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Metal to Ligand Charge-Transfer Photochemistry of Metal–Metal-Bonded Complexes. 7.[†] Photochemistry of $(CO)_4CoM(CO)_3(bpy)$ (M = Mn, Re; bpy = 2,2′-Bipyridine): Photocatalytic Disproportionation of the Manganese Complex in the Presence of PR_3

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This article describes the photochemistry of the complexes $(CO)_4CoM(CO)_3(bpy)$ (M = Mn, Re). Irradiation of the Mn complex in the absence of a nucleophile produced $Mn_2(CO)_6(bpy)_2$. No such reaction was observed for the Re complex, although $Re(CO)_3(bpy)$ radicals could be detected by spin-trapping with tBu-ṄO. In the presence of PR_3 or in a coordinating solvent (S), ionic photoproducts $[M(CO)_3(bpy)L]^+[Co(CO)_4]^-$ (L = PR_3, S) were formed. In the case of the Mn complex the reactions with PR_3 appeared to be photocatalytic with quantum yields varying from 7 to 60 mol/einstein. When CBr_4 was added to the above solutions, $M(CO)_3(bpy)Br$ was formed and all other reactions were suppressed. A remarkable reaction of the Re complex is its photodisproportionation in toluene at 230 K into the contact ion pair $\{Re(CO)_3(bpy)^+ \cdot Co(CO)_4^-\}$. This reaction was also completely suppressed by adding CBr_4. The mechanisms of these reactions are discussed in terms of a homolytic cleavage of the metal–metal bond from the $^3\sigma\sigma^*$ state, giving rise to the formation of a reactive 16-electron $M(CO)_3(bpy)$ radical species.

Introduction

Mechanistic studies in the field of organometallic photochemistry have mainly been confined to transition-metal carbonyls. This also holds for the photochemical reactions of metal–metal-bonded complexes, for which most mechanistic information is available for the carbonyl dimers $M_2(CO)_{10}$ (M = Mn, Re), $Cp_2Fe_2(CO)_4$, $Cp_2M_2(CO)_6$ (M = Mo, W), and their derivatives.[1-5] Both homolytic splitting of the metal–metal bond and loss of CO appeared to be primary photoprocesses of these dimers. The homolysis reaction takes place from the repulsive $^3\sigma\sigma^*$ state of the metal–metal bond, while release of CO presumably occurs from a close-lying ^{3}LF state.[2] Under normal conditions the homolysis reaction is the dominating process. The CO-loss reaction is best observed by using low concentrations of the substituting ligand, by scavenging the radicals with e.g. CCl_4, or by irradiating the complex in viscous or rigid media. All but one of the homo- and heterodinuclear complexes studied so far appeared to react via these two primary photoprocesses. The only exception is the complex $Cp(CO)_2FeCo(CO)_4$, for which a heterolytic splitting of the metal–metal bond has been postulated to occur in a CO-doped argon matrix at 10 K.[6] Substitution of two carbonyl groups of such a dimer by 2,2′-bipyridine (bpy) or another α-diimine ligand produces a complex with an extra metal to bpy charge transfer (MLCT) transition at low energy (λ_{max} = 450–600 nm). Thus, $Mn_2(CO)_{10}$ has its lowest energy absorption band at 340 nm and $Mn_2(CO)_8(bpy)$ at about 550 nm, depending on the solvent used. In recent years we have studied in detail the spectroscopic and photochemical properties of several such α-diimine complexes with a low ^{3}MLCT state, both mono- and binuclear.[7-22] Detailed studies on the photochemistry of the mononuclear complexes $M(CO)_4L$ (M = Cr, Mo, W),[7,15,18] $Fe(CO)_3L$,[9,10,17] and $Ni(CO)_2L$[19] (L = α-diimine) have shown that the ^{3}MLCT states of these complexes are not very reactive. High quantum yields ($\Phi > 0.1$) were only obtained when a reactive ^{3}LF state was populated, either by heating or by higher energy excitation.

In contrast with this, high photochemical quantum yields were obtained for the metal–metal-bonded α-diimine complexes $(CO)_5MM'(CO)_3L$ (M = M′ = Mn, Re),[2,5,11-14,23,24] $Ph_3SnM(CO)_3L$ (M = Mn, Re),[20-22] and $Cp(CO)_2FeRe(CO)_3L$[25] (L = α-diimine), even upon irradiation at the very low energy side of the MLCT band. Moreover, most of these complexes showed the same homolytic splitting of the metal–metal bond as the unsubstituted carbonyls from which they are derived.

These observations can best be explained with the energy level diagram proposed by Meyer and Caspar[2] (Figure 1), in which energy transfer takes place intramolecularly from the lowest unreactive ^{3}MLCT state to the repulsive $^3\sigma\sigma^*$ state of the metal–metal bond. Because of the repulsive character of this latter state, energy transfer can already take place at very low energy. This diagram also explains the observation of a similar photochemistry for the substituted and unsubstituted metal–metal-bonded carbonyls.

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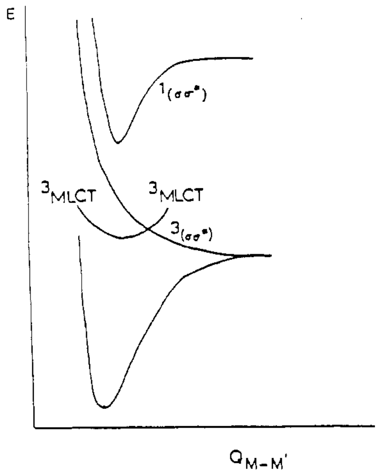

Figure 1. Schematic energy level diagram for metal–metal-bonded carbonyls with a low-energy ^{3}MLCT state.

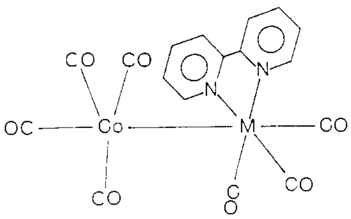

Figure 2. Proposed structure of $(CO)_4CoM(CO)_3(bpy)$.

However, some of these complexes appeared to behave differently by showing release of CO instead of homolytic cleavage of the metal–metal bond, even upon irradiation at low energy ($\lambda_{irr} \simeq 600$ nm). The quantum yields of this CO-loss reaction, which has been observed for the complexes $Ph_3SnMn(CO)_3(\alpha\text{-diimine})$,[22] $(CO)_5ReMn(CO)_3(\alpha\text{-diimine})$,[14] and $(CO)_5MnMn(CO)_3(\alpha\text{-diimine})$[5,23] (only at $T < 200$ K), were high (0.3–0.9 mol/einstein) and rather constant throughout the MLCT band. Since similar high and wavelength-independent quantum yields were obtained for the homolysis reaction of the other complexes, both reactions were assumed to occur from the same $^3\sigma\sigma^*$ state. Apparently, this state is antibonding not only between the two metal atoms but also between Mn and the CO ligands.

Another aspect of these metal–metal-bonded α-diimine complexes is the occurrence of a photocatalytic disproportionation in the presence of nucleophiles. Such reactions have been observed for the complexes $(CO)_5MnMn(CO)_3(\alpha\text{-diimine})$[14] and interpreted as an electron transfer chain (ETC) reaction initiated by the adducts formed by the nucleophile and the 16-electron radical species $Mn(CO)_3(\alpha\text{-diimine})$.

For a better understanding of the above photochemical and photocatalytic reactions of these metal–metal-bonded complexes, we have extended our photochemical studies to the complexes $(CO)_4CoM(CO)_3(bpy)$ (M = Mn, Re; see Figure 2). Up to now, the photochemical properties of these complexes have not been published. The synthesis and IR data of the corresponding phenanthroline complexes were first reported by Kruck et al.[26,27] For the bpy complexes in this study, however, an alternative synthetic route has been used (see Experimental Section). If a 1,4-diaza-1,3-butadiene (R-DAB) molecule is used as the α-diimine ligand, the complexes $CoMn(CO)_6(R\text{-DAB})$ are formed instead.[28] In these complexes the R-DAB ligand is σσ-N,N′-coordinated to Mn and η^2-CN-coordinated to Co, instead of σσ-N,N′ to Mn as for bpy. The structure, proposed for the complexes under study (Figure 2), is based on previous (NMR and X-ray) structural studies on $XM(CO)_3(\alpha\text{-diimine})$ (M = Mn, Re; X = Br, $Mn(CO)_5$, $Re(CO)_5$, Ph_3Sn, $CpFe(CO)_2$) complexes, which all have their α-diimine ligand in the equatorial plane of the $Mn(CO)_3(\alpha\text{-diimine})$ fragment. In the course of this study reactions have been performed with the following PR_3 ligands: R = *n*-butyl (nBu), cyclohexyl (cHx), phenyl (Ph), methoxy (OMe), phenoxy (OPh).

Experimental Section

Materials and Preparations. The phosphines and solvents were purified by distillation or sublimation and kept under a nitrogen atmosphere. All manipulations were carried out under an inert atmosphere.

$(CO)_4CoMn(CO)_3(bpy)$. A solution of $Na[Co(CO)_4]$ was prepared by adding 2 mL of $NaK_{2.8}$ to a solution of 7.5 g of $Co_2(CO)_8$ (Strem Chemicals, freshly sublimed) in 40 mL of THF. The solution was filtered twice over a glass filter with pores of 10–12 μm (G-4) in order to remove unreacted $NaK_{2.8}$. To the solution was added 2 g of $Mn(CO)_3(bpy)Br$ in 50 mL of THF with the exclusion of light. The $Mn(CO)_3(bpy)Br$ complex had been synthesized from $Mn(CO)_5Br$[29] according to a known procedure.[30] The combined solution was then stirred for 4 h. The THF was evaporated, and 100 mL of benzene was added. The solution was filtered and the volume reduced to 5 mL by evaporation under reduced pressure. The product was purified by column chromatography (Merck, silica gel, 60 mesh, activated by heating for 3 h under vacuum at 180 °C) in the dark, using ether as the eluent. The dark red ether fraction was evaporated to dryness, and the residue was carefully washed with *n*-pentane and dried; yield 41% of $(CO)_4CoMn(CO)_3(bpy)$ (red solid). The complex is air- and light-sensitive.

$(CO)_4CoRe(CO)_3(bpy)$. One gram of $Re(CO)_3(bpy)Br$, synthesized according to ref 31, was stirred for 1.5 h with a slight excess of Ag(OTF) (OTF = trifluoromethanesulfonate) in 50 mL of THF. $[Re(CO)_3(bpy)(THF)](OTF)$ was then formed, and AgBr precipitated. To the filtered solution was added a solution of $Na[Co(CO)_4]$ in THF, prepared by reaction of 4.3 g of $Co_2(CO)_8$ with 1.4 mL of $NaK_{2.8}$ in 40 mL of THF. The solution was stirred overnight and then evaporated to dryness. To the solid residue was added 50 mL of benzene, and the red solution, obtained after filtration, was evaporated to dryness. The red-orange solid was washed twice with 20 mL of *n*-hexane and carefully dried; yield 30%.

Spectra. Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 UV/vis spectrophotometer, equipped with a Model 3600 data station; resonance Raman spectra were obtained on a Jobin-Yvon HG 2S Ramanor spectrophotometer using an SP Model 171 argon ion laser as the excitation source. IR spectra were recorded on a Nicolet 7199 B FTIR interferometer with a liquid-nitrogen-cooled Hg, Cd, Te detector (32 scans, resolution 0.5 cm^{-1}). ESR spectra were measured on a Varian E6 spectrometer with 100-kHz modulation. The microwave frequency was measured with a Hewlett-Packard 5432 A MWF counter. The magnetic field was measured with an AEG "Kernresonanz Magnetfeld Messer". During the ESR measurements a 100-W Hg lamp with a cutoff light filter was used as the excitation source.

Photochemistry. For the photochemical reactions an SP 2020 argon ion laser was used as the irradiation source. Photochemical quantum yields were measured by irradiating low-temperature solutions of the complexes ($\simeq 10^{-3}$ M) in dry, carefully degassed toluene in quartz cells. The photon flux was calculated from the laser power, which was measured by a Coherent Model 201 (1 mW–30 W) or a Model 212 (1 μW–10 mW) power meter. Corrections were applied for reflections of the light within the cell, for transmission of the laser beam, and for absorption of light by the photoproduct.

In order to obtain reliable values for the very high quantum yields of the photocatalytic disproportionation reactions of the Mn complexes, the UV/vis apparatus had to be modified. Irradiations were carried out in the sample compartment of this spectrophotometer in order to exclude all disturbing stray light. During irradiation both the detector and analyzing light beam of the spectrophotometer were blocked. The absorption spectral changes during the reaction were then monitored at a fixed wavelength (usually the maximum of the MLCT band) by deblocking the analyzing beam and detector for a short moment. The laser light, which was introduced into the sample compartment by way of a glass fiber, was passed through a photographic shutter, thus enabling the use of reliable short irradiation times.

Results

Spectroscopic Properties. The CO stretching frequencies of both complexes, derived from their IR spectra, are collected in Table I.

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Table I. Infrared ν(CO) Frequencies of $(CO)_4CoM(CO)_3(bpy)$ (M = Mn, Re) and Their Photoproducts

complex	solvent; *T*, K	ν(CO), cm^{-1}
$(CO)_4CoMn(CO)_3(bpy)$ (I)	toluene; room temp	2046, 1998, 1971, 1951, 1937, 1910
$Mn_2(CO)_6(bpy)_2$	toluene; 203	1982, 1936, 1887, 1869
$Mn(CO)_3(bpy)Br$	toluene; 203	2027, 1948, 1913
$[Mn(CO)_3(bpy)(2\text{-}MeTHF)]^+$	2-MeTHF; 133	2038, 1940, 1931
$[Mn(CO)_3(bpy)(PR_3)]^+$		
R = nBu	2-MeTHF; 203	2032, 1953, 1924
R = cHx	2-MeTHF; 203	2031, 1952, 1922
R = Ph	2-MeTHF; 203	2037, 1961, 1930
R = OMe	2-MeTHF; 203	2046, 1972, 1938
R = OPh	2-MeTHF; 203	2054, 1984, 1945
$(CO)_4CoRe(CO)_3(bpy)$ (II)	toluene; room temp	2048, 2010, 1968, 1949, 1935, 1900
$Re(CO)_3(bpy)Br$	toluene; 203	2022, 1923, 1897
$[Re(CO)_3(bpy)(2\text{-}MeTHF)]^+$	2-MeTHF; 133	2033, 1924, 1916
$[Re(CO)_3(bpy)(PR_3)]^+$		
R = nBu	2-MeTHF; room temp	2033, 1944, 1917
R = cHx	2-MeTHF; room temp	2033, 1943, 1915
R = Ph	2-MeTHF; room temp	2037, 1951, 1923
R = OMe	2-MeTHF; room temp	2045, 1962, 1930
R = OPh	2-MeTHF; room temp	2052, 1979, 1938
$[Re(CO)_3(bpy)]^+$ (in $\{Re(CO)_3(bpy)^+{\cdot}Co(CO)_4^-\}$)	toluene; 203	2034, 1930, 1919

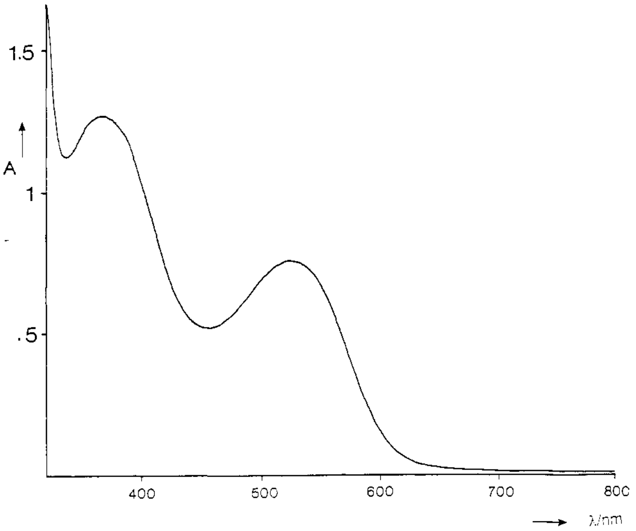

Figure 3. Electronic absorption spectrum of $(CO)_4CoMn(CO)_3(bpy)$ in toluene at room temperature.

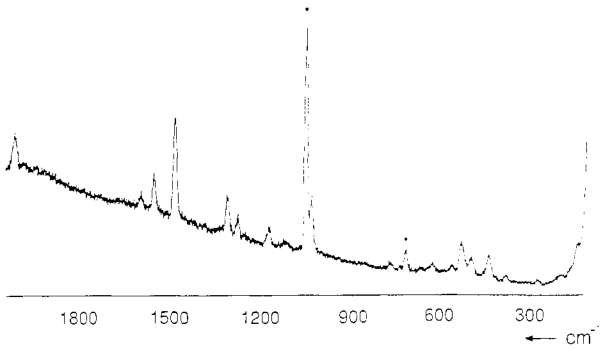

Figure 4. Resonance Raman spectrum of $(CO)_4CoRe(CO)_3(bpy)$ in a KNO_3 disk at 110 K (λ_{exc} = 514.5 nm; dots denote peaks due to NO_3^-).

The absorption spectrum of the complex $(CO)_4CoMn(CO)_3(bpy)$ (I) in toluene, presented in Figure 3, shows a band at 366 nm, which has the characteristic position and intensity of the $\sigma_b \rightarrow \sigma^*$ transition of the metal–metal bond.[1,2,5] The band at 540 nm, which is always present in the spectra of metal–metal-bonded complexes possessing an α-diimine ligand,[1,2,5] belongs to one or more metal to α-diimine (MLCT) transitions. The complex $(CO)_4CoRe(CO)_3(bpy)$ (II) has its MLCT band at somewhat higher energy ($\lambda_{max} \simeq$ 460 nm). There has been some controversy about the nature of the metal d orbital involved in this transition. For the corresponding complexes $(CO)_5MM(CO)_3$(α-diimine) (M = Mn, Re), Morse and Wrighton[24] assigned this low-energy band to a σ_b(M–M) $\rightarrow \pi^*$(α-diimine) transition. This assignment was based on the observation of a homolytic splitting of the metal–metal bond of these complexes upon irradiation into this band. It was, however, shown by us, both for these $(CO)_5MM(CO)_3$(α-diimine) complexes[13] and for the $Ph_3SnM(CO)_3$(α-diimine) (M = Mn, Re) analogues,[20] that this low-energy band belongs to one or more MLCT transitions from (a) metal d_π orbital(s) not involved in the metal–metal bond. Strong evidence for this assignment was the observation in the resonance Raman (RR) spectra of these complexes of only very weak RR effects for ν_s(M–M). This means that the metal–metal bond of these complexes is hardly affected by this MLCT transition. Figure 4 presents the RR spectrum of complex II, obtained by excitation with the 514.5-nm laser line, in preresonance with the MLCT band (λ_{max} = 454 nm in 2-MeTHF). This spectrum was recorded from a solution of the complex in a KNO_3 pellet at 110 K ($\simeq$3 mg of complex dissolved in 200 mg of KNO_3). Complex I decomposed under these circumstances. Resonance enhancement of Raman intensity is observed for bipyridine vibrations[32,33] at 1607, 1563, 1492, 1323, 1276, 1175, and 1023 cm^{-1}. The band at 2045 cm^{-1} belongs to the stretching vibration of the axial CO ligand of the $Re(CO)_3(bpy)$ moiety. Metal–CO stretching and deformation modes are observed in the 400–600-cm^{-1} frequency region. No RR effect is, however, observed for any vibration between 100 and 200 cm^{-1}, where ν(Co–Re) is expected to occur. This means that also for this complex the low-energy MLCT transition hardly affects the metal–metal bond. The MLCT character is evident from the RR effects observed for the bpy stretching modes. Similar RR spectra were obtained for other bpy complexes with a low MLCT state, such as $Ru(bpy)_3^{2+}$.[34-36] The occurrence of a RR effect for $\nu(CO)_{ax}$ points to a delocalization of the MLCT state over this carbonyl ligand. A similar effect was observed for the complexes $M(CO)_4L$ (M = Cr, Mo, W),[7] $Ph_3SnM(CO)_3L$ (M = Mn, Re),[20] $(CO)_5MM'(CO)_3L$ (M, M' = Mn, Re),[13] and $Ni(CO)_2L$[19] (L = α-diimine) and was then explained with a through-space overlap between the π^* orbitals of the carbonyl and α-diimine ligands. Additional evidence for the MLCT character of the low-energy transition is the solvent dependence of its absorption maximum. For complex I λ_{max} shifts from 539 to 522 nm upon going from toluene to 2-MeTHF. For complex II the band shifts from 472 to 454 nm. This positive solvatochromism is a common property of the MLCT bands of transition-metal carbonyls possessing a bpy ligand.[37,38]

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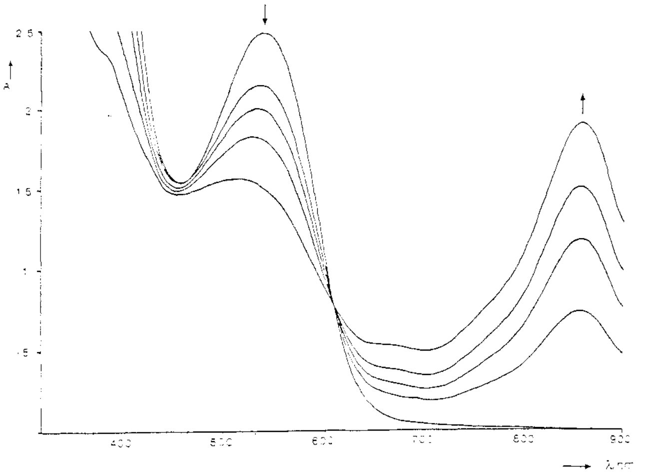

Figure 5. UV/vis spectral changes accompanying the photochemical reaction of $(CO)_4CoMn(CO)_3(bpy)$ in toluene at room temperature (λ_{irr} = 514.5 nm).

Photochemical Reactions. $(CO)_4CoMn(CO)_3(bpy)$ (I). Reactions were performed in both the absence and presence of a nucleophile. First of all, a solution of the complex was irradiated at room temperature with λ = 514.5 nm, and the UV/vis spectral changes accompanying this reaction are presented in Figure 5. The product spectrum shows the characteristic low-energy absorption band (λ_{max} = 855 nm) of a binuclear complex $Mn_2(CO)_6(bpy)_2$,[11,24] which was also identified by its IR CO stretching frequencies at 1982, 1934, 1885, and 1866 cm^{-1} [11] (see Table I). This complex is formed by dimerization of the radicals $Mn(CO)_3(bpy)$, produced from complex I by homolytic splitting of the metal–metal bond:

$$(CO)_4CoMn(CO)_3(bpy) \xrightarrow{h\nu} Co(CO)_4 + Mn(CO)_3(bpy) \quad (1)$$

$$2Mn(CO)_3(bpy) \rightarrow Mn_2(CO)_6(bpy)_2 \quad (2)$$

A previous photochemical study on the complexes $(CO)_5MnMn(CO)_3L$[11] (L = α-diimine) has shown that the equilibrium of reaction 2 lies far to the right since no $Mn(CO)_3(bpy)$ radicals could be detected with ESR. Later,[21] they have, however, been trapped by tBu-ṄO, a well-known spin-trapping agent. In contrast with this, the corresponding radicals $Mn(CO)_3(tBu\text{-}DAB)$ could be detected and analyzed with ESR without using a spin trap.[21] Apparently, the bulky *tert*-butyl groups of the diazabutadiene ligand prevent the dimerization of the radicals. The ESR spectrum of this latter radical showed that the unpaired electron is mainly localized at the α-diimine ligand and that the $Mn(CO)_3(\alpha\text{-diimine})$ radicals are therefore 16-electron radical complexes $Mn^+(CO)_3(\alpha\text{-diimine})^{\bullet -}$.

Unfortunately, no reaction product of the $Co(CO)_4$ radicals could be detected in the IR spectrum. A similar negative result was obtained by Abrahamson and Wrighton upon irradiation of $(\eta^5\text{-}C_5H_5)(CO)_3MCo(CO)_4$ (M = Mo, W) in the presence of CCl_4.[39] $(\eta^5\text{-}C_5H_5)M(CO)_3Cl$ was then formed, but no clear product of the $Co(CO)_4$ radicals was detected.

The same reaction occurred upon irradiation of the above toluene solution of I at 230 K. When, however, a solution of I in 2-MeTHF was irradiated with λ = 514.5 nm at 133 K, a completely different reaction was observed. $[Co(CO)_4]^-$ was then formed, as evidenced by its strong IR band at 1886 cm^{-1}.[40] Besides, weaker bands were observed at 2038, 1940, and 1931 cm^{-1}, which are assigned to the $[Mn(CO)_3(bpy)(2\text{-}MeTHF)]^+$ cation. This assignment is based on the close agreement between these frequencies and those of the cation $[Mn(CO)_3(iPr\text{-}DAB)(2\text{-}MeTHF)]^+$ (iPr = isopropyl; 2043, 1939, and 1928 cm^{-1}), produced by irradiation of $(CO)_5MnMn(CO)_3(iPr\text{-}DAB)$[11] in 2-MeTHF at 133 K and of the closely related cation $[Mn(CO)_3(iPr\text{-}DAB)(THF)]^+$ (2037 and 1937 cm^{-1}), which had been prepared separately.[11]

Table II. Quantum Yields of Photochemical Reactions of $(CO)_4CoM(CO)_3(bpy)$ (M = Mn, Re), Measured in Toluene at 233 K

complex	reactant	Φ, mol/einstein
$(CO)_4CoMn(CO)_3(bpy)$ (I)	$P(nBu)_3$	60[a]
	$P(cHx)_3$	27[a]
	$P(OMe)_3$	21[a]
	$P(OPh)_3$	12[a]
	PPh_3	7[a]
$(CO)_4CoRe(CO)_3(bpy)$ (II)	$P(nBu)_3$	0.65[b]
	$P(cHx)_3$	0.31[b]
	$P(OMe)_3$	0.30[b]
	$P(OPh)_3$	0.16[b]
	PPh_3	0.25[b]
	CBr_4	0.34[b]
	...	0.10[b]

[a] Estimated error 20%; a 200-fold excess of PR_3 was used; λ_{irr} = 514.5 nm. [b] Estimated error 10%; a 500-fold excess of PR_3 or CBr_4 was used; λ_{irr} = 476.5 nm.

Apparently, the following reaction had occurred:

$$(CO)_4CoMn(CO)_3(bpy) \xrightarrow[133\ K,\ 2\text{-}MeTHF\ (S)]{h\nu} [Mn(CO)_3(bpy)S]^+ + [Co(CO)_4]^- \quad (3)$$

Raising the temperature of the solution caused a back-reaction of the ions to the parent compound. In order to establish whether the above reaction proceeded via a homolytic or heterolytic splitting of the metal–metal bond, the reaction was also performed in the presence of CBr_4, which is an effective radical scavenger because of its relatively low C–Br bond energy.[41] No ions were then formed, but instead $Mn(CO)_3(bpy)Br$ was produced, as evidenced by its CO stretching frequencies at 2027, 1948, and 1913 cm^{-1}.[30] In a later section the mechanism of this reaction will be discussed in light of these results.

Additional bands were obtained at 2122 (w), 2072 (m), 2061 (w), and 2041 (s) cm^{-1}. $Co_2(CO)_8$ has its CO stretching frequencies in toluene at 2071 (s), 2040 (s), 2021 (s), 1860 (w), and 1847 (w) cm^{-1}, while the CO vibrations of $Co_3(CO)_9(CCl_3)$ in benzene were observed at 2109, 2061, 2044, and 2030 cm^{-1},[39] so a mixture of $Co_2(CO)_8$ and $Co_3(CO)_9CBr_3$ may have been formed here. It should be emphasized that the $Co(CO)_4$ radicals are known to be not very reactive with respect to CX_4 (X = Cl, Br).[42] Since the secondary reactions of the $Co(CO)_4$ radicals, formed by the homolysis reaction, are still not very clear, they are the subject of a more detailed study.

The photochemical reactions with phosphines had to be carried out at low temperature ($T < 230$ K) in order to avoid thermal reactions between both species. Irradiation with λ = 514.5 nm of such a low-temperature solution of I in toluene or 2-MeTHF in the presence of PR_3 caused the formation of $[Co(CO)_4]^-$ (ν(CO) = 1886 cm^{-1}) and of $[Mn(CO)_3(bpy)(PR_3)]^+$. The formation of the cation was evident from the close agreement between its CO stretching frequencies in the case of R = nBu (2032, 1953, and 1924 cm^{-1}) and those of the cation in the ionic compound $[Mn(CO)_3(bpy')(P(nBu)_3)]^+[Mn(CO)_5]^-$ (bpy' = 4,4'-Me_2-bpy; 2032, 1953, and 1930 cm^{-1}).[14] The latter compound, prepared by irradiation of a solution of $(CO)_5MnMn(CO)_3(bpy')$ and $P(nBu)_3$ in THF at room temperature, could be characterized as a stable photoproduct at this temperature by IR and ^1H and ^{31}P NMR spectroscopy. A similar thermal stability was observed for

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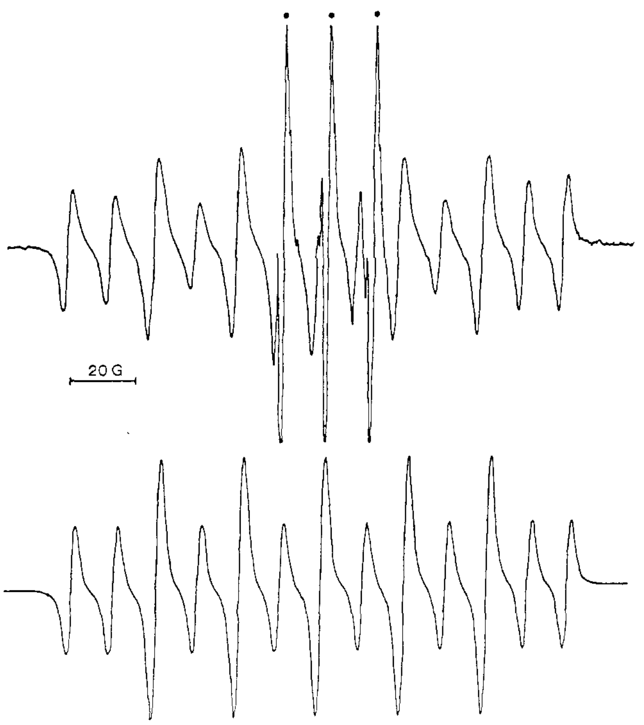

Figure 6. (Top) ESR spectrum of the spin adduct (tBu-$\dot{N}$O)Re(CO)$_3$(bpy) in toluene at room temperature (dots denote peaks due to tBu$_2\dot{N}$O). (Bottom) Simulated spectrum.

the photoproducts [Mn(CO)$_3$(bpy)(PR$_3$)]$^+$[Co(CO)$_4$]$^-$. On the basis of these results, the following reaction is assumed to occur:

$$(CO)_4CoMn(CO)_3(bpy) + PR_3 \xrightarrow[T < 230\ K]{h\nu} [Mn(CO)_3(bpy)(PR_3)]^+ + [Co(CO)_4]^- \quad (4)$$

Table I clearly demonstrates the dependence of the CO stretching frequencies of the cation on the basicity of the PR$_3$ ligand. A similar effect has been observed for the Re cations.

A remarkable aspect of this disproportionation reaction 4 is its high quantum yield. For all five PR$_3$ ligands used (R = nBu, cHx, Ph, OMe, and OPh), the reaction proceeded photocatalytically with quantum yields varying from 7 (R = Ph) to 60 mol/einstein (R = nBu) (Table II). During these quantum yield determinations a 200-fold excess of PR$_3$ was used and the laser power was 0.5–1 mW. The detailed mechanism of this photocatalytic reaction will be discussed below.

(CO)$_4$CoRe(CO)$_3$(bpy) (II). All photochemical reactions were performed by irradiation with λ = 476.5 nm into the MLCT band (λ_{max} = 454 nm in 2-MeTHF) of complex II. Irradiation of a room-temperature solution of II in toluene or 2-MeTHF did not produce a photoproduct. So, in contrast to the case for complex I, no dimeric species Re$_2$(CO)$_6$(bpy)$_2$ was formed. This does not, however, imply that no reaction occurred. On the contrary, homolysis of the metal–metal bond in such a (CO)$_4$CoM(CO)$_3$(bpy) (M = Mn, Re) complex may be followed either by dimerization of the M(CO)$_3$(bpy) radicals to give M$_2$(CO)$_6$(bpy)$_2$ or by a fast back-reaction of the Co(CO)$_4$ and M(CO)$_3$(bpy) radicals to give the parent compound. The first reaction was observed for complex I; the second one may very well take place for complex II. Unfortunately, this proposal could not be confirmed by flash photolysis, since the power of the exciting dye-laser line in the visible was too low for this purpose. There is, however, evidence for the formation of Re(CO)$_3$(bpy) radicals from ESR measurements on this system. To a 10^{-4} M solution of complex II in toluene was added a 3-fold excess of tBu-$\dot{N}$O, which is an effective radical trap, forming the spin adduct A-$\dot{N}$O-tBu with radicals A.[21,43,44] Irradiation of this solution by a Hg lamp provided with a 450 nm cutoff light filter at −55 °C did not produce an ESR signal. Raising the temperature of the solution stepwise to room temperature and using the same irradiation time (1 s) at each temperature caused a regular increase of the ESR signal. A maximum was reached at room temperature, and the ESR spectrum of the tBu-$\dot{N}$O-Re(CO)$_3$(bpy) spin adduct, formed at this temperature, is shown in Figure 6, together with the simulated spectrum. The *g* value is 2.0085. The coupling constants a_{Re} = 27.35 G and $a_{N(NO)}$ = 13.68 G, derived from these spectra, are in good agreement with the values obtained by Andréa et al. for similar spin adducts.[21] The lines marked with a dot belong to tBu$_2\dot{N}$O and are therefore not present in the simulated spectrum.

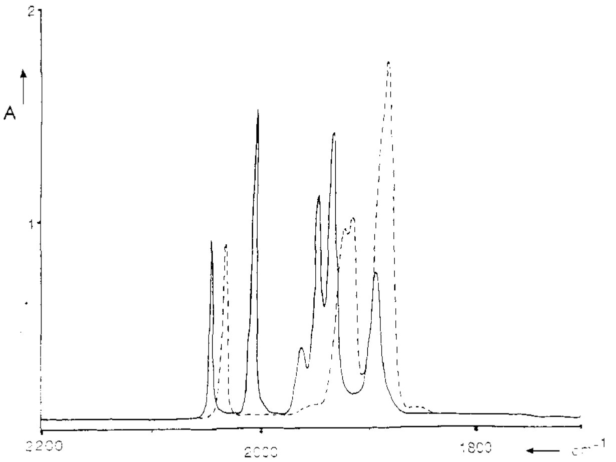

Figure 7. IR spectra (CO stretching region) of (CO)$_4$CoRe(CO)$_3$(bpy) (—) and its photoproduct (- - -) in 2-MeTHF at 133 K (λ_{irr} = 476.5 nm).

The formation of radicals upon irradiation of complex II was also evident from its photochemical reaction with CBr$_4$ in toluene at 230 K. Re(CO)$_3$(bpy)Br was then formed with CO stretching frequencies at 2022, 1923, and 1897 cm^{-1}. Additional bands at 2072 and 2038 cm^{-1} belong to Co$_2$(CO)$_8$. The 2021-cm^{-1} band of Co$_2$(CO)$_8$ will be hidden under the 2022-cm^{-1} band of Re(CO)$_3$(bpy)Br; the weak bands at 1860 and 1847 cm^{-1} of this dimer could not be detected.

Although a solution of complex II in 2-MeTHF did not produce a photoproduct at room temperature, the following reaction was observed in this solvent upon irradiation at 133 K:

$$(CO)_4CoRe(CO)_3(bpy) \xrightarrow[133\ K,\ 2\text{-}MeTHF\ (S)]{h\nu} [Re(CO)_3(bpy)(S)]^+ + [Co(CO)_4]^- \quad (5)$$

The IR spectra of both the parent compound and the photoproduct of this reaction are shown in Figure 7. The cation frequencies (2033, 1924, and 1916 cm^{-1}) closely correspond to those of the cation [Re(CO)$_3$(bpy)(THF)]$^+$ (2035, 1932, and 1911 cm^{-1}), which was prepared separately. The strong band at 1886 cm^{-1} belongs to the tetrahedral [Co(CO)$_4$]$^-$ ion.

Raising the temperature of the solution to room temperature resulted in a complete back-reaction of the ions to the parent compound.

Irradiation of a solution (*T* = 230 K) of II and of one of several phosphines in toluene or 2-MeTHF resulted again in the formation of an ionic photoproduct:

$$(CO)_4CoRe(CO)_3(bpy) + PR_3 \xrightarrow[230\ K]{h\nu} [Re(CO)_3(bpy)(PR_3)]^+ + [Co(CO)_4]^- \quad (6)$$

The CO stretching frequencies of the cations, presented in Table I, closely correspond to those of the Mn analogues and strongly depend on the nucleophilic character of the PR$_3$ ligand. The quantum yields of these reactions, determined for a 500-fold excess of PR$_3$, vary between 0.16 and 0.65 mol/einstein (Table II). These

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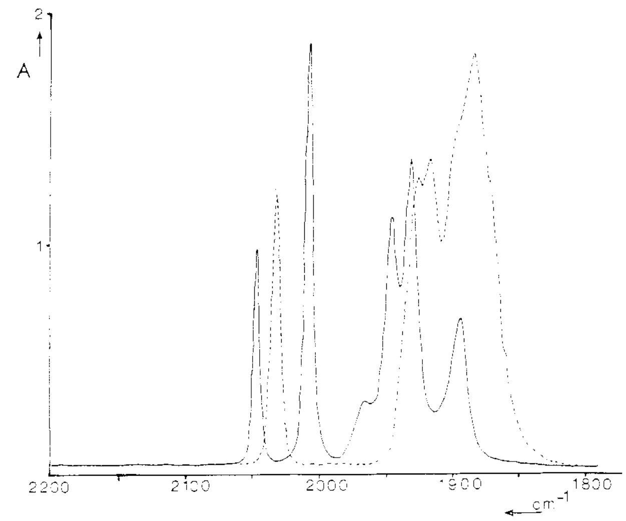

Figure 8. IR spectra (CO stretching region) of $(CO)_4CoRe(CO)_3(bpy)$ (—) and its photoproduct (- - -) in toluene at 230 K (λ_{irr} = 476.5 nm).

values are much lower than those obtained for complex I, and the reactions are clearly not photocatalytic in this case.

According to eq 3–6 both complexes I and II disproportionate in a coordinating solvent and also in the presence of a PR_3 ligand. However, complex II appeared to disproportionate already in toluene. Figure 8 presents the IR spectrum of the photoproduct obtained by irradiation of complex II in toluene at 230 K. The bands at 2034, 1930, and 1919 cm^{-1} point to the formation of a $[Re(CO)_3(bpy)]^+$ cation, although these frequencies are nearly as low as those of the corresponding $[Re(CO)_3(bpy)(2\text{-}MeTHF)]^+$ cation (Table I). This cannot be due to coordination of a solvent molecule here since toluene is too weak a base. This frequency lowering is therefore caused by a direct interaction between the cation and anion in a contact ion pair. This interaction is also responsible for the splitting of the degenerate stretching vibration of the $[Co(CO)_4]^-$ ion around 1885 cm^{-1} (see Figure 8). The reaction therefore proceeds according to eq 7.

$$(CO)_4CoRe(CO)_3(bpy) \xrightarrow[\text{toluene, 230 K}]{h\nu} \{Re(CO)_3(bpy)^+{\cdot}Co(CO)_4^-\} \quad (7)$$

In 2-MeTHF at 133 K this contact ion pair is no longer present since the solvent molecules then coordinate to the cation, producing $[Re(CO)_3(bpy)(2\text{-}MeTHF)]^+$ and the tetrahedral anion $[Co(CO)_4]^-$. Because of this, the CO stretching mode of this anion is observed as a narrow band in the IR spectrum (Figure 7).

Edgell et al.[45–47] have shown that, if $Na^+[Co(CO)_4]^-$ is dissolved in very polar solvents such as DMSO, DMF, and CH_3CN, the cation is completely surrounded by solvent molecules, preventing the formation of contact ion pairs. In less polar solvents, however, contact ion pairs appeared to be formed. The authors concluded from these findings that the solvent polarity or electron-donating ability determines the contact ion pair formation.

The above reaction is accompanied by the disappearance of the low-energy MLCT band. Raising the temperature of the solution caused a complete back-reaction to the parent compound.

The above reaction is remarkable since disproportionation of metal–metal-bonded carbonyls has only been observed so far in coordinating solvents or in the presence of nucleophiles.[2–5] Only in one case, the disproportionation of $(\eta^5\text{-}C_5H_5)(CO)_2FeCo(CO)_4$ into $[(\eta^5\text{-}C_5H_5)Fe(CO)_3]^+$ and $[Co(CO)_4]^-$ in a CO-doped argon matrix at 10 K,[6] has a heterolytic splitting of the metal–metal bond been postulated so far. For the reaction under study the following observations are all in favor of homolysis of the metal–metal bond as the primary photoprocess. First of all, the quantum yields for the reaction of II with CBr_4 (500-fold excess) and for the disproportionation of II, both in toluene at 230 K, differ only by a factor of 3 (0.34 and 0.10 mol/einstein, respectively; see Table II). So, if these reactions proceed via different primary photoprocesses, both are expected to occur independently upon irradiation of II in the presence of CBr_4. This, is, however, not the case since only $Re(CO)_3(bpy)Br$ was formed during this reaction. The occurrence of a thermal reaction between $[Re(CO)_3(bpy)]^+$ and CBr_4 could be excluded by adding CBr_4 to an in situ prepared toluene solution of $\{Re(CO)_3(bpy)^+{\cdot}Co(CO)_4^-\}$ at 230 K. No reaction was then observed. Moreover, the complex $[Re(CO)_3(bpy)(THF)]^+(OTF)^-$, prepared by adding at room temperature Ag(OTF) to a THF solution of $Re(CO)_3(bpy)Br$, did not react with CBr_4 (large excess) at this temperature. This result points to a common primary photoprocess, viz. homolysis of the metal–metal bond for both the disproportionation and the reaction with CBr_4. This conclusion is confirmed by the results of the following experiment.

From a solution of complex II in toluene a small volume was injected into an IR cell. The stock solution was kept in the dark. The solution in the IR cell was then irradiated at 230 K for 5 min by a 40-mW, 590-nm laser line. This gave rise to 40% conversion of the parent compound into $\{Re(CO)_3(bpy)^+{\cdot}Co(CO)_4^-\}$. To the stock solution was then added a small amount of the complex $(CO)_5MnRe(CO)_3(bpy)$, which is known to undergo efficient splitting of the metal–metal bond upon MLCT excitation. Mixing these two metal–metal-bonded species did not cause a thermal reaction. From this solution again a small volume was injected into the IR cell and the photochemical experiment was repeated with the same irradiation source. The photoproduction of extra $Re(CO)_3(bpy)$ radicals had a dramatic influence on the rate of conversion of complex II into $\{Re(CO)_3(bpy)^+{\cdot}Co(CO)_4^-\}$. The reaction was already completed after 3 min of irradiation. The only Mn-containing product was $Mn_2(CO)_{10}$, which means that the $Mn(CO)_5$ radicals did not take part in the reaction. The above results clearly show that the disproportionation reaction is not the result of a heterolytic splitting of the metal–metal bond as the primary photoprocess but of a homolysis reaction followed by electron transfer. The mechanism of this reaction will be discussed further in the next section in relationship to the other reactions of complexes I and II.

Discussion

There is good evidence that all photochemical reactions described in the preceding section proceed via homolytic splitting of the metal–metal bond. Thus, irradiation of complex I in a noncoordinating solvent produced $Mn_2(CO)_6(bpy)_2$ by dimerization of the $Mn(CO)_3(bpy)$ radicals. For complex II no such dimer was observed, although the ESR spectra showed that $Re(CO)_3(bpy)$ radicals were formed upon irradiation of II. However, from the fact that these $Re(CO)_3(bpy)$ radicals could not be detected as free radicals, as in the case of $(CO)_5MnRe(CO)_3(bpy)$[11] and $Ph_3SnRe(CO)_3(bpy)$,[21] but only by spin trapping with tBu-NO, it can be concluded that their lifetime is only short, presumably because of a fast back-reaction to the parent compound.

Further evidence for the homolysis reaction is the formation of $M(CO)_3(bpy)Br$ as the only photoproduct upon irradiation of these complexes in the presence of CBr_4.

In the presence of PR_3, in 2-MeTHF at 133 K and in toluene at 230 K (only in the case of complex II), ionic photoproducts were formed. Also in these cases, however, the primary photoprocess is a homolytic and not a heterolytic splitting of the metal–metal bond since all reactions were suppressed by adding a radical scavenger to the solution. In order to explain the formation of the ionic photoproducts after the homolysis reaction, it has to be realized that, according to the ESR spectra, the unpaired electron mainly resides on the bpy ligand.[21] This means that the radicals are 16-electron $Mn^+(CO)_3(bpy)^{\bullet-}$ species, which can readily take up a nucleophile such as PR_3 or 2-MeTHF (at low temperature only). Some of these radical adducts $L'M(CO)_3(bpy)$ have been characterized by ESR.[21] They are highly

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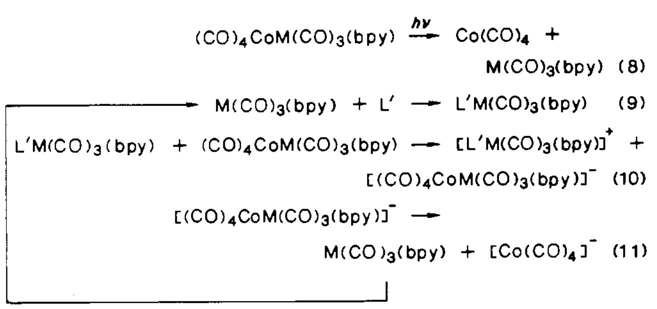
reducing agents, which can transfer an electron to the parent compound, thus initiating an electron transfer chain reaction,[3,4,48] as shown in reactions 8–11. These reactions are indeed photo-



$$(CO)_4CoM(CO)_3(bpy) \xrightarrow{h\nu} Co(CO)_4 + M(CO)_3(bpy) \quad (8)$$

$$M(CO)_3(bpy) + L' \rightarrow L'M(CO)_3(bpy) \quad (9)$$

$$L'M(CO)_3(bpy) + (CO)_4CoM(CO)_3(bpy) \rightarrow [L'M(CO)_3(bpy)]^+ + [(CO)_4CoM(CO)_3(bpy)]^- \quad (10)$$

$$[(CO)_4CoM(CO)_3(bpy)]^- \rightarrow M(CO)_3(bpy) + [Co(CO)_4]^- \quad (11)$$

catalytic in the case of complex I since quantum yields higher than 1 were obtained for all PR_3 ligands. The quantum yields strongly depend on the steric and electronic properties of PR_3 (Table II). Φ is largest for the basic and not very bulky $P(nBu)_3$ ligand and decreases when the ligand becomes less basic and bulkier. The size of L′ will mainly influence the rate of reaction 9, its nucleophilic character that of reaction 10.

Similar photocatalytic disproportionation reactions have been observed by us for the analogous complexes $(CO)_5MnMn(CO)_3(\alpha\text{-diimine})$, which also produce $Mn(CO)_3(\alpha\text{-diimine})$ radicals upon irradiation into the MLCT band.[14] Stiegman and Tyler[3,4,49] and McCullen and Brown[50] observed photodisproportionation of the dimers $Mn_2(CO)_{10}$, $Cp_2M_2(CO)_6$ (M = Mo, W), and $Cp_2Fe_2(CO)_4$ in the presence of an electron-donating ligand or in a coordinating solvent. In that case, however, the reducing agent is most probably a 19-electron radical species with the unpaired electron mainly localized at the central metal atom. In the case of complex II the disproportionation is not photocatalytic. This is understandable in view of the above observation that the $Re(CO)_3(bpy)$ radicals are only short-lived because of a fast back-reaction to the parent compound. However, although the quantum yields for complex II are much lower than for complex I, their values show a similar dependence on the steric and electronic properties of the PR_3 ligands (Table II). This again points to a similar reaction mechanism for both complexes. A very interesting result of this study is the photodisproportionation of complex II in toluene at $T \leq 230$ K. This reaction was suppressed by addition of CBr_4, which means that the primary photoprocess is homolysis of the Co–Re bond. The $Re(CO)_3(bpy)$ radicals, produced by this reaction, cannot form an adduct according to reaction 9, since toluene is only a very weak base. Apparently, this radical can already transfer an electron to the parent compound or to $Co(CO)_4$ without formation of such a radical adduct. As far as we know, such a reaction has never been observed before. In all cases known, the 16- or 17-electron radicals first form an adduct with a basic ligand before transferring an electron to the parent compound.

All reactions described in this article are therefore the result of a homolytic cleavage of the metal–metal bond from the $^3\sigma\sigma^*$ states of the complexes. Apparently these states, which become populated by energy transfer from the lowest ^{3}MLCT states (see Figure 1), have a much weaker metal–metal than metal (Mn or Re)–CO bond here, since under no circumstances was release of CO observed upon irradiation into the MLCT band (see Introduction).

Acknowledgment. H. Harmsen is thanked for modifying the UV/vis spectrophotometer and the glass fibers for the quantum yield measurements of the photocatalytic reactions. W. G. J. de Lange is thanked for the preparation of the Re complex and R. Sitters for his assistance during the ESR measurements. The Netherlands Foundation of Chemical Research (SON) and the Netherlands Organization for the Advancement of Pure Research (NWO) are thanked for financial support.

Registry No. I, 117828-09-8; II, 117828-10-1; $P(nBu)_3$, 998-40-3; $P(cHx)_3$, 2622-14-2; $P(OMe)_3$, 121-45-9; $P(OPh)_3$, 101-02-0; PPh_3, 603-35-0; CBr_4, 558-13-4; $Mn_2(CO)_6(bpy)Br$, 97570-76-8; $Mn(CO)_3(bpy)Br$, 38173-71-6; $[Mn(CO)_3(bpy)(2\text{-MeTHF})]^+$, 117828-12-3; $[Mn(CO)_3(bpy)(P(nBu)_3)]^+$, 117828-13-4; $[Mn(CO)_3(bpy)(P(cHx)_3)]^+$, 117828-14-5; $[Mn(CO)_3(bpy)(PPh_3)]^+$, 117894-33-4; $[Mn(CO)_3(bpy)(P(OMe)_3)]^+$, 117828-15-6; $[Mn(CO)_3(bpy)(P(OPh)_3)]^+$, 117828-16-7; $Re(CO)_3(bpy)Br$, 40231-87-6; $[Re(CO)_3(bpy)(2\text{-MeTHF})]^+$, 117828-17-8; $[Re(CO)_3(bpy)(P(nBu)_3)]^+$, 117828-18-9; $[Re(CO)_3(bpy)(P(cHx)_3)]^+$, 117828-19-0; $[Re(CO)_3(bpy)(PPh_3)]^+$, 117828-20-3; $[Re(CO)_3(bpy)(P(OMe)_3)]^+$, 117828-21-4; $[Re(CO)_3(bpy)(P(OPh)_3)]^+$, 117828-22-5; $[Re(CO)_3(bpy)]^+$, 117828-11-2; 2-MeTHF, 96-47-9.

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Luminescent Tetrametallic Complexes of Ruthenium

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Tetrametallic complexes constructed around the metal core $Ru(dpp)_3^{2+}$ (where dpp = 2,3-bis(2-pyridyl)pyrazine) have been prepared and characterized. The complexes, which have the general formula $Ru[(dpp)ML_2]_3^{n+}$, where $ML_2 = Ru^{II}(bpy)_2$ (n = 8), $Ru^{II}(phen)_2$ (n = 8), and $Ru^{II}(tpy)Cl$ (n = 5) and bpy = 2,2′-bipyridine, phen = 1,10-phenanthroline, and tpy = 2,2′:6′,2″-terpyridine, are prepared from the reaction of $Ru(dpp)_3^{2+}$ with ML_2Cl_2 in ethanol/water. The tetrametallic complexes luminesce at room temperature in acetonitrile with emissions characteristic of a single ruthenium center with excited-state lifetimes in the 100-ns range. Electrochemically, the most facile reductions occur at the dpp ligand, and the lowest energy oxidation is a single peak associated with the three peripheral ruthenium centers.

Introduction

In an earlier publication,[3] we described the preparation of the highly luminescent complex $Ru(dpp)_3^{2+}$ (dpp = 2,3-bis(2-pyridyl)pyrazine). The significance of this complex is that it can form the core of new polymetallic species that may have application in excited-state energy- and electron-transfer reactions.[4] Multidentate bridging ligands have only recently received much attention in the construction of polymetallic systems.[5] However, the extent of electronic coupling present in the ground state of

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