Metal to Ligand Charge-Transfer Photochemistry of Metal–Metal-Bonded Complexes. 12.[†] The Primary Photoprocess of $(CO)_5ReMn(CO)_3(\alpha$-diimine) Complexes Studied by Temperature- and Pressure-Dependent Photochemistry and Pico- and Nanosecond Flash Photolysis

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Photoreactions of $(CO)_5ReMn(CO)_3(\alpha$-diimine) complexes have been studied at different temperatures and pressures and by time-resolved UV–vis absorption spectroscopy on pico- to millisecond time scales. Irradiation into the MLCT absorption band in CH_2Cl_2 or in toluene/CCl_4 mixtures produces $Re(CO)_5Cl$ and $Mn(CO)_3(\alpha$-diimine)Cl whereas the substituted product $(CO)_5ReMn(CO)_2(PPh_3)(\alpha$-diimine) is formed in the presence of PPh_3. Irradiation with 9,10-phenanthrenequinone leads to semiquinone radical complexes. Similar quantum yield values were obtained for all these reactions and also for various photoreactions taking place in mixtures of 9,10-phenanthrenequinone and PPh_3. These observations indicate that all the final products are formed from the same primary photoproduct that was characterized spectroscopically in low-temperature solutions as a CO-(semi)bridged $(CO)_4Re(\mu$-CO)-$Mn(CO)_2(\alpha$-diimine) species formed by CO photodissociation from the parent complex. Very similar apparent volumes of activation found for the reaction of $(CO)_5ReMn(CO)_3$(4,4′-dimethyl-2,2′-bipyridine) with CH_2Cl_2 (17.2 ± 1.3 cm^3 mol^{-1}) and PPh_3 (15.7 ± 0.5 cm^3 mol^{-1}) are again consistent with the involvement of an identical primary photoprocess in both reactions. Moreover, the apparent activation volumes are similar to those of thermal CO-loss reactions in analogous complexes. Finally, picosecond (0 ps–10 ns) and nanosecond (20 ns–200 μs) laser flash photolysis suggested that the formation of $(CO)_4Re(\mu$-CO)$Mn(CO)_2(\alpha$-diimine) is the only primary photoprocess, the usual Re–Mn bond homolysis being absent. Picosecond data indicate that it is a very rapid, most probably subpicosecond, process.

Introduction

Mechanistic studies in the field of organometallic photochemistry have mainly been confined to transition metal carbonyls. Among these complexes, the metal–metal-bonded species $M_2(CO)_{10}$ (M = Mn, Re), $Cp_2Fe_2(CO)_4$, and $Cp_2M_2(CO)_6$ (M = Mo, W) appeared to undergo both metal–metal-bond homolysis and release of CO as primary photoprocesses.[1-4] Recently, we studied in detail the photochemistry of a series of related complexes $L_nM'M(CO)_3(\alpha$-diimine) (L_nM' = $(CO)_5Mn$, $(CO)_5Re$, $(CO)_4Co$, $Cp(CO)_2Fe$, Ph_3Sn; M = Mn, Re; α-diimine = bpy, phen, etc.), which contain a metal–metal bond and show an intense metal to α-diimine charge-transfer (MLCT) band in the visible spectral region.[5-9] Irradiation into this MLCT band gave rise to homolysis of the metal–metal bond and/or to release of CO from the $M(CO)_3(\alpha$-diimine) fragment. Rhenium complexes $L_nM'Re(CO)_3(\alpha$-diimine) exhibited M′–Re bond homolysis only, while both reactions were observed for some of corresponding $L_nM'Mn(CO)_3(\alpha$-diimine) complexes.

Quinones appeared to react with the primary photoproducts of both reactions, giving rise to the formation of different complexes.[9] $M(CO)_3(\alpha$-diimine) (M = Mn, Re) radicals formed by homolysis of the M′–M bond react with 9,10-phenanthrenequinone (PhenQ) by an one-electron oxidative addition to produce $M(CO)_3(\alpha$-diimine)(PhenSQ) (SQ = semiquinone radical anion). On the other hand, the CO-loss products of the type $(CO)_5MMn(CO)_2(\alpha$-diimine) (M = Mn, Re) reacted with PhenQ to give[9] ultimately $Mn(\alpha$-diimine)$(PhenSQ)_2$. This compound was also found[9] to be the only product of the photolysis of $Ph_3SnMn(CO)_3(\alpha$-diimine) which is known[10] to undergo CO dissociation as the only photochemical reaction.

The behavior of the $(CO)_5ReMn(CO)_3(\alpha$-diimine) complexes is exceptional in the $L_nM'M(CO)_3(\alpha$-diimine) family. Their photolysis leads to CO photosubstitution whereas radical-coupling products, *i.e.* $Mn_2(CO)_6(\alpha$-diimine$)_2$ and $Re_2(CO)_{10}$ do not appear among the primary photoproducts.[9] This indicates that the Re–

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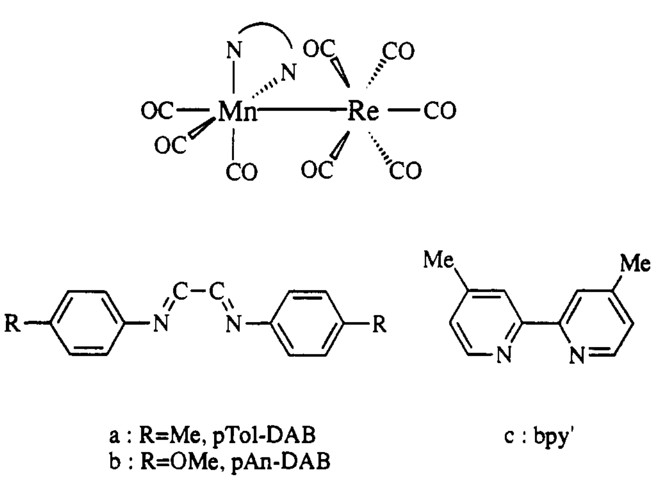

Figure 1. General structures of the $(CO)_5ReMn(CO)_3(\alpha\text{-diimine})$ complexes, **1**, and of the α-diimine ligands used.

Mn bond does not dissociate upon MLCT excitation. In contrast with this conclusion, the complexes $(CO)_5ReMn(CO)_3(\alpha\text{-diimine})$ were found[9] to react photochemically with PhenQ to give not only $Mn(\alpha\text{-diimine})(PhenSQ)_2$ but also the oxidative-addition product $Mn(CO)_3(\alpha\text{-diimine})(PhenSQ)$. Photoreaction with CH_2Cl_2 affords Cl-abstraction products $Re(CO)_5Cl$ and $Mn(CO)_3(\alpha\text{-diimine})Cl$. Preliminary experiments[9] have indicated that all these reactions occur with very similar quantum yields of about 0.4–0.5, indicating that the same primary process is involved in all these diverse photoreactions. From these results alone, it was not clear whether this behavior of the $(CO)_5ReMn(CO)_3(\alpha\text{-diimine})$ complexes is caused by a higher reactivity of their CO-loss products toward PhenQ and CH_2Cl_2 or if these complexes yet undergo, similarly to their congeners, both homolysis and release of CO as primary photoprocesses.

In order to solve this problem and to learn more about the primary photoprocess(es) of these compounds, we have studied in detail the photoreactions of three $(CO)_5ReMn(CO)_3(\alpha\text{-diimine})$ complexes, **1**. The structures of the complexes and α-diimine ligands used, 1,4-di-*p*-tolyl-1,4-diaza-1,3-butadiene (pTol-DAB, **a**), 1,4-di-*p*-anisyl-1,4-diaza-1,3-butadiene (pAn-DAB, **b**), and 4,4'-dimethyl-2,2'-bipyridine (bpy', **c**), are depicted in Figure 1.

Experimental Section

Materials and Preparations. THF and 2-MeTHF were freshly distilled from a sodium–benzophenone mixture. Toluene was carefully dried by refluxing with sodium. $CaCl_2$ was used as a drying agent for CH_2Cl_2 and 2-chlorobutane. All solvents were distilled, stored, and handled under nitrogen. PPh_3 (Aldrich and Strem) was recrystallized from hexane or ethanol, 9,10-phenanthrenequinone, (PhenQ), Aldrich, and 4,4'-dimethyl-2,2'-bipyridine (bpy', **c**), Merck, were used as received. Complexes **1**[11–13] and both 1,4-di-*p*-tolyl-1,4-diaza-1,3-butadiene (pTol-DAB, **a**) and 1,4-di-*p*-anisyl-1,4-diaza-1,3-butadiene (pAn-DAB, **b**) ligands[14] were synthesized by literature procedures.

Spectroscopic Measurements. IR spectra were recorded on a Nicolet 7199B FTIR spectrophotometer using a MCT detector cooled by liquid nitrogen (32 scans, resolution 1.0 cm^{-1}). A Bio-Rad 3240-SPC (16 scans, resolution 2.0 cm^{-1}) instrument was used in some experiments. Electronic absorption spectra were measured on a Perkin-Elmer Lambda 5 UV–vis spectrophotometer connected to a Model 3600 data station. Low-temperature UV–vis and IR measurements were performed using an Oxford Instruments DN 1704/54 liquid-nitrogen cryostat.

Continuous-Wave Photochemistry. An SP 2025 argon ion laser and a CR 590 tunable dye laser with Rhodamine 6G dye were used as light sources in the temperature-dependent photochemical experiments. The light-sensitive samples used for the quantum yield determinations were prepared in a carefully blinded room, illuminated with red light. They were placed in a specially constructed light-tight compartment equipped with shutters that allowed us to record the spectra but prevented the stray light from entering the sample.[7] Photon fluxes were measured with a Coherent Model 210 ($P_\lambda > 15$ mW) or Model 212 ($P_\lambda < 15$ mW) power meter. The experimental setup was tested with ferrioxalate actinometry. To measure quantum yields, the photochemical reactions of **1a** were followed by the spectral changes in the UV–vis region and the decay of the MLCT absorption band was monitored. Corrections were applied for light absorption by the photoproduct of reaction 2 (*vide infra*). No correction was necessary for reactions 1 and 3. Although all reactions investigated occurred isosbestically to (near) completion, quantum yields were evaluated only from data obtained for conversions not exceeding 15%. Lower conversions were used when necessary, especially in reactions involving PhenQ and in competition reactions. Incident light intensity was usually 4.3×10^{-8} einstein s^{-1}, as corresponds to the 10-mW average laser power at 514.5 nm. Initial concentrations of **1a** were in the range 3×10^{-5}–1×10^{-4} M. Extinction coefficients at the irradiation wavelengths were determined from those at the band maxima: 1.05×10^4 M^{-1} cm^{-1} at 571 nm for **1a** in CH_2Cl_2; 5260 M^{-1} cm^{-1} at 571 nm for the product of reaction 2, $(CO)_5ReMn(CO)_2(PPh_3)(pTol\text{-}DAB)$. The latter value was determined after completion of the photolysis.

Pressure dependence of photochemical quantum yields was measured according to a procedure described previously.[15] Samples were irradiated under five different pressures between 0.1 and 150 MPa in a pillbox quartz cell[16] that was placed inside a two-window high-pressure cell.[17] The solutions were stirred by a Teflon-coated magnetic stirrer during irradiation. Solutions of complex **1a** in CH_2Cl_2 were irradiated by the 577-nm line selected by an interference filter from the output of an Oriel 100-W high-pressure mercury lamp. Light intensities were measured by a Si photodiode which was calibrated at 577 nm by an Aberchrome 999P actinometer.[18] The incident light intensity was kept in the range (1.3–1.4) $\times 10^{-9}$ einstein s^{-1}. Quantum yields were evaluated as described above. Values listed in Table 4 are the averages of at least four independent measurements.

Flash Photolysis. Picosecond laser flash photolysis measurements were performed using the equipment[19] of the Canadian Centre for Picosecond Laser Spectroscopy at Concordia University, Montreal. A Q-switched Quantel YG 402 G Nd:YAG laser, which provided 30-ps pulses at 1064 nm, was used. Excitation pulses at 532 nm, energy $\simeq$ 2 mJ/pulse, were obtained by frequency doubling. Transient absorption spectra were measured at selected delay times after the sample excitation using probe pulses of a white continuum (425–675 nm) generated by focusing part of the fundamental laser beam on a cell with D_3PO_4. Delay times between the excitation and probe pulses were varied in the 0 ps–10 ns range. An optical multichannel analyzer, EG&G PAR OMA II, with a silicon-enhanced vidicon array detector was used to collect the data. Difference transient absorption spectra were obtained by subtracting the spectra measured with and without previous sample excitation. Each spectrum is an average of 8–10 measurements. Toluene solutions of **1a** were placed in a 2-mm quartz cell and well stirred between laser excitations. Absorbance of the sample solution at the 532-nm excitation wavelength was maintained in the range 0.3–0.6.

The nanosecond laser flash photolysis study employed a Quantel GCR-3 pulsed Nd:YAG laser which provided 1064-nm, 5-ns pulses at a maximum repetition rate of 10 Hz. The pump beam (532 nm, 10 mJ/pulse) was obtained by frequency doubling using KDP crystals. A right-angle optical system using a 1-cm flow-through cell was used for the excitation/analyzing setup. A pulsed Müller SVX 1450 Xe lamp was employed as a light source for the detection beam. The data collection system consisted of a Model 1460 OMA-III console equipped with a 1302 fast pulser, a 1304 gate pulser, and a 1421 MCP-gated diode array detector. Solutions of **1a** and **1b** in deoxygenated toluene were allowed to flow through the spectral cell after each laser pulse to ensure that a fresh sample was always excited. The measurements were carried out at ambient

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Table 1. Spectral Data for Complexes **1a–c** and Their Photoproducts

compound	solvent, temp[a]	ν(CO) bands, cm^{-1}	λ,[b] nm	ref
$(CO)_5ReMn(CO)_3$(pTol-DAB) (**1a**)	THF, RT	2095, 2025, 2006, 1990, 1971, 1905, 1896	560	45
$(CO)_5ReMn(CO)_3$(pAn-DAB) (**1b**)	THF, RT	2094, 2026, 2006, 1988, 1970, 1903, 1896	576	45
	CH_2Cl_2, RT	2095, 2027, 2005, 1990, 1971, 1905, 1894	577	
$(CO)_5ReMn(CO)_3$(bpy′) (**1c**)	THF, RT	2072, 1972, 1885	552	45
$(CO)_5ReMn(CO)_2(PPh_3)$(pTolDAB)	THF, RT	2091, 1993, 1956, 1890, 1839	586	*c*
$(CO)_5ReMn(CO)_2(PPh_3)$(pAn-DAB)	THF, RT	2087, 1991, 1953, 1886, 1835	584	*c*
	CH_2Cl_2, RT	2089, 1990, 1957, 1887, 1831	592	*c*
$(CO)_5ReMn(CO)_2(PPh_3)$(bpy′)	THF, RT	2060, 1974, 1958, 1932, 1881, 1827	650	*c*
$(CO)_5ReMn(CO)_2(PBu^n_3)$(bpy′)	2-MeTHF, RT	2056, 1973, 1954, 1928, 1878, 1821	695	*c*
$(CO)_4Re(\mu\text{-}CO)Mn(CO)_2$(bpy′)	2-MeTHF, 143 K	2059, 1974, 1952, 1922, 1860, 1802	714	*d*
	2-ClBut, 143 K	2059, 1975, 1954, 1926, 1861, 1803	714	*d*
	THF, 173 K	2058, 1971, 1951, 1923, 1862, 1804	730	*d*
	Tol, 183 K	2062, 1983, 1954, 1928, 1863, 1805	740	*d*
$Re(CO)_5Cl$	CH_2Cl_2, RT	2143, 2084, 2046, 1986		9
$Re(CO)_4$(2-MeTHF)Cl	2-MeTHF, 143 K	2093, 2010, 1989, 1969		*e*
$Re(CO)_4(PPh_3)Cl$	CH_2Cl_2, RT	2106		*e*
$Re(CO)_4(PPhMe_2)Cl$	CH_2Cl_2, RT	2105, 2010, 2000, 1942		29
$Mn(CO)_3$(bpy′)Cl	CH_2Cl_2, RT	2028, 1936, 1918		9
$Mn(CO)_3$(pAn-DAB)Cl	CH_2Cl_2, RT	2032, 1944, 1917		*f*
$Mn(CO)_3$(pTol-DAB)Cl	CH_2Cl_2, RT	2034, 1942, 1922		*f*
$Mn(CO)_3$(bpy′)(PhenSQ)	THF, RT	2022, 1929, 1909		9
$Mn(CO)_3$(pTol-DAB)(PhenSQ)	THF, RT	2022, 1929, 1902		*g*
Mn(pTol-DAB)$(PhenSQ)_2$	THF, RT		695	*d*
$Mn(py)_2(DBSQ)_2$	Tol, RT		423 781	*h*
$Re_2(CO)_7(PhenSQ)_2$	KBr, RT	2113, 2015, 1985, 1933, 1914, 1894		*i*
$Re_2(CO)_{10}$	CH_2Cl_2, RT	2068, 2009, 1981		9
	Tol, RT	2070, 2011, 1970		
$Mn_2(CO)_6$(bpy′$)_2$	2-MeTHF, RT	1979, 1932, 1882, 1836	850	11
	THF, 173 K	1973, 1928, 1877, 1857	836	*d*
	Tol, 183 K		837	*d*

[a] Tol = toluene, 2-ClBut = 2-chlorobutane, KBr = in KBr pellet, RT = room temperature. [b] Wavelength corresponding to the maximum of the MLCT absorption band. [c] This work; see refs 11 and 46 for identical or similar complexes. [d] This work. [e] This work, see ref 29 for comparison with analogous compounds. [f] This work; assigned by analogy with similar complexes described in ref 9 and in: Staal, L. H.; Oskam, A.; Vrieze, K. *J. Organomet. Chem.* **1979**, *170*, 235. [g] This work; assigned by analogy with $Mn(CO)_3$(bpy′)(PhenSQ).[9] [h] Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpont, C. G. *J. Am. Chem. Soc.* **1984**, *106*, 2041. [i] deLearie, L. A.; Pierpont, C. G. *J. Am. Chem. Soc.* **1987**, *109*, 703.

temperature, and the spectra are average results of at least 10 measurements. Flash photolytic experiments in CH_2Cl_2 were prevented by the formation of microbubbles upon the laser flash.

Results

Room-Temperature Photochemistry. At room temperature, complexes **1a–c**, dissolved in CH_2Cl_2, reacted according to reaction 1 when irradiated into their visible absorption band. In the presence of an excess PPh_3, photosubstitution 2 occurred in both THF and CH_2Cl_2. The photoproducts were identified by comparing their IR and UV–vis spectra with those of the same or structurally closely related complexes characterized previously; see Table 1. Spectral changes that accompanied reactions of **1a** are presented in Figures 2 and 3. Isosbestic points are well preserved until complete conversion, indicating that neither side reactions nor product (photo)decomposition occurs. Very similar spectral changes were observed during irradiation of complex **1b**. In the case of complex **1c**, reaction 2 could only be followed during short irradiation times since its photoproduct decomposed upon further irradiation. In addition to these reactions, complexes **1** were found to add 9,10-phenanthrenequinone (PhenQ) oxidatively:

$$\mathbf{1} \xrightarrow[\mathrm{CH_2Cl_2}]{h\nu} \mathrm{Re(CO)_5Cl} + \mathrm{Mn(CO)_3(\alpha\text{-diimine})Cl} \qquad (1)$$

$$\mathbf{1} + \mathrm{PPh_3} \xrightarrow[\mathrm{THF\ or\ CH_2Cl_2}]{h\nu} \mathrm{(CO)_5ReMn(CO)_2(PPh_3)(\alpha\text{-diimine})} + \mathrm{CO} \qquad (2)$$

$$\mathbf{1} + \mathrm{PhenQ} \xrightarrow[\mathrm{THF}]{h\nu} \mathrm{Re_2(CO)_7(PhenSQ)_2} + \mathrm{Mn(CO)_3(\alpha\text{-diimine})(PhenSQ)} + \mathrm{Mn(\alpha\text{-diimine})(PhenSQ)_2} \qquad (3)$$

This reaction was studied in more detail for **1a**. The first two products were identified by IR and UV–vis spectra (Table 1), whereas Mn(α-diimine)$(PhenSQ)_2$ was tentatively assigned on the basis of absorption spectra in the visible region (Table 1, ref 9).

The photosubstitution of CO by PPh_3 (reaction 2) is fully competitive with the Cl abstraction from CH_2Cl_2 since irradiation of both **1a** and **1b** in CH_2Cl_2 solution containing excess of PPh_3 afforded $(CO)_5ReMn(CO)_2(PPh_3)$(α-diimine) as the only product. A similar competition was found between the photoreactions of **1a** with CCl_4 and PPh_3 in toluene solutions. At the **1a**/PPh_3/CCl_4 reactant ratio 1/100/50, reaction 2 is responsible for the formation of about 90% of the reaction products. On the other hand, a mixture of $(CO)_5ReMn(CO)_2(PPh_3)$(α-diimine) and chlorine-containing products $Re(CO)_5Cl$, $Re(CO)_4(PPh_3)Cl$, and $Mn(CO)_3$(pTol-DAB)Cl of the Cl abstraction was formed at the 1/50/100 reactant ratio. The intensities of the corresponding IR bands indicate that the Cl-containing species amount to more than 50% of the products.

A more quantitative picture of the photoreactions of **1a**, *i.e.* the CO substitution (2), the Cl abstraction (1), and the oxidative addition (3), and of their competition was obtained from quantum yield data. The isosbestic character of all reactions studied and the absence of any secondary photochemistry (*vide infra*) substantiate the use of quantum yield values based on the disappearance of the reactant, **1a**. Cl abstraction was studied in neat CH_2Cl_2 that was used both as a reactant and as a solvent. The reaction with 9,10-phenanthrenequinone (PhenQ) was

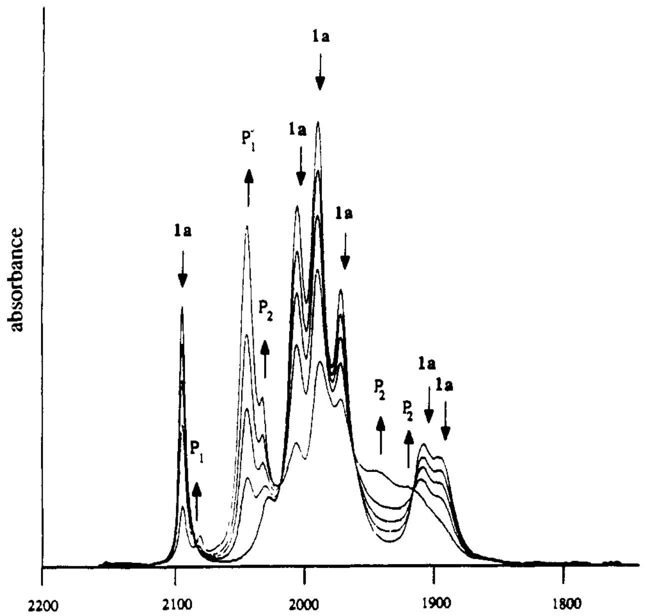

Figure 2. IR spectral changes in the ν(CO) region monitored during the photoreaction of **1a** in CH_2Cl_2 upon 514.5-nm irradiation at ambient temperature. P_1 = $Re(CO)_5Cl$; P_2 = $Mn(CO)_3$(pTol-DAB)Cl.

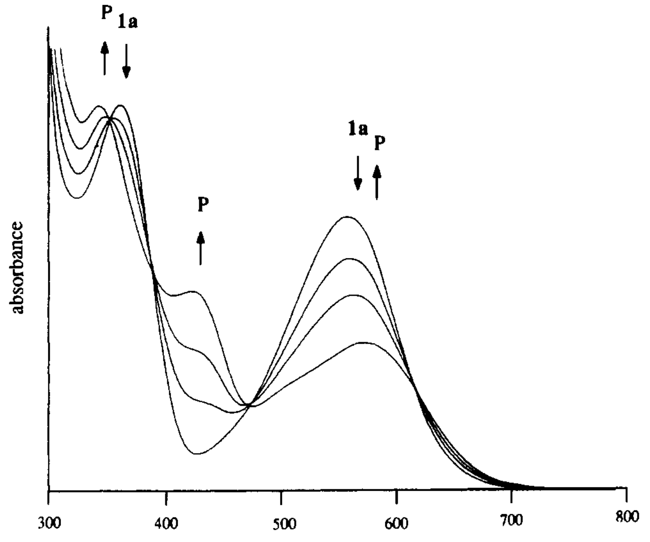

Figure 3. UV–vis spectral changes monitored during the photoreaction of an **1a**/PPh_3 (1/200) mixture in CH_2Cl_2 upon 514.5-nm irradiation. P = $(CO)_5ReMn(CO)_2(PPh_3)$(pTol-DAB).

Table 2. Quantum Yields[a] for the Photoconversion of **1a** Measured in Various Mixtures of **1a**, PPh_3, and PhenQ in CH_2Cl_2 or THF

λ_{irr},[b] nm	**1a**; CH_2Cl_2	**1a**/PhenQ (1/50); THF	**1a**/PPh_3 (1/200); THF	**1a**/PPh_3 (1/200); CH_2Cl_2	**1a**/PhenQ/PPh_3 (1/50/200); THF
458	0.49	0.59	0.57		
514.5	0.42[c]	0.51[c]	0.51	0.44	0.56
592	0.65	0.58	0.50		

[a] Estimated error in ϕ: 10%. Irradiated with Ar^+ laser. [b] Laser power approximately 10 mW at all λ_{irr}. [c] From ref 9.

Table 3. Pressure Dependence of Quantum Yields of Photoreactions 1 (ϕ_1) and 2 (ϕ_2) Measured for Complex **1a**[a]

p, MPa	ϕ_1	ϕ_2	p, MPa	ϕ_1	ϕ_2
0.1	0.58 ± 0.03	0.56 ± 0.02	100	0.38 ± 0.03	0.40 ± 0.04
5.0	0.56 ± 0.03	0.54 ± 0.04	150	0.33 ± 0.03	0.32 ± 0.03
50	0.50 ± 0.04	0.47 ± 0.05			

[a] The concentration of **1a** was in the range 3×10^{-5}–1×10^{-4} M. ϕ_2 was measured in the presence of 3.6×10^{-2} M PPh_3. Irradiation was done with the 577-nm spectral line of a mercury lamp.

followed in THF solutions containing PhenQ in 50-fold excess over **1a**. The photosubstitution (2) was studied both in THF and CH_2Cl_2 containing PPh_3 in 200-fold excess. Competition between the oxidative addition of PhenQ and substitution by PPh_3 was tested by measuring the quantum yield of **1a** disappearance upon irradiation of a 1/50/200 mixture of **1a**/PhenQ/PPh_3 in THF solutions which afforded a mixture of products of reactions 2 and 3.

The results collected in Table 2 clearly show that all quantum yield values are very similar and that they do not show any systematic dependence on the excitation energy. (The rather large value, 0.65, measured for reaction 1 at 592 nm is probably caused by less accurate measurement of the weak absorbance in the region of a sharply decreasing absorption band.) More importantly, quantum yields measured for different reactions may be regarded as nearly identical. For example, at 514.5 nm in CH_2Cl_2, quantum yields of 0.42 and 0.44 were found for reactions 1 and 2, respectively, whereas identical values, 0.51, were obtained for reactions 2 and 3 in THF. The small difference between the data obtained in CH_2Cl_2 and THF is, most probably, due to a solvent effect. It should be also noted that the quantum yield values obtained under laser excitation are very close to those measured with a mercury lamp of intensity at least 30 times lower; see Table 3. Involvement of secondary photolysis or radical-coupling reactions in the photochemical mechanism is thus unlikely.

Pressure-Dependent Quantum Yields. In order to obtain more detailed information on the nature of the primary photoprocess(es) involved, the dependence of the quantum yields, ϕ, on applied pressure[20–23] was investigated for reactions 1 and 2 using complex **1a**. Since the Cl abstraction from CH_2Cl_2 does not compete with the substitution by PPh_3 in CH_2Cl_2 solutions (*vide supra*), this solvent was also used for the pressure dependence studies of reaction 2. Quantum yields of both reactions were found to decrease with increasing pressure, as is demonstrated by the data in Table 3. Apparent volumes of activation,[20–27] ΔV^*, were obtained[21] from the slopes of linear plots of $(\ln[\phi/(1-\phi)]$ *vs* pressure. (Correlation coefficients were 0.992 and 0.999 for the data obtained on reactions 1 and 2, respectively.) The value found for reaction 1, $\Delta V^* = +17.2 \pm 1.3$ cm^3 mol^{-1}, is very close to the value measured for reaction 2, $\Delta V^* = +15.7 \pm 0.5$ cm^3 mol^{-1}. These values are sufficiently similar to imply that the same primary step is involved in both reactions. (Plots of ln ϕ *vs* pressure are also linear and yield apparent ΔV^* values that are again similar for reactions 1 and 2, +9.4 and +8.8 cm^3 mol^{-1}, respectively. However, the values obtained from the $\ln[\phi/(1-\phi)]$ *vs* pressure dependencies are preferred as they have a better defined physical meaning,[21] *i.e.* the difference of the volume of activation of the reaction itself and the nonradiative excited-state deactivation.[21]

Low-Temperature Photochemistry. Irradiation of complexes **1** in fluid solutions at low temperatures (in 2-MeTHF at 143 K or in toluene at 183 K) led to release of CO, as seen from the appearance of a weak IR band of free CO at 2132 cm^{-1}. For **1a**, the IR spectra showed that $(CO)_5ReMn(CO)_2(PPh_3)$(pTol-DAB) was formed as the only stable product upon low-temperature

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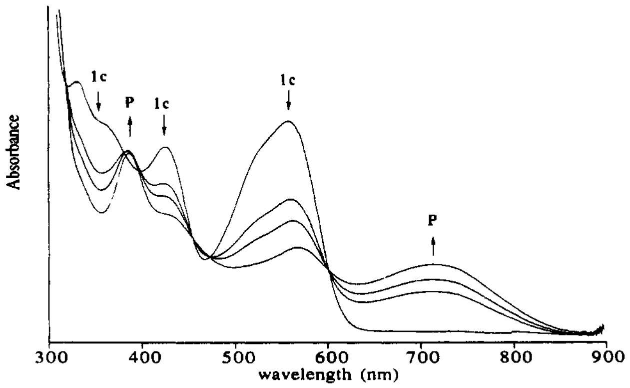

Figure 4. UV–vis spectral changes monitored during the 514.5-nm irradiation of **1c** in 2-chlorobutane solution at 143 K. P = $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$. Irradiation times: 0, 6, 14, 23.5 min. Laser power: 10 mW.

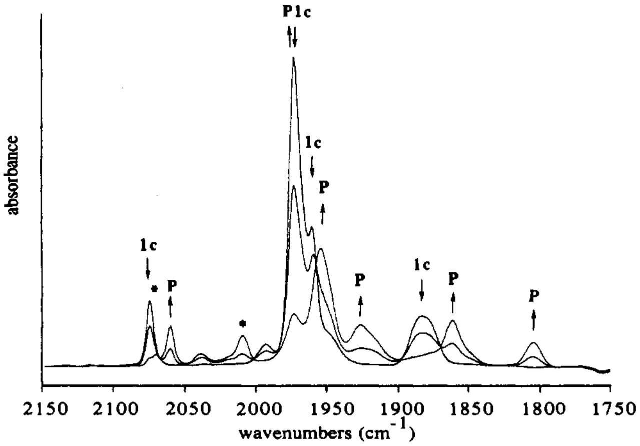

Figure 5. IR spectral changes in the $\nu(CO)$ region monitored during the 514.5-nm irradiation of **1c** in 2-chlorobutane solution at 143 K. P = $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$; * = $Re_2(CO)_{10}$. Irradiation times: 0, 1, 7.5 min. Laser power: 12 mW.

irradiation in the presence of PPh_3, indicating the same reaction mechanism at low and ambient temperatures. Unfortunately, the primary photoproducts of complexes **1a** and **1b** were too unstable (both thermally and photochemically) to be studied in detail with IR spectroscopy. Only a weak band of the primary photoproduct was observed between 700 and 710 nm for both complexes in the UV–vis spectrum. On the other hand, irradiation of the complex $(CO)_5ReMn(CO)_3(bpy')$ (**1c**) produced more stable primary species whose properties will now be discussed.

UV–vis and FTIR spectra measured during the 514.5-nm irradiation of the fluid solution of **1c** in 2-chlorobutane at 143 K are shown in Figures 4 and 5, respectively. Both sets of spectra exhibit well-developed isosbestic points. The photoproduct is characterized by an absorption band at 714 nm and by a typical IR band at 1803 cm^{-1}. Other IR bands as well as spectral data obtained in other solvents are collected in Table 1. It is obvious that the CO stretching frequencies are nearly the same in all solvents studied regardless their different coordinative properties. This excludes the formation of a solvent-substituted species $(CO)_5ReMn(CO)_2(S)(bpy')$ as a primary photoproduct at low temperature. Instead, the appearance of a low-frequency band at 1803 cm^{-1} points to the formation of the CO-bridged species $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$. This assignment is supported by comparison with the IR spectra of related substituted complexes $(CO)_5ReMn(CO)_2(L)(\alpha\text{-diimine})$ (Table 1, ref 30). The $\nu(CO)$ bands are at very similar positions, except for the lowest-frequency one (1803 cm^{-1} for the bridged species) which shifts to higher frequencies (1839–1821 cm^{-1}) in the substituted complexes as the μ-CO ligand regains its terminal position. The rather low CO stretching frequency found for $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$, *i.e.* 1803 cm^{-1}, is well within the range typical for bridging CO ligands, but this value alone does not allow us to distinguish between the symmetrical bridging and semibridging coordinations. For comparison, the analogous $(CO)_4Re(\mu\text{-}CO)Mn(CO)_4$[28] complex exhibits a $\nu(CO)$ band for the semibridging CO ligand at 1760 cm^{-1}. The value of 1816 cm^{-1} observed for $(CO)_4Mn(\mu\text{-}CO)Mn(CO)_2(bpy')$[6] was also assigned to semibridging μ-CO, however, without any other independent evidence distinguishing between these two forms of coordination. In conclusion, the low-temperature IR spectrum clearly identifies the primary product of the **1c** photolysis as the bridged $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$ complex, but it leaves the question of the specific mode of μ-CO coordination open. The visible absorption band of $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$ may be assigned to the Mn → bpy′ MLCT transition as evidenced by its solvatochromism (Table 1). At longer times of irradiation, a very small amount of $Re_2(CO)_{10}$ was detected in the IR spectra alongside the dominant $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$ photoproduct.

The photoreaction of **1c** occurs identically also in 2-MeTHF at 143 K. When the photolyzed 2-MeTHF solution was warmed in the dark to 153, 193, and 233 K, the bands due to $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$ decreased and the parent $(CO)_5ReMn(CO)_3(bpy')$ complex (**1c**) was largely regenerated by the back-reaction with CO still present in the tight spectral cell. As well, minor formation of the $Mn_2(CO)_6(bpy')_2$ coupling product was detected by a small absorbance increase at approximately 830 nm. Photolysis of **1c** in toluene and THF at 173 and 183 K, respectively, yielded again the bridged $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$ product (see Table 1 for the spectral data), together with small amounts of $Re_2(CO)_{10}$ and $Mn_2(CO)_6(bpy')_2$. Warming the THF solution to 233 K led to a disappearance of the IR and vis absorption bands of $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$ with a concomitant rise of the bands belonging to the starting complex and also to the secondary products $Mn_2(CO)_6(bpy')_2$ and $Re_2(CO)_{10}$. These species were the only stable products observed during the photolysis at 233 K. $Re_2(CO)_{10}$ was detected by the IR spectra, whereas $Mn_2(CO)_6(bpy')_2$ was manifested by its $\nu(CO)$ IR bands as well as by absorption bands at 837 nm (toluene) and 822 nm (THF).

Under all reaction conditions employed (solvent, temperature), $Mn_2(CO)_6(bpy')_2$ and $Re_2(CO)_{10}$ were formed only in very low concentrations. This is, for example, demonstrated in Figure 5 by the low intensity of the IR band of $Re_2(CO)_{10}$ at 2010 cm^{-1}, especially if we take into account its high extinction coefficient. Moreover, the spectral bands of both radical-coupling products increased at the expense of $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$ during prolonged irradiation or during gradual warming of the irradiated solutions in the dark. They were missing in the spectra recorded at the beginning of irradiation of the 2-MeTHF and 2-chlorobutane solutions at 143 K, while the bands due to $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$ were already present. All these observations indicate that both radical-coupling products $Mn_2(CO)_6(bpy')_2$ and $Re_2(CO)_{10}$ do not originate from radicals formed in a primary photoprocess but that they are only minor secondary products of thermal and/or photochemical decomposition of $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$.

The same bridged $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$ species was formed upon irradiation of a solution of **1c** in 2-MeTHF containing CCl_4 or PPh_3 at 143 K. However, a thermal reaction between the CO-(semi)bridged complex and these reagents occurred while the temperature was raised to about 200 K. For the reaction with CCl_4, the IR spectral changes resemble those observed earlier[6] for an analogous photoreaction of $(CO)_4Mn(\mu\text{-}CO)Mn(CO)_2(bpy')$. In both cases, the $\nu(CO)$ bands of a tetracarbonyl product appeared. The reaction of $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$, photoproduced from **1c**, yielded a product with $\nu(CO)$ bands at

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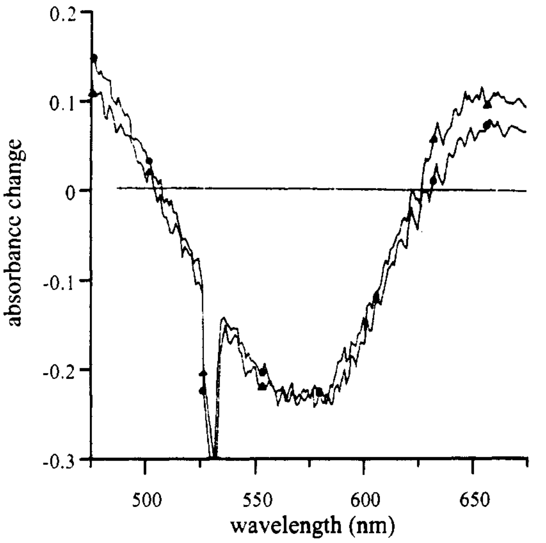

Figure 6. Difference absorption spectra measured 20 ps (●) and 10 ns (▲) after the 532-nm, 30-ps excitation of a toluene solution of **1a** at ambient temperature.

2093, 2010 (sh), 1989, and 1969 cm^{-1}, whereas the dimanganese complexes gave a product characterized by IR bands at 2069, 1999, 1983, and 1968 cm^{-1}, assigned[6] to Mn(CO)$_4$(2-MeTHF)-Cl. Because of this analogy and also because of the close correspondence with the ν(CO) bands of Re(CO)$_4$(PR$_3$)Cl complexes,[29] the product of the thermal reaction of (CO)$_4$Re-(μ-CO)Mn(CO)$_2$(bpy′) with CCl$_4$ was assigned as Re(CO)$_4$(2-MeTHF)Cl. Only weak bands belonging to Mn(CO)$_3$(bpy′)Cl[9] were detected. The thermal reaction of the CO-(semi)bridged complex (CO)$_4$Re(μ-CO)Mn(CO)$_2$(bpy′) with PPh$_3$ at about 200 K gave rise to the formation of (CO)$_5$ReMn(CO)$_2$(PPh$_3$)(bpy′), as manifested by its IR and visible spectra (Table 1). In the presence of more basic PBu$^n_3$, the substituted product (CO)$_5$-ReMn(CO)$_2$(PBu$^n_3$)(bpy′) was observed already at 143 K in 2-MeTHF. No CO-bridged intermediate was found in that case. The competition between the reactions of the CO-bridged complex with CCl$_4$ and PPh$_3$ was followed by raising the temperature of the photolyzed solution of the mixture **1c**/PPh$_3$/CCl$_4$ in the molar ratio 1/100/100 in 2-MeTHF from 143 to about 200 K. Only the substitution product (CO)$_5$ReMn(CO)$_2$(PPh$_3$)(bpy′) was then formed without any evidence of halogen abstraction. Obviously, PPh$_3$ coordination is even more kinetically favored over the halogen abstraction at low temperature than at room temperature (*vide supra*).

Picosecond and Nanosecond Flash Photolysis. In order to establish the nature of the primary photoprocess involved in reactions 1 and 2 and to estimate their time scales, picosecond and nano- to millisecond time-resolved absorption spectra were measured for room-temperature solutions of complexes **1a** and **1b** in toluene. The samples were excited by the 532-nm line of the Nd:YAG laser, close to the maximum of the MLCT band (≅570 nm). The picosecond spectra of **1a** were taken at several probe delays between 0 ps and 10 ns after the excitation. Figure 6 shows the difference absorption spectra measured at probe delays of 20 ps and 10 ns. These spectra exhibit bleaching at 570 nm which corresponds to the depletion of the ground state. The bleached absorption is a negative mirror image of the ground-state absorption with no evidence for any prominent transient absorption around 550 nm, where the Re(CO$_5$)$^\bullet$ radical is known[30] to absorb strongly. A new absorption band appears in the red spectral region. Its formation is very rapid, being completed within the 30-ps excitation pulse. It is persistent over the next 10 ns. The same transient spectra were obtained when the sample was excited with the 355-nm laser pulse.

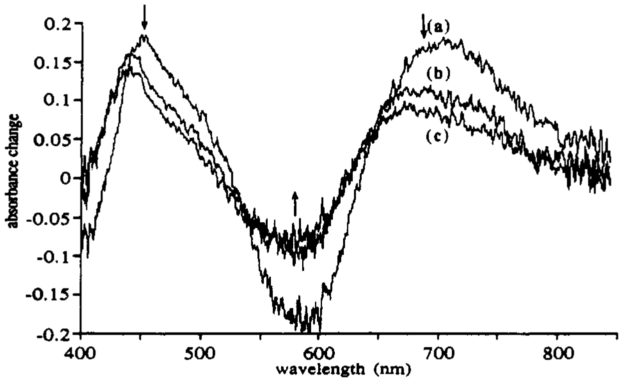

Figure 7. Difference absorption spectra measured 20 ns (a), 2 μs (b), and 5 μs (c) after the 532-nm, 5-ns excitation of a CO-saturated toluene solution of **1b** at ambient temperature. Spectrum a is identical with that measured in the absence of CO. Almost no decay was observed if no CO was present.

A nanosecond transient absorption spectrum obtained for **1a** in toluene solutions 20 ns after excitation at 532 nm agrees with the picosecond data. It exhibits bleached ground-state absorption and a new strong transient absorption in the red spectral region with an apparent maximum at about 710 nm. Nano- to millisecond spectra were also measured for solutions of **1b** in toluene, neat 2-MeTHF, 2-MeTHF containing 10- and 200-fold excess of PPh$_3$, and THF. Spectra were taken at several probe delays between 20 ns and 200 μs. Essentially identical transient spectra were obtained in all solvents investigated; see Figure 7, curve a. The spectra showed only very little changes with time. The presence of PPh$_3$ had virtually no effect. On the other hand, significant decay of both the bleached and transient absorption between 20 ns and 2 μs was observed in CO-saturated solution; see Figure 7. The bleached ground-state absorption (≅570 nm) and new absorptions in the violet (400–500 nm) and, especially, in the red (>600 nm) spectral regions are well developed already within the excitation laser pulse (5 ns). The spectral maxima apparent in Figure 7 are only virtual because of a strong overlap with the broad bleached ground-state absorption. Its subtraction, attempted for the spectra measured in toluene, permitted us to estimate the shapes and maxima of absorption bands corresponding to the photoproduct. Its transient absorption was found to be quite high throughout the whole visible spectral region with a broad maximum at 705 nm and a weak shoulder at 510 nm apparent on the absorption profile increasing into the UV spectral region.

The shapes of the absorption bands and their time changes do not allow an unequivocal assignment of the transient absorption spectra. Regeneration of the starting complex by the back-reaction with CO, apparent from Figure 7, indicates that the photointermediate is either (CO)$_4$Re(μ-CO)Mn(CO)$_2$(pAn-DAB), analogous to the (semi)bridged complex characterized at low temperature for **1c**, or the solvent-substituted species (CO)$_5$ReMn(S)(CO)$_2$(pAn-DAB). The very small effect of the solvent nature on the transient spectra and the position of the low-energy band around 710 nm favor an assignment to (CO)$_4$Re-(μ-CO)Mn(CO)$_2$(pAn-DAB). It is, however, not clear why the back-reaction of this intermediate with CO is rather rapid, whereas only very minor changes were observed in the transient spectra on a ns–ms time scale when PPh$_3$ was added to the solution. This different behavior may be due to the associative nature of the reactions of the bridged intermediate with CO and PPh$_3$.

Importantly, no evidence for the absorption of Re(CO)$_5^\bullet$ around 550 nm[30] was found in any of the nanosecond absorption spectra measured. Apparently, no radicals are formed by a 532-nm

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(29) See, *e.g.*: Singleton, E.; Moelwyn-Hughes, J. I.; Garner, A. W. B. *J. Organomet. Chem.* **1970**, *21*, 449.

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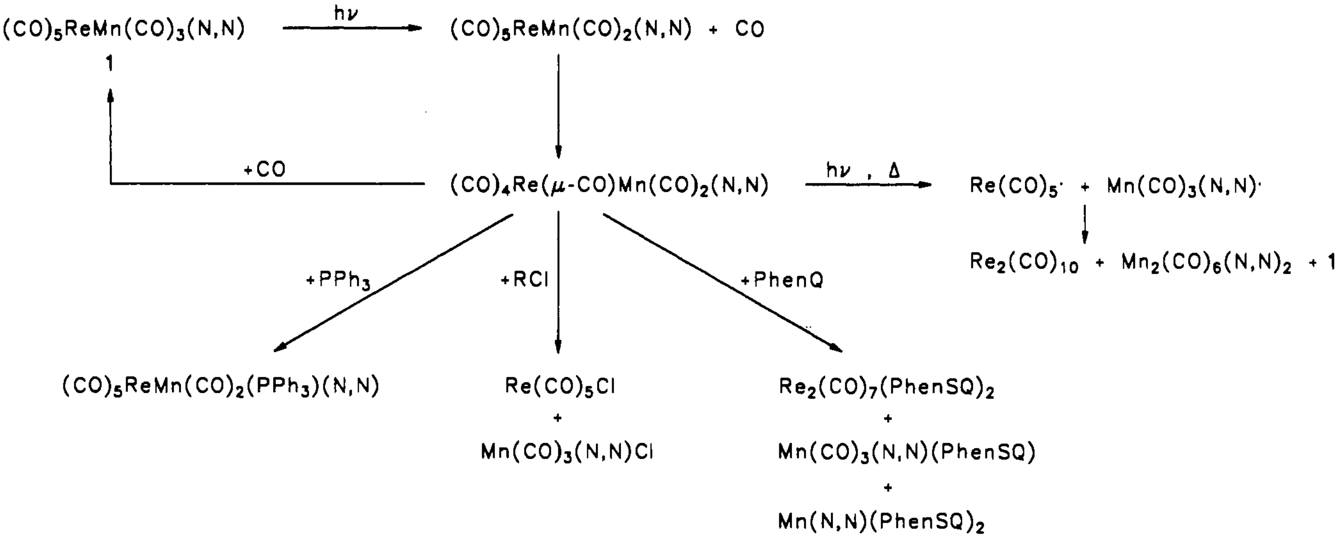
Scheme 1. Reactivity of $(CO)_5ReMn(CO)_3$(α-diimine) Complexes, **1**, under Irradiation with Visible Light



excitation of either **1a** or **1b** in any of the solvents investigated. Moreover, indirect evidence against the primary photochemical formation of a $Mn(CO)_3$(pAn-DAB)$^\bullet$ radical comes from the absence of any transient absorption bands at wavelengths longer than 750 nm at time delays between 20 ns and 200 μs. This clearly shows that the radical-coupling product $Mn_2(CO)_6$(pAn-DAB)$_2$ is not formed in significant concentrations by a 532-nm laser pulse excitation.

The nanosecond spectra of complex **1c** indicated rather complicated behavior which was attributed to secondary photochemistry of the primary photoproduct in the polychromatic analyzing beam. Extensive secondary photochemistry of **1c** was also observed under CW irradiation at room temperature (*vide supra*).

Discussion

All three $(CO)_5ReMn(CO)_3$(α-diimine) complexes investigated, **1a–c**, exhibit two types of photoreactivity when irradiated into their Mn → diimine MLCT absorption band. First, a chlorine abstraction (eq 1) from CCl_4 and CH_2Cl_2 and oxidative addition of 9,10-phenanthrenequinone (eq 3) involve the oxidation of the Re and Mn atoms. Second, in the presence of a Lewis base PPh_3, photosubstitution (eq 2) takes place, producing $(CO)_5ReMn(CO)_2(PPh_3)$(α-diimine). The mechanism of these reactions has been elucidated using quantum yields and their pressure dependence, low-temperature photochemistry, and laser flash photolysis in the ps–ms time range. Experimental difficulties, mainly different stabilities of the primary and final products, prevented carrying out all these experiments on all three complexes, **1a–c**. Nevertheless, the identity of their overall photochemical behavior allowed us to combine mechanistic information obtained by various methods on individual complexes **1a–c** to arrive at a common mechanistic picture shown in Scheme 1. The mechanism proposed is rather different from that found for analogous $L_nMM'(CO)_3$(α-diimine) complexes, where the substitution originates from the CO-loss photoproducts and the Cl-containing products are formed by secondary reactions of simultaneously produced radicals.

As was discussed under Results, reactions 1–3 were found to take place with nearly identical quantum yields. Moreover, quantum yields of the Cl-abstraction (1) and substitution (2) of **1a** exhibit very similar pressure dependencies that afford also very similar values of the apparent activation volumes, ΔV^*. Making the usual assumption[22] that the volume of activation corresponding to nonradiative excited-state deactivation is very small, we can assign the apparent activation volumes observed experimentally to the photochemical reaction itself. Quantum yields and their pressure dependencies were measured at a very large excess of the reactants (CH_2Cl_2, PPh_3, PhenQ), which ensured efficient "trapping" of primary photointermediate(s) to form the final products. Moreover, the reactions studied took place without any complicating side or followup reactions. Under these conditions, the overall quantum yield and the apparent activation volume are determined by the primary photoprocess only. Hence, the identity of the quantum yields and of the apparent activation volumes observed for reaction 1–3 implies an identical nature of the primary photoprocess involved in these different reactions.

Low-temperature studies identified the primary photoproducts spectroscopically as a symmetrically bridged or semibridged $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2$($\alpha$-diimine) complex and free CO. No spectral evidence that would indicate primary photochemical homolytic splitting of the Re–Mn bond in **1** was obtained. The primary photochemical step may thus be described as a photochemical CO dissociation from the Mn center accompanied by a change of the coordination of one Re-bound CO from terminal to bridged:

$$(CO)_5ReMn(CO)_3(\alpha\text{-diimine}) \xrightarrow[-CO]{h\nu} (CO)_5ReMn(CO)_2(\alpha\text{-diimine}) \rightarrow\rightarrow (CO)_4Re(\mu\text{-}CO)Mn(CO)_2(\alpha\text{-diimine}) \quad (4)$$

It is not possible to decide whether it takes place concertedly or if a very fast followup intramolecular rearrangement is involved.

Laser flash photolysis suggests that reaction 4, established by low-temperature experiments, constitutes the only primary photoprocess also at room temperature. Spectral evidence was observed neither for the formation of $Re(CO)_5^\bullet$ in the ps–ns time domain nor for the formation of the $Mn_2(CO)_6$(α-diimine)$_2$ radical-coupling product on the μs–ms time scale. This indicates that no primary photochemical homolysis of the Re–Mn bond in **1** takes place even at room temperature. The intense transient absorption in the red spectral region was assigned to $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2$($\alpha$-diimine). Its intensity decreases in the presence of free CO due to a recombination reaction shown in Scheme 1. Picosecond transient spectroscopy shows that reaction 4 occurs very rapidly, being completed within the 30-ps excitation pulse.

Formulation of the primary photoprocess as reaction 4 is also consistent with the observed large positive apparent volumes of activation (average: +16.5 cm^3 mol^{-1}) that point to a highly dissociative mechanism. Moreover, there is a close correspondence between the values obtained for reactions 1 and 2 and those reported earlier for the rate-determining loss of CO in thermal substitution reactions of metal carbonyl complexes, *e.g.* +21 cm^3 mol^{-1} for $HRu_3(CO)_{11}^-$,[24] +22 cm^3 mol^{-1} for $Mn(CO)_5Br$,[25] +21 cm^3 mol^{-1} for $Mn(CO)_5Cl$,[26] and +14 cm^3 mol^{-1} for $Cr(CO)_4$-phen.[27] This observation indicates that the primary reaction step of both reactions 1 and 2 involves CO dissociation; see Scheme 1. On the other hand, the values found for reactions 1 and 2 are larger than those reported for photochemical CO dissociation from mononuclear complexes[15,22,31,32] like $Cr(CO)_6$ (7.0–9.3 cm^3 mol^{-1}), $Mo(CO)_6$ (14.0 cm^3 mol^{-1}), $W(CO)_6$ (8.8 cm^3 mol^{-1}), $W(CO)_5(py)$ (5.7 cm^3 mol^{-1}, and $Cr(CO)_4$phen (9.6 or 3.0 cm^3 mol^{-1}, depending on the excitation wavelength). In these mononuclear complexes, apparent volumes of activation are usually composed of several contributions, including those due to coordination of the solvent and of liberated CO to the vacant coordination site. This problem is absent in (4) because the vacant site is very rapidly blocked by the intramolecular rearrangement to the bridged species. Such a rearrangement amounts to only very little structural change and is thus assumed to involve only a very small (probably negative) volume change which might even be compensated for by a small volume increase caused by elongation of the Re–Mn bond. Therefore, the apparent volume of activation of reaction 4 is expected to be determined essentially by the volume of activation of the CO dissociation and, hence, to be close to the activation volumes observed in thermal dissociative CO substitutions.

It may thus be concluded that the CO dissociation (4) is the only primary photoprocess of MLCT-excited $(CO)_5ReMn(CO)_3$(α-diimine) complexes. In order to account for the formation of different photoproducts in reactions 1–3, it has to be assumed that the same primary photoproduct, $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2$($\alpha$-diimine), undergoes reactions with PPh_3 as well as with CH_2Cl_2, CCl_4, and PhenQ, as shown in Scheme 1. This assumption was confirmed at low temperatures by the direct observation that photoproduced $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2(bpy')$ reacts thermally with PPh_3 and CCl_4 to afford $(CO)_5ReMn(CO)_2(PPh_3)(bpy')$ and Cl-containing products, $Re(CO)_5Cl$ and $Mn(CO)_3(bpy')Cl$, respectively.

The high reactivity of the $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2$($\alpha$-diimine) primary photoproduct toward CH_2Cl_2 and CCl_4 is rather surprising. The propensity of analogous coordinatively unsaturated binuclear metal carbonyls to undergo Cl abstractions and oxidative additions has already been demonstrated. Thus, the $(CO)_4M(\mu\text{-}CO)M(CO)_4$ (M = Mn, Re) complexes react with *o*-quinones[33] to form $M(CO)_4$(*o*-semiquinone) radical species. Semibridged $(CO)_4Mn(\mu\text{-}CO)Mn(CO)_4$ produced by irradiation of $Mn_2(CO)_{10}$ in alkane glass yielded[34] only a negligible amount of $Mn(CO)_5Cl$ upon raising the temperature in the presence of CCl_4. Indirect evidence for a low-yield Cl abstraction from CCl_4 by a photoproduced $Mn_2(CO)_9$ was also obtained from a detailed quantum yield study[35] carried out at room temperature. The kinetics of oxidative addition of Bu^n_3SnH and Et_3SiH to photogenerated $L(CO)_3Mn(\mu\text{-}CO)Mn(CO)_3L$ species (L = CO, PMe_3, PBu^n_3, PPr^i_3) was also studied in detail.[36,37] All these reactions involve a transfer of electron density from the metal–metal bond to the reactant molecule. Therefore, the M–M bond dissociates concertedly with the reactant coordination, and monomeric products containing oxidized metal atoms, M^I, are ultimately formed. $Mn(CO)_5Cl$ is thus produced in the reaction with CCl_4, whereas oxidative addition of Bu^n_3SnH leads[36,37] to $HMn(CO)_4L$ and $Bu^n_3SnMn(CO)_3L$. For dinuclear carbonyl complexes containing diimine ligands, an efficient reaction of bridged $(CO)_4Mn(\mu\text{-}CO)Mn(CO)_2(bpy')$, photoproduced from $Mn_2(CO)_8(bpy')$, with CCl_4, CH_2Cl_2, and PhenQ was demonstrated.[6,9] Unbridged $Ph_3SnMn(CO)_2$(α-diimine) complexes,[10] which are formed by a CO photodissociation from $Ph_3SnMn(CO)_3$(α-diimine), add oxidatively PhenQ.[9] However, their reactions with CCl_4 and CH_2Cl_2 are very inefficient,[9,10] apparently because of the great strength[38] of the Sn–Mn bond. The CO-loss products of **1a–c**, *i.e.* $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2$($\alpha$-diimine) complexes, are the first dinuclear carbonyl species that abstract the Cl atom efficiently from CH_2Cl_2 despite the presence of a strong[4] Re–Mn bond. This (semi)bridged intermediate also readily reacts with potential ligands L to produce $(CO)_4ReMn(CO)_2(L)$(α-diimine). For L being a strong ligand (PPh_3, PBu^n_3), this substitution product is stable. However, if L is a redox-active species like PhenQ, CH_2Cl_2, or CCl_4, the initial substitution of the μ-CO ligand by L is accompanied with a rearrangement of electron density and Cl abstraction or oxidative addition takes place as described by reactions 1 and 3, respectively. Weakening of the Re–Mn bond in the (semi)bridged species would aid these reactions. This is manifested by much larger quantum yields of the photoreactions of CCl_4 and CH_2Cl_2 with complexes **1a–c** than with[9] $Ph_3SnMn(CO)_3(bpy')$, whose primary photoproduct,[10] $Ph_3SnMn(CO)_2(bpy')$, does not contain a (semi)bridged CO ligand and whose strong Sn–Mn bond is thus essentially unperturbed. This explanation is also consistent with the observed competition between the CO substitution by PPh_3 and Cl abstraction or PhenQ oxidative addition. This is just a result of a competition for the coordination site in the $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2$($\alpha$-diimine) intermediate, which favors strongly coordinating phosphines over chlorocarbons or PhenQ. The observation of the formation of products typical for radical reactions in the entirely nonradical processes (1) and (3) also highlights our previous conclusion[33] that, for reactions of dinuclear complexes, spin-trapping techniques cannot unequivocally distinguish between radical and nonradical pathways,[33] unless accompanied by mechanistic studies.

The $(CO)_5ReMn(CO)_3$(α-diimine) complexes are exceptional among dinuclear transition-metal carbonyls, as they undergo efficient ($\phi \cong 0.5$) CO dissociation as the only primary photochemical process, the usual metal–metal-bond homolysis being absent even at room temperature. The identities of the picosecond spectra obtained under the 355- and 532-nm excitation, together with the excitation-wavelength independence of the photochemical quantum yield, suggest that the reaction takes place rapidly from a low-lying excited state that is very efficiently populated regardless the nature of the directly excited Franck–Condon state. The questions remain as to what the nature of this reactive excited state is and why its population does not lead to dissociation of the Re–Mn bond. It cannot be excluded that the CO dissociation occurs from the directly excited MLCT state.[39] However, such a MLCT reactivity is usually low and characterized by a pronounced excitation-wavelength dependence of photochemical quantum yields,[39,40] which was not observed here. A clue to the identification of the reactive excited state comes from the fact that efficient CO dissociation takes place only from the $-Mn(CO)_3$(α-diimine) fragment of the $L_nM'Mn(CO)_3$(α-diimine) complexes. Analogous $L_nM'Re(CO)_3$(α-diimine) complexes do not undergo photochemical CO dissociation. The reactive $-Mn(CO)_3$(α-diimine) fragment contains a first-row Mn atom, for which smaller ligand-field splitting of d orbitals, as compared with that of Re, is expected. This points to the presence of a repulsive low-lying $d_\pi \rightarrow d_{\sigma^*}$ (LF) state (d_{σ^*} being a d orbital antibonding with respect to the Mn–CO bond). Rapid nonra-

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diative population of such a state from the $d_\pi \rightarrow \pi^*$ (MLCT) state(s) would lead to an efficient CO dissociation. Evidence for the presence of an easily accessible low-lying reactive LF state was recently presented for several organometallic complexes of Mn(I).[41]

The photochemistry of dinuclear carbonyls which do undergo efficient M′–M-bond homolysis, *e.g.* $(CO)_5MRe(CO)_3$(α-diimine) (M = Mn, Re), is usually interpreted[42,43] by population of the spectroscopically silent $\sigma \rightarrow \pi^*$ excited state that corresponds to the electron excitation from the σ(M–Re) bonding orbital to the diimine π^* orbital. As shown by the UPS spectra,[44] the σ orbital is the HOMO, and hence, $\sigma \rightarrow \pi^*$ is the lowest-lying excited state in these complexes. Its rapid and efficient population from the spectroscopic $d_\pi \rightarrow \pi^*$ MLCT states is quite conceivable, as it involves only an electronic transition from the σ orbital to a lower-lying half-occupied d_π orbital. The $d_\pi \rightarrow d_{\sigma^*}$ state lies much higher because of the large ligand-field splitting of Re(I) d orbitals. Thus, the M–Re bond dissociation dominates the photoreactivity. For the complexes **1**, the strength of the Re–Mn bond is comparable to that of the M–Re bond in $(CO)_5MRe(CO)_3$(α-diimine).[44] However, for complexes **1** that contain the $Mn(CO)_3$(α-diimine) fragment, the separation between the manganese d_π and d_{σ^*} orbitals is so small that the $d_\pi \rightarrow d_{\sigma^*}$ state becomes the lowest-lying state. Consequently, the Re–Mn bond does not photodissociate and, instead, CO dissociation from the $d_\pi \rightarrow d_{\sigma^*}$ state prevails. Going to the $(CO)_5MnMn(CO)_3$(α-diimine) complexes, the σ orbital rises in energy[44] and, consequently, the $\sigma \rightarrow \pi^*$ excited state is stabilized to an energy similar to that of the $d_\pi \rightarrow d_{\sigma^*}$ state. Hence, $(CO)_5MnMn(CO)_3$(α-diimine) complexes exhibit both Mn–Mn-bond homolysis and CO dissociation.[6]

Conclusions

MLCT excitation of $(CO)_5ReMn(CO)_3$(α-diimine) complexes leads to a very fast CO dissociation from the Mn center as the only primary photoprocess. No Re–Mn bond homolysis takes place as the primary photochemical step. The photoproduced $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2$($\alpha$-diimine) species containing a (semi)-bridging CO ligand react with phosphines (L) to produce $(CO)_5ReMn(CO)_2(L)$(α-diimine). On the other hand, Cl abstraction or oxidative addition take place between $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2$($\alpha$-diimine) and redox-active reactants CCl_4, CH_2Cl_2, and PhenQ; see Scheme 1. This high reactivity of $(CO)_4Re(\mu\text{-}CO)Mn(CO)_2$($\alpha$-diimine) is explained by the presence of a readily available coordination site on the Mn atom, together with a weakening of the Re–Mn bond. The relative importance of metal–metal-bond homolysis and CO dissociation as the primary photoprocesses in MLCT-excited $L_nM'M(CO)_3$(α-diimine) complexes appears to be determined by the relative energetic positions of $d_\pi \rightarrow \pi^*$ (MLCT), $\sigma_{M'M} \rightarrow \pi^*$, and $d_\pi \rightarrow d_{\sigma^*}$ (LF) excited states. The last is sufficiently low-lying only in complexes containing the $-Mn(CO)_3$(α-diimine) fragment. Only the $L_nM'Mn(CO)_3$(α-diimine) complexes thus undergo efficient CO dissociation as primary photoprocess.

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