIDNP 300-MHz ^{1}H probe, equipped with a glass fiber (o.d. = 0.8 cm). An Oriel AG 150-W high pressure xenon lamp provided with a water cooling and a 420-nm cutoff filter was used as the irradiation source. Upon irradiation at 233 K the bands of the starting complex decreased and broadened, indicating the formation of paramagnetic species, most probably by photodecomposition of the *mer* product (see hereafter). Due to this broadening new product bands could not be observed. Attempts to isolate any of the complexes *mer*-XMn(CO)$_3$(α-diimine) (α-diimine = bpy, iPrPyCa, pTolPyCa) also failed due to their thermal instability above 213 K.

Formation of Mn$_2$(CO)$_6$(bpy)$_2$ normally takes place by dimerization of Mn$^+$(CO)$_3$(bpy$^{•-}$) radicals.[14a,17] In order to prove that these radicals were indeed formed, the reaction was also followed by ESR spectroscopy. Irradiation of a solution of *fac*-BrMn(CO)$_3$(bpy) in THF in the presence of the spin-trapping agent tBuNO resulted in the formation of the fairly stable radical (tBuNO$^{•-}$)(Mn$^+$(CO)$_3$(bpy)) (a_N(NO) = 14.32 G, a_{Mn} = 6.53 G).[28] The Mn$^+$(CO)$_3$(bpy$^{•-}$) radical, with the unpaired electron residing in the lowest π* orbital of bpy,[28] was too

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[26] (a) Angelici, R. J.; Basolo, F.; Poë, A. J. *J. Am. Chem. Soc.* **1963**, *85*, 2215. (b) Reimann, R. H.; Singleton, E. *J. Am. Chem. Soc., Dalton Trans.* **1973**, 841. (c) Wuyts, L. F.; van der Kelen, G. P. *Inorg. Chim. Acta* **1977**, *23*, 19. (d) Bond, A. M.; Colton, R.; McDonald, M. E. *Inorg. Chem.* **1978**, *17*, 2842. (e) Bombin, F.; Carriedo, G. A.; Miguel, J. A.; Riera, V. *J. Am. Chem. Soc., Dalton Trans.* **1981**, 2049. (f) Carriedo, G. A.; Riera, V. *J. Organomet. Chem.* **1981**, *205*, 371. (g) Bond, A. M.; Colton, R.; McCormick, M. J. *Inorg. Chem.* **1977**, *16*, 155.

[27] (a) Christensen, P.; Hamnett, A.; Muir, A. V. G.; Timney, J. A. *J. Chem. Soc., Dalton Trans.* **1992**, 1455. (b) Morrison, S. L.; Timney, J. A.; Turner, J. J. Presented at CONCOORD XXII Paris, May 1992.

[28] Andréa, R. R.; de Lange, W. G. J.; van der Graaf, T.; Rijkhoff, M.; Stufkens, D. J.; Oskam, A. *Organometallics* **1988**, *7*, 1100.

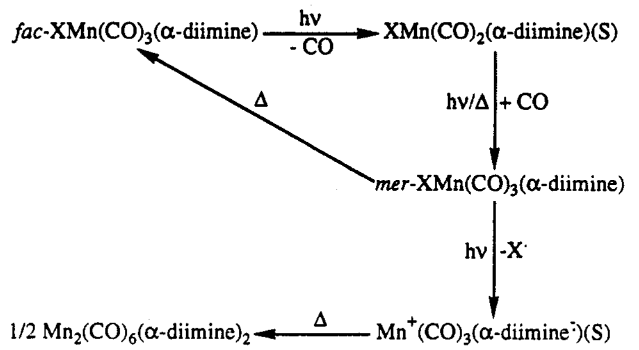
short-lived at room temperature to be detected without using a spin-trapping agent.

Although irradiation of a solution of *fac*-XMn(CO)$_3$(RPyCa) in THF (R = iPr, pTol) gave rise to the same photoreaction as for the bpy complex, almost no dimer was formed in this case. As can be seen from the low-temperature data, to be discussed hereafter, this is mainly due to the fact that the radical complexes of these RPyCa ligands are very unstable and easily decompose before they can dimerize.

So, irradiation of *fac*-XMn(CO)$_3$(bpy) leads to the formation of Mn$_2$(CO)$_6$(bpy)$_2$ with the complex *mer*-XMn(CO)$_3$(bpy) and the radical Mn$^+$(CO)$_3$(bpy$^{\bullet-}$) as intermediates. On the other hand, the related complexes *fac*-Ph$_3$SnMn(CO)$_3$(α-diimine)[29] and *fac*-(CO)$_5$ReMn(CO)$_3$(α-diimine)[17,30] lose CO upon irradiation into their lowest MLCT band. In order to find out if a similar CO-loss reaction is the primary photoprocess of this *fac* to *mer* isomerization, a nanosecond flash photolysis experiment was performed on a solution of *fac*-BrMn(CO)$_3$(iPrPyCa) in THF. The solution was irradiated with the 532-nm line of a Nd:YAG laser at the long-wavelength side of the lowest-energy absorption band of the complex. All spectra, taken at time delays from 10 ns to 4 μs, showed the presence of a transient with an absorption band at 710 nm which did not decrease in intensity within this time domain. On the basis of the results of low-temperature IR experiments (vide infra) this band is assigned to the CO-loss product BrMn(CO)$_2$(iPrPyCa)(THF). In the case of toluene this primary photoproduct will not be stabilized by the solvent molecule and will therefore partly decompose before the secondary reaction to give the *mer* isomer. This explains the low yield of the reaction in toluene. Already for the reaction in THF the primary photoproduct BrMn(CO)$_2$(iPrPyCa)(THF) appeared to be too unstable, thermally and photochemically (vide infra), to be observed as an intermediate of the *fac* to *mer* isomerization upon CW irradiation. Contrary to this, the corresponding pyridine-substituted complex BrMn(CO)$_2$(pTolPyCa)(pyridine) (ν(CO): 1938 (s), 1862 (s) cm^{-1}) was formed as a stable complex upon irradiation of *fac*-BrMn(CO)$_3$(pTolPyCa) in neat pyridine. The formation of this product is further proof for the occurrence of a CO-loss reaction as a primary photoprocess.

The above results, and the low-temperature data to be discussed hereafter, show that the complexes *fac*-XMn(CO)$_3$(α-diimine) react by irradiation into their lowest-energy absorption band according to Scheme 1. From these experiments it cannot, however, be established whether an equatorial or axial CO ligand is substituted in the first step of the reaction, how XMn(CO)$_2$(α-diimine)(S) (S = solvent) is converted into *mer*-XMn(CO)$_3$(α-diimine), and how *mer*-XMn(CO)$_3$(α-diimine) reacts to give Mn$_2$(CO)$_6$(α-diimine)$_2$. In order to answer these questions the photoreaction was also studied at low temperatures, in both the absence and presence of PR$_3$.

Scheme 1



Photolysis at $T \leq 183$ K in the Absence and Presence of PR$_3$. Irradiation of a solution of *fac*-BrMn(CO)$_3$(α-diimine) in 2-MeTHF at 135 K gave rise to subsequent formation of the intermediates and final product of Scheme 1. The IR and UV/vis data of these products are presented in Table 3. With the exception of the last step, all reactions involved in the conversion of the parent compound appeared to be photochemical at this low temperature. The first reaction might in principle cause the substitution of either an equatorial or axial CO ligand, leading to the formation of four possible isomers of BrMn(CO)$_2$(α-diimine)(2-MeTHF). According to the IR spectra, only one isomer had been formed with two CO bands at 1921–1926 (vs) and 1842–1857 (m) cm^{-1}. The observation of a very strong highest frequency band excludes the formation of the *trans,cis* isomer, with two carbonyls *trans* to each other in axial positions and the Br$^-$ and 2-MeTHF ligands *cis* to each other within the equatorial plane. However, since the other three possible isomers, one having the *cis,trans* conformation, the other two being *cis,cis* isomers, may only slightly differ in their CO-stretching frequencies, the molecular structure of the product cannot directly be derived from the IR data. In order to establish which isomer had in fact been formed, the reaction of *fac*-BrMn(CO)$_3$(iPrPyCa) in 2-MeTHF at 135 K was also performed in the presence of excess P(OMe)$_3$ (1:50). Irradiation of this solution caused the formation of the solvent-substituted bicarbonyl complex BrMn(CO)$_2$(iPrPyCa)(2-MeTHF). By raising the temperature of the solution to 170 K the solvent molecule was replaced by P(OMe)$_3$, as evidenced by the shift of the CO-stretching frequencies from 1923 (vs) and 1846 (m) cm^{-1} to 1948 (s) and 1864 (s) cm^{-1}, respectively, and of the lowest-energy absorption band from 700 to 610 nm. An analogous P(OMe)$_3$-substituted complex BrMn(CO)$_2$(iPrPyCa)(P(OMe)$_3$ was prepared by refluxing *fac*-BrMn(CO)$_3$(iPrPyCa) and an excess P(OMe)$_3$ in THF. In this reaction either an axial or an equatorial CO ligand may be substituted by P(OMe)$_3$, leading to the formation of different isomers. However, only one product was formed. The CO-stretching frequencies (1945 (s) and 1875 (s) cm^{-1}) as well as the lowest-energy absorption band (λ_{max} = 495 nm) of this product, which could also be formed by reaction 6 (vide infra), differed from those of the above photosubstitution product prepared at 170 K. In order to determine the structures of these thermally and photochemically formed isomers, the product of the reflux reaction was characterized by ^{13}C NMR spectroscopy. The spectrum of *fac*-BrMn(CO)$_3$(iPrPyCa) showed three ^{13}CO resonances (225.19, 224.57, and 221.70 ppm), whereas only two such resonances (226.57 and 225.99 ppm) were observed for the thermally synthesized BrMn(CO)$_2$(iPrPyCa)(P(OMe)$_3$) complex. On the basis of recent results of Garcia Alonso et al. for the

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[29] Andréa, R. R.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1989**, *28*, 318.

[30] (a) Kokkes, M. W.; Stufkens, D. J.; Oskam, A. *Inorg. Chem.* **1985**, *24*, 2934. (b) van der Graaf, T.; Bal Reddy, K.; van Eldik, R.; Langford, C. H.; Rossenaar, B. D.; Stufkens, D. J.; Vlcek, A., Jr. To be published.

Table 3. CO-Stretching Frequencies and Maxima of the Lowest-Energy Absorption Bands of the Products Formed upon Photolysis of *fac*-$BrMn(CO)_3$(α-diimine) in 2-MeTHF at 135 K, unless Stated Otherwise

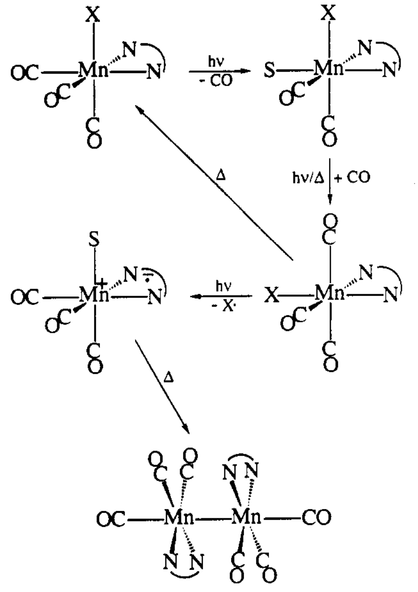
complex	ν(CO) (cm^{-1})	λ_{max} (nm)
$BrMn(CO)_2$(bpy)(2-MeTHF)	1921 (vs), 1842 (m)	630
$BrMn(CO)_2$(iPrPyCa)(2-MeTHF)	1923 (vs), 1846 (m)	700
$BrMn(CO)_2$pTolPyCa)(2-MeTHF)	1926 (vs), 1857 (m)	740
mer-$BrMn(CO)_3$(bpy)	2043 (vw), 1948 (vs), 1903 (m)	510, 375
mer-$BrMn(CO)_3$(iPrPyCa)	2044 (vw), 1951 (vs), 1905 (m)	500, 395
mer-$BrMn(CO)_3$(pTolPyCa)	2042 (vw), 1952 (vs), 1916 (m)	490, 385
$[Mn(CO)_3(bpy)]^-$	1917 (s), 1823 (m), 1815 (sh)	560
$[Mn(CO)_3(iPrPyCa)]^-$	1921 (s), 1819 (m), 1813 (sh)	530
$[Mn(CO)_3(pTolPyCa)]^-$	1924 (s), 1842 (m)	540
$Mn_2(CO)_6(bpy)_2$[a]	1980 (m), 1963 (w), 1936 (vs) 1886 (m), 1866 (m)	840, 740 (sh) 650, 455, 395
$Mn_2(CO)_6(iPrPyCa)_2$[a]	1990 (m), 1972 (w), 1941 (vs) 1894 (m), 1974 (m)	*b*
$Mn^+(CO)_3(bpy^{\bullet-})(P(nBu)_3)$	2012 (s), 1923 (s), 1891 (s)	525, 490
$Mn^+(CO)_3(bpy^{\bullet-})(P(OMe)_3)$	2024 (s), 1942 (s), 1909 (s)	525, 490
$Mn^+(CO)_3(iPrPyCa^{\bullet-})(P(nBu)_3)$	2009 (s), 1921 (s), 1889 (s)	500–400[c]
$Mn^+(CO)_3(iPrPyCa^{\bullet-})(P(OMe)_3)$	2018 (s), 1937 (s), 1902 (s)	500–400[c]

[a] In THF at room temperature. [b] Bands could not be detected due to low concentration. [c] Broad band consisting of several transitions of $iPrPyCa^{\bullet-}$.

related complexes (COMe)$Mn(CO)_3$(α-diimine) and *cis*-,*trans*-(COMe)$Mn(CO)_2$(α-diimine)L (α-diimine = bpy, phen, tBuDAB; L = $P(OMe)_3$, PEt_3, CNtBu),[31] the two close-lying ^{13}CO resonances of $BrMn(CO)_2$(iPrPyCa)-($P(OMe)_3$) are assigned to equatorial CO ligands. We are dealing here with the *cis,trans* isomer, in which the two carbonyls are in a *cis* position and the Br^- and $P(OMe)_3$ ligands are *trans* to each other. The low-temperature product will therefore have a *cis,cis* conformation in which Br^- occupies an axial position and $P(OMe)_3$ an equatorial one, or vice versa. The corresponding low-temperature complex $BrMn(CO)_2$(iPrPyCa)(2-MeTHF) will also have a *cis,cis* conformation, since its lowest-energy absorption band is rather close in energy to that of the *cis,cis*-$P(OMe)_3$ complex and far separated from the band of its *cis,trans* isomer. In addition, there is a near coincidence between the absorption band of this *cis,cis*-$BrMn(CO)_2$(iPrPyCa)-(2-MeTHF) complex and the solvent-substituted complex $BrMn(CO)_2$(iPrPyCa)(THF), formed by flash photolysis of the starting complex at room temperature (vide supra). This primary photoproduct of the reaction will therefore also have a *cis,cis* conformation. The question remains whether the *cis,cis* isomer has the Br^- ion in an axial or equatorial position. Although it cannot be excluded that rearrangement processes occur within 10 ns after the flash and at temperatures as low as 135 K, it is still more likely that the Br^- ion has retained its axial position and that the solvent molecule has replaced an equatorial carbonyl ligand. This isomer is therefore proposed to be formed as depicted in Scheme 2.

In the second step of Scheme 1 the complex BrMn-$(CO)_2$(α-diimine)(S) is converted into *mer*-$BrMn(CO)_3$-(α-diimine), most probably by photochemical loss of the weakly bonded solvent molecule. Free CO, still present in the solution after the first reaction step, will then react with the five-coordinated $BrMn(CO)_2$(α-diimine) complex to give $BrMn(CO)_3$(α-diimine). If the coordinatively unsaturated $BrMn(CO)_2$(α-diimine) species retains its structure during this reaction, only the *fac* isomer will be re-formed. Alternatively, by internal rearrangement, the *mer* isomer may be formed and this is apparently the case for the complexes under study. In order to establish whether irradiation of $BrMn(CO)_2$(α-diimine)(S) gave rise to the formation of both the *fac* and *mer* isomers, the following experiment was performed. A solution of *fac*-$BrMn(CO)_3$(iPrPyCa) in 2-MeTHF was irradiated at 150 K with 458-nm light. The starting complex was then partly converted into *cis,cis*-$BrMn(CO)_2$(iPrPyCa)(2-MeTHF). Next, the mixture was irradiated with 600-nm light, which only affects the bicarbonyl product. No increase of concentration was then observed for the parent complex *fac*-$BrMn(CO)_3$(iPrPyCa) and irradiation only produced *mer*-$BrMn(CO)_3$(iPrPyCa). This means that an internal rearrangement of the five-coordinated complex had taken place, which resulted in transfer of Br^- from an axial to an equatorial position. Subsequent reaction with CO then led to the formation of the complex *mer*-$BrMn(CO)_3$-(iPrPyCa). In order to establish whether the formation of *mer*-$BrMn(CO)_3$(α-diimine) out of $BrMn(CO)_2$(α-diimine)(2-MeTHF) can also take place thermally, a solution of $BrMn(CO)_2$(α-diimine)(2-MeTHF) (α-diimine = bpy, iPrPyCa), formed by irradiation of *fac*-$BrMn(CO)_3$(α-diimine) at 135 K, was raised in temperature. At 180 K $BrMn(CO)_2$(α-diimine)(2-MeTHF) then transformed into *mer*-$BrMn(CO)_3$(α-diimine). So, the second step of the reaction sequence can be initiated photochemically and

Scheme 2



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(31) Garcia Alonso, F. J.; Llamazares, A.; Riera, V.; Vivanco, M. *Organometallics* 1992, *11*, 2826.

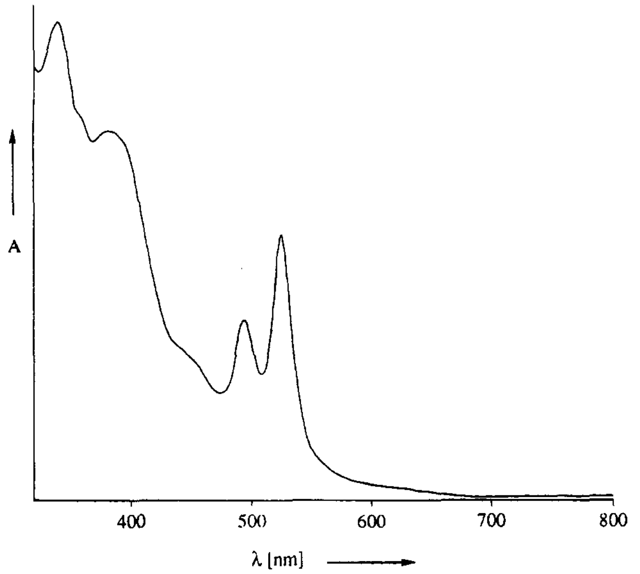

Figure 5. UV/vis spectrum of $Mn^+(CO)_3(bpy^{\bullet -})(P(OMe)_3)$ in 2-MeTHF at 135 K.

thermally. A further raise in temperature caused the back-reaction of *mer*-BrMn(CO)$_3$(α-diimine) to give *fac*-BrMn(CO)$_3$(α-diimine). No intermediates were observed in this back-reaction, which means that it took place without loss of any ligand.

The room temperature experiments have shown that both *mer*-XMn(CO)$_3$(bpy) and the radical complex $Mn^+(CO)_3(bpy^{\bullet -})$ are intermediates in the photoconversion of *fac*-XMn(CO)$_3$(bpy) into $Mn_2(CO)_6(bpy)_2$. Photolysis at low temperature was also performed in order to establish whether the radical complexes were in fact the photoproducts of these *mer* isomers. In this respect the low-temperature results were, however, remarkable. Irradiation of *fac*-BrMn(CO)$_3$(α-diimine) (α-diimine = bpy, iPrPyCa) in 2-MeTHF at 135 K in the presence of excess P(OMe)$_3$ or P(nBu)$_3$ gave rise to the formation of *mer*-BrMn(CO)$_3$(α-diimine) via the solvent-substituted complex BrMn(CO)$_2$(α-diimine)(2-MeTHF). Next, the *mer*-BrMn(CO)$_3$(α-diimine) complexes were converted photochemically into the radical complexes $Mn^+(CO)_3$(α-diimine$^{\bullet -}$)(PR$_3$) (Table 3) which show the characteristic intraligand transitions of (α-diimine$^{\bullet -}$) at about 500 nm[3e,32] (Figure 5).

So far these results are in line with the reaction mechanism of Scheme 1, which shows that the complexes *mer*-XMn(CO)$_3$(α-diimine) photodecompose into the 16-electron radical complexes $Mn^+(CO)_3$(α-diimine$^{\bullet -}$), which in turn form the 18-electron adducts $Mn^+(CO)_3$(α-diimine$^{\bullet -}$)(PR$_3$) in the presence of excess PR$_3$. The fate of the Br$^\bullet$ radicals is not yet clear.

When the same reaction was, however, performed in 2-MeTHF at 135 K in the absence of PR$_3$, a different product was obtained. Much lower CO-stretching frequencies were then observed for the photoproduct of *mer*-BrMn(CO)$_3$(α-diimine), viz. 1917 (s), 1823 (m), 1815 (sh) cm^{-1} for α-diimine = bpy, 1921 (s), 1819 (m), 1813 (sh) cm^{-1} for α-diimine = iPrPyCa, and 1924 (s), 1842 (m) cm^{-1} for α-diimine = pTolPyCa. In addition, these photoproducts exhibited an intense absorption band in the visible region (560 nm for α-diimine = bpy, 530 nm for α-diimine = iPrPyCa, 540 nm for α-diimine = pTolPyCa). For α-diimine = bpy these spectroscopic data are very similar to those of the five-coordinated anion [Mn(CO)$_3$(bpy)]$^-$ (IR ν(CO) 1912 (s), 1810 (s, br) cm^{-1}; UV/vis 565 nm), obtained by two successive one-electron reductions of *fac*-BrMn(CO)$_3$(bpy) in CH$_3$CN inside an OTTLE cell.[18] This anion will be isostructural with [Mn(CO)$_3$(DBCat)]$^-$ (DBCat = di-*tert*-butyl catecholate) for which the X-ray structure has been determined.[33] Thus, the type of photoproduct formed depends on the presence or absence of PR$_3$. The primary photoprocess will, however, be the same for both reactions and involves homolysis of the Mn–Br bond with formation of the radical complex $Mn^+(CO)_3$(α-diimine$^{\bullet -}$). In the absence of PR$_3$ solvent molecules will form adducts $Mn^+(CO)_3$(α-diimine$^{\bullet -}$)(S) which, apparently, undergo a disproportionation reaction to give [Mn(CO)$_3$(α-diimine)]$^-$ and a further not identified oxidation product. Raising the temperature of the solution to 170 K caused the thermal conversion of [Mn(CO)$_3$(α-diimine)]$^-$ into $Mn_2(CO)_6$(α-diimine)$_2$ for α-diimine = bpy, most probably with the $Mn^+(CO)_3$(α-diimine$^{\bullet -}$) radicals as intermediates. The mechanisms of this latter reaction and of the formation of the [Mn(CO)$_3$(α-diimine)]$^-$ anions are not yet clear and are the subject of further investigation.

Table 4. CO-Stretching Frequencies of the Products Formed upon Photolysis of *fac*-BrMn(CO)$_3$(α-diimine) in THF at Room Temperature in the Presence of PR$_3$ (R = nBu, OMe)

complex	ν(CO) (cm^{-1})
$Mn(CO)_3(bpy)(P(nBu)_3)^+$	2032 (s), 1953 (m), 1931 (m)
$Mn(CO)_3(iPrPyCa)(P(nBu)_3)^+$	2032 (s), 1954 (m), 1932 (m)
$Mn(CO)_3(pTolPyCa)(P(nBu)_3)^+$	2034 (s), 1961 (m), 1934 (m)
$Mn(CO)_2(bpy)(P(nBu)_3)_2^+$	1927 (s), 1857 (s)
$Mn(CO)_2(iPrPyCa)(P(nBu)_3)_2^+$	1928 (s), 1858 (s)
$Mn(CO)_2(pTolPyCa)(P(nBu)_3)_2^+$	1927 (s), 1858 (s)
$Mn(CO)_2(phen)(P(OMe)_3)_2^+ClO_4^-$ [a]	1968 (s), 1898 (s)
$Mn(CO)_2(bpy)(P(OMe)_3)_2^+$	1963 (s), 1892 (s)
$Mn(CO)_2(iPrPyCa)(P(OMe)_3)_2^+$	1963 (s), 1891 (s)
$Mn(CO)_2(pTolPyCa)(P(OMe)_3)_2^+$	1965 (s), 1894 (s)

[a] From ref 35.

When the photochemical reaction was performed in THF or toluene at 183 K, the same products were formed. However, in the case of toluene the yield of the reaction was again very low. These low-temperature data are all in favor of the reaction scheme presented in Schemes 1 and 2.

Photolysis at Room Temperature in the Presence of PR$_3$. The IR data for the products formed in the various photochemical reactions of *fac*-BrMn(CO)$_3$(α-diimine) with excess PR$_3$ are collected in Table 4. It should be noted that none of the complexes *fac*-BrMn(CO)$_3$(α-diimine) reacted thermally with PR$_3$ at room temperature.

Irradiation of a solution of *fac*-BrMn(CO)$_3$(α-diimine) with excess P(nBu)$_3$ (molar ratio 1:50) in THF gave rise to the following photocatalytic substitution reaction:

$$fac\text{-BrMn(CO)}_3(\alpha\text{-diimine}) + P(nBu)_3 \xrightarrow{h\nu} Mn(CO)_3(\alpha\text{-diimine})(P(nBu)_3)^+ + Br^- \quad (2)$$

A similar photocatalytic reaction has been observed before for the complexes (CO)$_5$MnMn(CO)$_3$(α-diimine) (reaction

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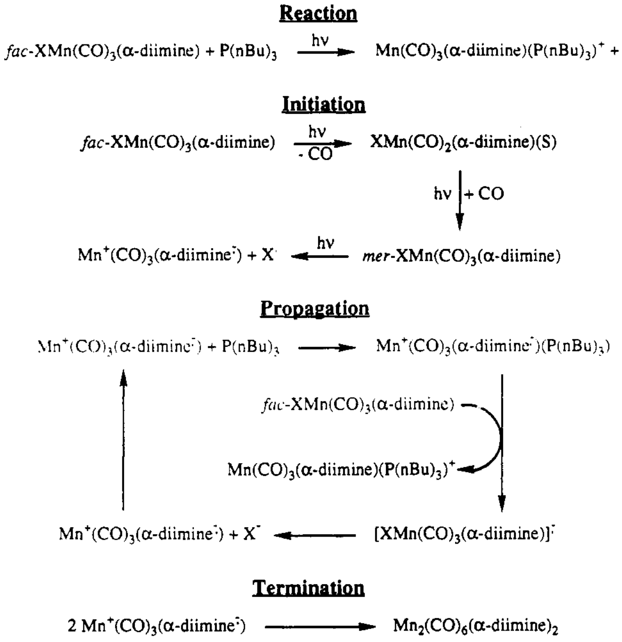
(32) (a) Krejcík, M.; Vlcek, A. A. *J. Electroanal. Chem. Interfacial Electrochem.* **1991**, *313*, 243. (b) Creutz, C. *Comments Inorg. Chem.* **1982**, *1*, 293.

(33) Hartl, F.; Vlcek, A., Jr.; deLearie, L. A.; Pierpont, C. G. *Inorg. Chem.* **1990**, *29*, 1073.

Scheme 3



3)[14b,17] and $(CO)_4CoMn(CO)_3(bpy)$ (reaction 4).[34] On the basis of these results reaction 2 is proposed to be an electron transfer chain (ETC) reaction, which proceeds according to the mechanism depicted in Scheme 3.

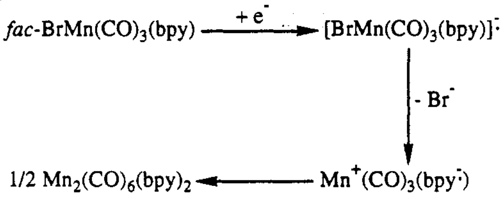
$$(CO)_5MnMn(CO)_3(\alpha\text{-diimine}) + P(nBu)_3 \xrightarrow{h\nu} Mn(CO)_3(\alpha\text{-diimine})(P(nBu)_3)^+ + Mn(CO)_5^- \quad (3)$$

$$(CO)_4CoMn(CO)_3(bpy) + P(nBu)_3 \xrightarrow{h\nu} Mn(CO)_3(bpy)(P(nBu)_3)^+ + Co(CO)_4^- \quad (4)$$

The key step in the reaction scheme is the transfer of the unpaired electron from the 18-electron radical species $Mn^+(CO)_3(\alpha\text{-diimine}^{\bullet-})(P(nBu)_3)$ to the starting complex. In order to demonstrate that such an electron transfer takes place, i.e. that reaction 2 is photocatalytic, the following experiment was performed. A solution of *fac*-$BrMn(CO)_3(bpy)$ and $P(nBu)_3$ (1:100) in THF was irradiated with a short light pulse. Hereafter, the change of absorption at 400 nm as a function of time was monitored with UV/vis spectroscopy. It appeared that the absorption decreased in time, which indicated that the conversion of *fac*-$BrMn(CO)_3(bpy)$ proceeded even when the solution was not further irradiated. This confirms that reaction 2 is indeed photocatalytic. Upon prolonged irradiation the product $Mn(CO)_3(bpy)(P(nBu)_3)^+$ was converted into a complex with CO bands at 1927 (s) and 1857 (s) cm^{-1}. On the basis of previous results[17] these bands are assigned to $Mn(CO)_2(bpy)(P(nBu)_3)_2^+$.

In order to confirm that *fac*-$BrMn(CO)_3(\alpha\text{-diimine})$ loses Br^- by one-electron reduction (Scheme 3), a solution of *fac*-$BrMn(CO)_3(bpy)$ in CH_3CN was electrochemically reduced inside an OTTLE cell.[18] The reduction, which was followed by IR spectroscopy, resulted in the formation of $Mn_2(CO)_6(bpy)_2$ as the only detectable product. The dimer formation most probably proceeded according to Scheme 4. Upon one-electron reduction Br^- was rapidly ejected from the reduced complex. The radicals thus formed dimerized to give $Mn_2(CO)_6(bpy)_2$.

Scheme 4



Irradiation of a solution of *fac*-$BrMn(CO)_3(\alpha\text{-diimine})$ with excess $P(OMe)_3$ (1:100) in THF gave rise to very fast formation of a bicarbonyl complex ((α-diimine = bpy) ν(CO) 1963 (s), 1892 (s) cm^{-1}; (α-diimine = iPrPyCa) ν(CO) 1963 (s), 1891 (s) cm^{-1}; (α-diimine = pTolPyCa) ν(CO) 1965 (s), 1894 (s) cm^{-1}). On the basis of the similarity between the CO-stretching frequencies of the products formed and those of $Mn(CO)_2(phen)(P(OMe)_3)_2^+ClO_4^-$ (ν(CO) in CH_2Cl_2: 1968 (s), 1898 (s) cm^{-1})[35] (Table 4) the following reaction is proposed to have occurred:

$$fac\text{-}BrMn(CO)_3(\alpha\text{-diimine}) + 2P(OMe)_3 \xrightarrow{h\nu} Mn(CO)_2(\alpha\text{-diimine})(P(OMe)_3)_2^+ + Br^- + CO \quad (5)$$

When, after completion of reaction 5, the solution was left in the dark, the complex $Mn(CO)_2(\alpha\text{-diimine})(P(OMe)_3)_2^+$ was thermally converted into a different bicarbonyl complex with frequencies 1950 (s) and 1865 (s) cm^{-1} for α-diimine = bpy, 1945 (s) and 1875 (s) cm^{-1} for α-diimine = iPrPyCa, and 1949 (s) and 1881 (s) cm^{-1} for α-diimine = pTolPyCa. Apparently, a substitution reaction had occurred in which a phosphine ligand was replaced by Br^-, leading to the formation of $BrMn(CO)_2(\alpha\text{-diimine})(P(OMe)_3)$ (reaction 6). ^{13}C NMR data for $BrMn(CO)_2(iPrPyCa)(P(OMe)_3)$ revealed that this complex has a *cis,trans* configuration; i.e. Br^- is coordinated *cis* to iPrPyCa and *trans* to $P(OMe)_3$ (vide supra). The occurrence of this reaction was confirmed by the thermal reaction of $Mn(CO)_3(\alpha\text{-diimine})^+Otf^-$ ($Otf^- = CF_3SO_3^-$) with excess $P(OMe)_3$ (1:100) in THF. Heating the reaction mixture for 2 h in the dark at 40 °C gave rise to the formation of the product $Mn(CO)_3(\alpha\text{-diimine})(P(OMe)_3)^+$. By subsequent irradiation of the reaction mixture in the presence of excess $P(OMe)_3$ the tricarbonyl product was completely converted into $Mn(CO)_2(\alpha\text{-diimine})(P(OMe)_3)_2^+$. When the reaction mixture was then left in the dark, no new bicarbonyl complex was formed, due to the absence of Br^- in this case.

$$Mn(CO)_2(\alpha\text{-diimine})(P(OMe)_3)_2^+ + Br^- \xrightarrow{\Delta} BrMn(CO)_2(\alpha\text{-diimine})(P(OMe)_3) + P(OMe)_3 \quad (6)$$

Mechanistic Aspects

As discussed in the previous sections, irradiation of *fac*-$XMn(CO)_3(\alpha\text{-diimine})$ complexes into their lowest-energy visible absorption band gives rise to the reaction sequence depicted in Schemes 1 and 2. The primary photoprocess is loss of CO, leading to the formation of $XMn(CO)_2(\alpha\text{-diimine})(S)$. Previous studies have shown that the related

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complexes *fac*-(Ph_3E)Mn$(CO)_3$(α-diimine) (E = Ge, Sn, Pb)[29] and *fac*-$(CO)_5$ReMn$(CO)_3$(α-diimine)[17,30] also lose CO upon visible excitation. Just as for the complexes CpMn$(CO)_2$L (L = (substituted) pyridine),[8] these CO-loss reactions most likely occur from a LF state close in energy to the lowest MLCT state. The low energy of this LF state is a consequence of the small ligand-field splitting of Mn(I). Quite recently, CASSCF/MRCI calculations of the ground and excited states of *fac*-HMn$(CO)_3$(HDAB) (DAB = 1,4-diaza-1,3-butadiene) have shown that this complex has two ^{3}LF states below the ^{1}MLCT states, which probably lead to release of CO.[36]

In the second step of the reaction the bicarbonyl complex is converted into *mer*-XMn$(CO)_3$(α-diimine). This reaction takes place thermally as well as photochemically. In both cases the weakly bonded solvent molecule will be released. The coordinatively unsaturated species XMn$(CO)_2$(α-diimine) reacts back with CO to give *mer*-XMn$(CO)_3$(α-diimine). It is noteworthy that the bicarbonyl complex is only converted into the *mer* isomer, both thermally and photochemically. This indicates that the most stable configuration of the five-coordinated intermediate is a square pyramid with X, α-diimine, and CO in the basal plane.

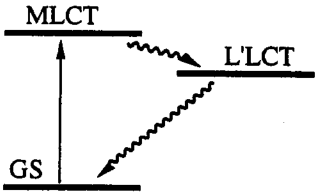
Irradiation of *mer*-XMn$(CO)_3$(α-diimine) leads to the formation of the radicals $Mn^+(CO)_3$(α-diimine$^{\bullet-}$), as shown by the ESR spectra at room temperature and by the formation of rather stable $Mn^+(CO)_3$(α-diimine$^{\bullet-}$)(PR_3) adducts at 135 K in 2-MeTHF. For α-diimine = bpy these radicals dimerize to give $Mn_2(CO)_6(bpy)_2$. At first sight there seems to be a relationship with the photochemical formation of $Mn_2(CO)_{10}$ out of $Mn(CO)_5X$ (X = halide).[37] In that case, however, the complexes $Mn(CO)_4X$, formed by CO dissociation, and the halide-bridged dimer $Mn_2(CO)_8X_2$ were intermediates in the reaction.

An important result of this study is the observation of different primary photoprocesses for the *fac* and *mer* isomers of XMn$(CO)_3$(α-diimine). The former complexes lose CO; the *mer* isomers produce $Mn^+(CO)_3$(α-diimine$^{\bullet-}$) radicals.

As mentioned above, the CO-loss reaction of the *fac* isomers most probably occurs from a LF state close in energy to the lowest CT state. Going from the *fac* to the *mer* isomers, the CT transitions shift to lower energy (Tables 1 and 3, Figure 4). Since a similar shift is not expected for the lowest LF states, the *fac* to *mer* isomerization will increase the energy difference between the CT and LF states. As a result, the reactive LF states may not be occupied anymore and this explains the absence of a CO-loss reaction for the *mer* complexes.

The photoproduction of $Mn^+(CO)_3$(α-diimine$^{\bullet-}$) radicals by irradiation of *mer*-XMn$(CO)_3$(α-diimine) is a novel reaction of this type of XM$(CO)_3$(α-diimine) (M = Mn, Re) complex. It closely resembles the photochemistry of the metal–metal bonded complexes L_nMRe$(CO)_3$(α-diimine) (L_nM = $(CO)_5$Mn, $(CO)_5$Re, $(CO)_4$Co, Cp$(CO)_2$Fe, Ph_3Sn)[1d,12] and the metal–alkyl complexes *fac*-(R)Re$(CO)_3$(α-diimine) (R = Me, Et, benzyl),[13] which also produce $Re^+(CO)_3$(α-diimine$^{\bullet-}$) radicals upon irradiation into their visible absorption band. In a recent article,[30] we have suggested that these complexes represent a special class of chromophore–quencher (C–Q) complexes, in which the MLCT state is quenched by intramolecular electron transfer. Most well-known are the C–Q complexes $DRe^+(CO)_3$(α-diimine), in which D represents an organic donor.[3k–n,38–41] Excitation of such a complex ion to its MLCT state is followed by electron transfer from D to Re, producing a complex in its L′LCT state (see Scheme 5). From this state the complex returns to its ground state by nonradiative decay on a nanosecond time scale. A direct electronic transition to the L′LCT state is not expected, due to lack of overlap between the orbitals of D and the α-diimine. A similar two-state diagram has been proposed by us for the above-mentioned metal–metal and metal–alkyl bonded α-diimine complexes.[30] The L′LCT state then represents a reactive $\sigma_b\pi^*$ state, σ_b being the metal–metal/metal–alkyl bonding orbital and π^* the lowest empty orbital of the α-diimine ligand. Contrary to the L′LCT state of the $DRe^+(CO)_3$(α-diimine) complexes, the $\sigma_b\pi^*$ state is then reactive, giving rise to the formation of radicals. Support for such a two-state diagram with a reactive $\sigma_b\pi^*$ state has recently been obtained by us for the complexes *fac*-(R)Re$(CO)_3$(α-diimine) (R = Me, Et).[13] Going from R = Me to Et, the L′LCT ($\sigma_b\pi^*$) state will decrease in energy with respect to the MLCT state so that it can be occupied more easily. The experiments confirmed these expectations, since the photodecomposition quantum yields increased from only ~10^{-2} for R = Me to nearly 1 in the case of the Et complexes.

Scheme 5



It is, however, questionable if the same two-state diagram of Scheme 5 can explain the photochemistry of the *mer*-XMn$(CO)_3$(α-diimine) complexes, since the characters of the CT states are so different. Recent MO calculations have shown that the highest filled orbitals of both *fac*- and *mer*-XMn$(CO)_3$(bpy) have strong metal–halide antibonding character, the halide contribution being predominant, and that their energies increase on going from the *fac* to the *mer* isomer.[21d] This energy increase causes the first absorption band to shift to longer wavelength (Figure 4). The transitions from the corresponding set of metal–halide bonding orbitals to bpy are predominantly MLCT in character and give rise to the more intense absorption band of the *mer* isomer at ca. 380 nm.

Comparing these data with those of the metal–metal and metal–alkyl bonded complexes, we can conclude that the *mer*-XMn$(CO)_3$(bpy) complexes have allowed electronic transitions to both the MLCT and L′LCT states. The character of the L′LCT state is, however, different from that of the metal–metal and metal–alkyl bonded complexes, since the electron does not originate from a metal–halide σ-bonding orbital but from a metal–halide π-antibonding orbital. It is therefore not clear how

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occupation of this L′LCT state can lead to a metal–halide homolysis reaction, since the metal–halide bond is expected to be strengthened with respect to the ground state instead of weakened. Maybe, just as for the metal–metal and metal–alkyl bonded complexes, the metal–halide σ_b orbital is rather high in energy for *mer*-XMn(CO)$_3$(bpy), so that the reactive $\sigma_b\pi^*$ state can be occupied after excitation to the L′LCT state. Work is in progress to obtain more insight into the excited state properties of these *mer* isomers.

Conclusion

The above results show that irradiation of the complexes *fac*-XMn(CO)$_3$(α-diimine) into their lowest-energy CT band gave rise to the efficient formation of the 16-electron radical complex Mn$^+$(CO)$_3$(α-diimine$^{\bullet-}$). Subsequent intermediates in this process were XMn(CO)$_2$(α-diimine)(S) (S = solvent molecule) and the highly unstable complex *mer*-XMn(CO)$_3$(α-diimine). For α-diimine = bpy the Mn$^+$(CO)$_3$(α-diimine$^{\bullet-}$) radicals dimerized to give Mn$_2$(CO)$_6$(α-diimine)$_2$. In the presence of PR$_3$ (R = nBu, OMe) the radicals reacted to give the highly reducing 18-electron radical species Mn$^+$(CO)$_3$(α-diimine$^{\bullet-}$)(PR$_3$), which initiated the photocatalytic substitution of X$^-$ by PR$_3$ in the starting complex *fac*-XMn(CO)$_3$(α-diimine).

The primary photoprocesses of *fac*-XMn(CO)$_3$(α-diimine) (release of CO) and *mer*-XMn(CO)$_3$(α-diimine) (homolysis of the Mn–X bond) are proposed to occur from the LF state and the $\sigma_b\pi^*$ state, respectively.

Acknowledgment. Dr. J. A. Timney is thanked for placing at our disposal the program for the force field calculations, and Dr. F. Hartl, for his skillful help with the recording and interpretation of the spectroelectrochemical data. We wish to thank W. G. J. de Lange and Ch. Mahabiersing for technical assistance during the NMR measurements and A. Terpstra for technical assistance during the flash photolysis measurements. Thanks are due to the Netherlands Foundation for Chemical Research (SON) and the Netherlands Organization for the Advancement of Pure Research (NWO) for their financial support.

OM930762L