Metal to ligand charge-transfer photochemistry of metal-metal bonded complexes. The primary photoprocess of (CO)$_5$ReMn(CO)$_3$(alpha-diimine) complexes studied by temperature and pressure dependent photochemistry and pico-nanosecond flash photolysis
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Metal to Ligand Charge-Transfer Photochemistry of Metal–Metal-Bonded Complexes. 12† The Primary Photoprocess of (CO)$_5$ReMn(CO)$_3$(α-dimine) Complexes Studied by Temperature- and Pressure-Dependent Photochemistry and Pico- and Nanosecond Flash Photolysis

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Photoreactions of (CO)$_5$ReMn(CO)$_3$(α-dimine) 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$_2$Cl$_2$ or in toluene/CCl$_4$ mixtures produces Re(CO)$_2$Cl and Mn(CO)$_3$(α-dimine)Cl whereas the substituted product (CO)$_5$ReMn(CO)$_3$(PPh$_3$)(α-dimine) 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)$_5$Re(μ-CO)-Mn(CO)$_3$(α-dimine) species formed by CO photodissociation from the parent complex. Very similar apparent volumes of activation found for the reaction of (CO)$_5$ReMn(CO)$_3$(4,4'-dimethyl-2,2'-bipyridine) with CH$_2$Cl$_2$ (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)$_5$Re(μ-CO)Mn(CO)$_3$(α-dimine) is the only primary photoprocess, the usual Re–Mn bond homolysis being absent. Pico- and nanosecond 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$_2$Fe(CO)$_4$, and Cp$_2$M$_2$(CO)$_6$ (M = Mo, W) appear 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$_2$M'M(CO)$_3$(α-dimine) (L$_2$M' = (CO)$_3$Mn, (CO)$_3$Re, (CO)$_3$Co, Cp(CO)$_2$Fe, Ph$_3$Sn; M = Mn, Re; α-dimine = bpy, phen, etc.), which contain a metal–metal bond and show an intense metal to α-dimine 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 release of CO from the M(CO)$_3$(α-dimine) fragment. Rhenium complexes L$_2$M'–Re(CO)$_2$(α-dimine) exhibited M'–Re bond homolysis only, while both reactions were observed for some of corresponding L$_2$M'M(CO)$_3$(α-dimine) complexes.

Quinones appear to react with the primary photoproducts of both reactions, giving rise to the formation of different complexes.5 M(CO)$_3$(α-dimine) (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)$_3$(α-dimine)(PhenQ) (SO = semiquinone radical anion). On the other hand, the CO-loss products of the type (CO)$_5$MM(CO)$_3$(α-dimine) (M = Mn, Re) reacted with PhenQ to give ultimately Mn(α-dimine)(PhenSQ). This compound was found to be the only product of the photolysis of Ph$_3$SnMn(CO)$_3$(α-dimine) which is known to undergo CO dissociation as the only photochemical reaction.

The behavior of the (CO)$_5$ReMn(CO)$_3$(α-dimine) complexes is exceptional in the L$_2$M'M(CO)$_3$(α-dimine) family. Their photolysis leads to CO photosubstitution whereas radical-coupling products, i.e., Mn$_2$(CO)$_3$(α-dimine) and Re$_2$(CO)$_6$, do not appear among the primary photoproducts.9 This indicates that the Re-
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 spectroscopy was performed by literature procedures.

di-p-anisyl-1,4-diaza-1,3-butadiene (pAn-DAB, R = OMe, pAn-DAB) and both 1,4-di-p-tolyl-1,4-diaza-1,3-butadiene (pTol-DAB, a) and 4,4'-dimethyl-2,2'-bipyridine (bpy', e), are depicted in Figure 1.

Figure 1. General structures of the (CO)₅ReMn(CO)₃(a-diimine) complexes, 1, and of the a-diimine ligands used.

Mn bond does not dissociate upon MLCT excitation. In contrast with this conclusion, the complexes (CO)₅ReMn(CO)₃(a-diimine) were found⁶ to react photochemically with PhenQ to give not only Mn(a-diimine)(PhenSQ) but also the oxidative-addition product Mn(CO)₅(a-diimine)(PhenSQ). Photoreaction with CH₂Cl₂ affords Cl- abstraction products Re(CO)₅Cl and Mn(CO)₃(a-diimine)Cl. Preliminary experiments⁸ 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(a-diimine) complexes is caused by a higher reactivity of their CO-loss products toward PhenQ and CH₂Cl₂ or if these complexes yet undergo, similarly to their congeners, both homolysis and release of CO as primary photoproducts.

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(a-diimine) complexes, 1. The structures of the complexes and a-diimine ligands used, 1, 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', e), are depicted in Figure 1.

**Experimental Section**

**Materials and Preparations.** THF and 2-MeTHF were freshly distilled from a sodium–benzenophene mixture. Toluene was carefully dried by refluxing with sodium and CaCl₂; it was used as a drying agent for CH₂Cl₂ and 2-chlorobutane. All solvents were distilled, stored, and handled under nitrogen. PPh₃ (Aldrich, Merck) was recrystallized from hexane or 2-chlorobutane. All solvents were distilled, stored, and handled under nitrogen. PPh₃ (Aldrich and Strem) was recrystallized from hexane or 2-chlorobutane. All solvents were distilled, stored, and handled under nitrogen.

**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 vessel, 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 > 15 mW) or Model 212 (P < 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 photoproduce of reaction 2 (side infra). No correction was necessary for reactions 1 and 3. Although all reactions investigated occurred isosbectically 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 × 10⁻⁴ einstein s⁻¹, as compared to the 10⁻⁸ 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 CH₂Cl₂, 5260 M⁻¹ cm⁻¹ at 571 nm for the product of reaction 2, (CO)₅ReMn(CO)₃(PP₃)₂(pTol-DAB). The latter value was determined after completion of the photolysis.

**Flash Photoysis.** Picosecond laser flash photolysis measurements were performed using the equipment⁹ 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 as 2 mJ/pulse, were obtained by frequency doubling. Transient absorbance 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 onto a cell with D₂PO₃. 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 excited 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 photoysis 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 SXV 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 pulse, 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 temperature.

Photochemistry of Metal–Metal-Bonded Complexes


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

<table>
<thead>
<tr>
<th>compound</th>
<th>solvent, temp</th>
<th>ν(CO) bands, cm⁻¹</th>
<th>λ, nm</th>
<th>ref</th>
</tr>
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<tbody>
<tr>
<td>(CO)₂ReMn(CO)₂(pTol-DAB) (1a)</td>
<td>THF, RT</td>
<td>2095, 2025, 2006, 1990, 1971, 1905, 1896</td>
<td>560</td>
<td>45</td>
</tr>
<tr>
<td>(CO)₂ReMn(CO)₂(pAn-DAB) (1b)</td>
<td>THF, RT</td>
<td>2094, 2026, 2006, 1988, 1970, 1903, 1896</td>
<td>576</td>
<td>45</td>
</tr>
<tr>
<td>(CO)₂ReMn(CO)(bpy) (1c)</td>
<td>CH₂Cl₂, RT</td>
<td>2019, 1993, 1956, 1890, 1839</td>
<td>586</td>
<td>c</td>
</tr>
<tr>
<td>(CO)₂ReMn(CO)₂(PPh₃)(pTol-DAB)</td>
<td>THF, RT</td>
<td>2087, 1991, 1951, 1886, 1835</td>
<td>584</td>
<td>c</td>
</tr>
<tr>
<td>(CO)₂ReMn(CO)₂(PPh₃)(pAn-DAB)</td>
<td>CH₂Cl₂, RT</td>
<td>2089, 1990, 1887, 1831</td>
<td>592</td>
<td>c</td>
</tr>
<tr>
<td>(CO)₂ReMn(CO)(PPh₃)(bpy)’</td>
<td>THF, RT</td>
<td>2072, 1972, 1885</td>
<td>552</td>
<td>45</td>
</tr>
<tr>
<td>(CO)₂ReMn(CO)(PPh₃)₂(bpy)’</td>
<td>CH₂Cl₂, RT</td>
<td>2091, 1993, 1956, 1905, 1903</td>
<td>577</td>
<td></td>
</tr>
<tr>
<td>(CO)₂ReMn(CO)₂(PBu₃)(bpy)’</td>
<td>THF, RT</td>
<td>2087, 1991, 1951, 1886, 1835</td>
<td>584</td>
<td>c</td>
</tr>
<tr>
<td>(CO)₂Re(μ-CO)Mn(CO)₃(bpy)’(2-MeTHF)Cl</td>
<td>THF, RT</td>
<td>2060, 1974, 1958, 1932, 1881, 1827</td>
<td>650</td>
<td>c</td>
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<tr>
<td>Mn(CO)₃(pTol-DAB)Cl</td>
<td>THF, RT</td>
<td>2056, 1973, 1954, 1928, 1878, 1821</td>
<td>695</td>
<td>c</td>
</tr>
<tr>
<td>Mn(CO)₃(PAn-DAB)((PhenSQ)</td>
<td>THF, RT</td>
<td>2059, 1974, 1952, 1922, 1860, 1802</td>
<td>714</td>
<td>d</td>
</tr>
<tr>
<td>Mn(CO)₃(PBu₃)((PhenSQ)</td>
<td>CH₂Cl₂, RT</td>
<td>2059, 1975, 1954, 1926, 1861, 1803</td>
<td>714</td>
<td>d</td>
</tr>
<tr>
<td>Mn(CO)₃((PhenSQ)</td>
<td>THF, RT</td>
<td>2058, 1975, 1954, 1926, 1862, 1804</td>
<td>730</td>
<td>d</td>
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<tr>
<td>Tol, 183 K</td>
<td>2143, 2084, 2046, 1866</td>
<td>9</td>
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<td></td>
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<tr>
<td>Re(CO)₂(2-MeTHF)Cl</td>
<td>THF, 143 K</td>
<td>2010, 2000, 1942</td>
<td>29</td>
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<tr>
<td>Re(CO)₃(PPh₃)Cl</td>
<td>CH₂Cl₂, RT</td>
<td>2028, 1936, 1918</td>
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<tr>
<td>Mn(CO)₃(pAn-DAB)Cl</td>
<td>CH₂Cl₂, RT</td>
<td>2032, 1944, 1917</td>
<td>f</td>
<td></td>
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<tr>
<td>Mn(CO)₃((pTol-DAB)Cl</td>
<td>CH₂Cl₂, RT</td>
<td>2034, 1942, 1922</td>
<td>f</td>
<td></td>
</tr>
<tr>
<td>Mn(CO)₃(bpy)((PhenSQ)</td>
<td>THF, RT</td>
<td>2022, 1929, 1909</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Mn(CO)₃(pTol-DAB)((PhenSQ)</td>
<td>THF, RT</td>
<td>2022, 1929, 1909</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Mn(pTol-DAB)((PhenSQ)</td>
<td>THF, RT</td>
<td>695</td>
<td>d</td>
<td></td>
</tr>
<tr>
<td>Mn(pPh)₂(DBS₂)</td>
<td>Tol, RT</td>
<td>423</td>
<td>h</td>
<td></td>
</tr>
<tr>
<td>Re₂(CO)₃(PhenSQ)₂</td>
<td>KBr, RT</td>
<td>2113, 2015, 1985, 1933, 1914, 1894</td>
<td>6</td>
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</tr>
<tr>
<td>Re₂(CO)₁₀</td>
<td>CH₂Cl₂, RT</td>
<td>2068, 2009, 1981</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>Mn₂(CO)₆(bpy)₂</td>
<td>Tol, RT</td>
<td>2070, 2011, 1970</td>
<td></td>
<td></td>
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<tr>
<td>2-MeTHF, RT</td>
<td>1979, 1932, 1882, 1836</td>
<td>850</td>
<td>11</td>
<td></td>
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<tr>
<td>THF, 173 K</td>
<td>1973, 1952, 1878, 1857</td>
<td>836</td>
<td>d</td>
<td></td>
</tr>
</tbody>
</table>

* Tol = toluene, 2-Chlorobutane, KBr = in KBr pellet, RT = room temperature. Wavelength corresponding to the maximum of the MLCT absorption band. This work; see refs 11 and 46 for identical or similar complexes. This work; see ref 29 for comparison with analogous compounds. / This work; assigned by analogy with similar complexes described in refs 9 and in: Staal, L. H.; Oskam, A.; Vrieze, K. J. Organomet. Chem. 1979, 170, 235. * This work; assigned by analogy with Mn(CO)₃(bpy)((PhenSQ). * Lynch, M. W.; Hendrickson, D. N.; Fitzgerald, B. J.; Pierpoint, C. G. J. Am. Chem. Soc. 1984, 106, 2041. / deLearie, L. A.; Pierpont, C. G. J. Am. Chem. Soc. 1987, 109, 703.

Results

Room-Temperature Photochemistry. At room temperature, complexes 1a–e, dissolved in CH₂Cl₂, reacted according to reaction 1 when irradiated into their visible absorption band. In the presence of an excess PPh₃, photosubstitution 2 occurred in both THF and CH₂Cl₂. 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:

$$\text{I} + \text{PhenQ} \rightarrow \text{Re}_2(\text{CO})_3(\text{PhenSQ})_2 + \text{Mn}(\alpha\text{-diimine})(\text{PhenSQ}) + \text{Mn}(\alpha\text{-diimine})(\text{PhenSQ})_2$$

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 PPh₃ (reaction 2) is fully competitive with the C₁ abstraction from CH₂Cl₂ since irradiation of both 1a and 1b in CH₂Cl₂ solution containing excess of PPh₃ afforded (CO)₂ReMn(CO)₂(PPh₃) (α-diimine) as the only product. A similar competition was found between the photoreactions of 1a with CCl₄ and PPh₃ in toluene solutions. At the 1a/PPh₃/CCl₄ 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)₂ReMn(CO)₂(PPh₃) (α-diimine) and chlorine-containing products Re(CO)₃Cl, Re(CO)₄(PPh₃)Cl, and Mn(CO)₃(pTol-DAB)Cl of the C₁ abstraction was formed at the 1/50/100 reactant ratio. The intensities of the corresponding IR bands indicate that the C₁-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 C₁ 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. C₁ abstraction was studied in neat CH₂Cl₂ that was used both as a reactant and as a solvent. The reaction with 9,10-phenanthrenequinone (PhenQ) was
followed in THF solutions containing PhenQ in 50-fold excess over 1a. The photosubstitution (2) was studied both in THF and CH₂Cl₂ containing PPh₃ in 200-fold excess. Competition between the oxidative addition of PhenQ and substitution by PPh₃ was tested by measuring the quantum yield of la disappearance upon irradiation of a 1/200 mixture of 1a/PhenQ/PPh₃ 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 CH₂Cl₂, quantum yields of 0.42 and 0.44 were found for reactions 1 and 2, respectively, whereas identical values, 0.51,
The UV–vis spectral changes monitored during the 514.5-nm irradiation of 1e in 2-chlorobutane solution at 143 K. P = (CO)₄Re(μ-CO)Mn(CO)₃(bpy'). Irradiation times: 0, 6, 14, 23.5 min. Laser power: 10 mW.

Figure 4.

The IR spectral changes in the ν(CO) region monitored during the 514.5-nm irradiation of 1e in 2-chlorobutane solution at 143 K. P = (CO)₄Re(μ-CO)Mn(CO)₃(bpy'); * = Re₂(CO)₁₀. Irradiation times: 0, 1, 7.5 min. Laser power: 12 mW.

Figure 5.

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)₄ReMn(CO)₃(bpy') (1e) produced more stable primary species whose properties will now be discussed.

Irradiation in the presence of PPh₃, 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)₄ReMn(CO)₃(bpy') (1e) 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 1e 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 coordinate properties. This excludes the formation of a solvent-substituted species (CO)₄ReMn(CO)₃(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(μ-CO)Mn(CO)₃(bpy'). This assignment is supported by comparison with the IR spectra of related substituted complexes (CO)₄ReMn(CO)₃(L)(α-diimine) (Table 1, ref 30). The ν(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(μ-CO)Mn(CO)₃(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(μ-CO)Mn(CO)₃ complex exhibits a ν(CO) band for the semibridging CO ligand at 1760 cm⁻¹. The value of 1816 cm⁻¹ observed for (CO)₄Mn(μ-CO)Mn(CO)₃(bpy') 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 1e photolysis as the bridged (CO)₄Re(μ-CO)Mn(CO)₃(bpy') complex, but it leaves the question of the specific mode of μ-CO coordination open. The visible absorption band of (CO)₄Re(μ-CO)Mn(CO)₃(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 Re₂(CO)₁₀ was detected in the IR spectra alongside the dominant (CO)₄Re(μ-CO)Mn(CO)₃(bpy') photoproduct.

The photoreaction of 1e 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(μ-CO)Mn(CO)₃(bpy') decreased and the parent (CO)₄ReMn(CO)₃(bpy') complex (1e) was largely regenerated by the back-reaction with CO still present in the tight spectral cell. As well, minor formation of the Mn₂(CO)₄(bpy')₂ coupling product was detected by a small absorbance increase at approximately 830 nm. Photolysis of 1e in toluene and THF at 173 and 183 K, respectively, yielded again the bridged (CO)₄Re(μ-CO)Mn(CO)₃(bpy') product (see Table 1 for the spectral data), together with small amounts of Re₂(CO)₁₀ and Mn₂(CO)₄(bpy')₂. Warming the THF solution to 233 K led to a disappearance of the IR and visible absorption bands of (CO)₄Re(μ-CO)Mn(CO)₃(bpy') with a concomitant rise of the bands belonging to the starting complex and also to the secondary products Mn₂(CO)₄(bpy')₂ and Re₂(CO)₁₀. These species were the only stable products observed during the photolysis at 233 K. Re₂(CO)₁₀ was detected by the IR spectra, whereas Mn₂(CO)₄(bpy')₂ was manifested by its ν(CO) IR bands as well as by absorption bands at 837 nm (toluene) and 822 nm (THF).

Under all reaction conditions employed (solvent, temperature), Mn₂(CO)₄(bpy')₂ and Re₂(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 Re₂(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(μ-CO)Mn(CO)₃(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(μ-CO)Mn(CO)₃(bpy') were already present. All these observations indicate that both radical-coupling products Mn₂(CO)₄(bpy')₂ and Re₂(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(μ-CO)Mn(CO)₃(bpy')

The same bridged (CO)₄Re(μ-CO)Mn(CO)₃(bpy') species was formed upon irradiation of a solution of 1e in 2-MeTHF containing CCl₄ or PPh₃ 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 CCl₄, the IR spectral changes resemble those observed earlier for an analogous photoreaction of (CO)₂Mn(μ-CO)Mn(CO)₃(bpy'). In both cases, the ν(CO) bands of a tetracarboxyl complex appeared. The reaction of (CO)₄Re(μ-CO)Mn(CO)₃(bpy'), photoproduced from 1e, yielded a product with ν(CO) bands at 2829, 2150, 2100, 2050, 2000, 1950, 1900, and 1850 cm⁻¹.
with CC14 and PPh3 was followed by raising the temperature of the
photolyzed solution of the mixture lc/PPh3/CC14 in the molar
supra).

the Nd:YAG laser, close to the maximum of the MLCT band
complexes,29 the product of the thermal reaction of (C0)4Re-

and new absorptions in the violet (400-500 nm) and, especially,

which corresponds
to absorb strongly. A new absorption band appears 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 correspond-
ing 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)4Re(μ-CO)Mn(CO)2(pAn-
DAB), analogous to the (semi)bridged complex characterized at
low temperature for IC, or the solvent-substituted species
(CO)3ReMn(S)(CO)(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 PPh3 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 PPh3.

Importantly, no evidence for the absorption of Re(CO)5 around
550 nm20 was found in any of the nanosecond absorption spectra
measured. Apparently, no radicals are formed by a 532-nm

and nano- to millisecond time-resolved absorption spectra were
measured for room-temperature solutions of complexes la and

bleached absorption is a negative mirror image of the ground-
state absorption in the mixture la/PPh3/CC14. 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.

A nanosecond transient absorption spectrum obtained for la
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 Ib in
toluene, neat 2-MeTHF, 2-MeTHF containing 10- and 200-fold
excess of PPh3, 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 PPh3 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 correspond-
ing to the photoproduct. Its transient absorption was found to
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Importantly, no evidence for the absorption of Re(CO)5 around
550 nm20 was found in any of the nanosecond absorption spectra
measured. Apparently, no radicals are formed by a 532-nm

2093, 2010 (sh), 1989, and 1969 cm−1, whereas the dimanganic
complexes gave a product characterized by IR bands at 2069,
1999, 1983, and 1968 cm−1, assigned6 to Mn(CO)4(2-MeTHF)Cl.
Because of this analogy and also because of the close
correspondence with the (μ-CO) bands of Re(CO)4(PR3)Cl
complexes,29 the product of the thermal reaction of (CO)4Re-
(μ-CO)Mn(CO)2(bpy') with CCl4 was assigned as Re(CO)4(2-
MeTHF)Cl. Only weak bands belonging to Mn(CO)4(bpy')Cl6
were detected. The thermal reaction of the CO-(semi)bridged
complex (CO)4Re(μ-CO)Mn(CO)2(bpy') with PPh3 at about 200
K gave rise to the formation of (CO)4ReMn(CO)2(PPh3)(bpy'),
as manifested by its IR and visible spectra (Table 1). In the
presence of more basic PPh3, the substituted product (CO)4-
ReMn(CO)2(PPh3)(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 CCl4 and PPh3 was followed by raising the temperature of the
photolyzed solution of the mixture lc/PPh3/CC14 in the molar
eratio 1/100/100 in 2-MeTHF from 143 to about 200 K. Only
the substitution product (CO)4ReMn(CO)2(PPh3)(bpy') was then
formed without any evidence of halogen abstraction. Obviously,
PPh3 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 la and
Ib 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 la 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 radical is known30
to absorb strongly. A new absorption band appears in the red
spectral region. Its formation is very rapid, being completed

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

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 Ib 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.

(29) See, e.g.: Singleton, E.; Moelwyn-Hughes, J. I.; Garner, A. W. B. J.
(30) Yasufuku, K.; Noda, H.; Iwai, J.; Ohnani, H.; Hoshino, M.; Kobayashi,
T. Organometallics 1985, 4, 2174.
Scheme 1. Reactivity of (CO)$_2$ReMn(CO)$_3$(α-dimine) Complexes, 1, under Irradiation with Visible Light

\[
\begin{align*}
\text{(CO)$_2$ReMn(CO)$_3$(N,N)} & \xrightarrow{h\nu} \text{(CO)$_2$ReMn(CO)$_2$(N,N) + CO} \\
\text{(CO)$_2$ReMn(CO)$_3$(PPh$_3$)(N,N)} & \xrightarrow{h\nu, \Delta} \text{Re(CO)$_2$Cl + Mn(CO)$_3$(N,N)Cl} \\
& \quad \text{Re$_2$(CO)$_3$(PhenSO)$_2$} + \text{Mn(CO)$_3$(N,N)(PhenSO)} + \text{Mn(N,N)(PhenSO)$_2$} \\
& \quad \text{Re$_2$(CO)$_3$(PhenSO)$_2$} + \text{Mn(CO)$_3$(N,N)(PhenSO)} + \text{Mn(N,N)(PhenSO)$_2$}
\end{align*}
\]

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)$^*$ 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 photoprocess 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)$_2$ReMn(CO)$_3$(α-dimine) complexes investigated, 1a–c, exhibit two types of photoactivity when irradiated into their Mn-dimine MLCT absorption band. First, a chlorine abstraction (eq 1) from CCl$_4$ and CH$_2$Cl$_2$ and oxidative addition of 9,10-phenanthrenquinonone (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)$_2$ReMn-(CO)$_3$(PPh$_3$)(α-dimine). The mechanism of these reactions has been elucidated using quantum yields and their pressure dependences that afford also very similar values of the apparent activation volumes, AV.

The quantum yields and their pressure dependencies were measured at a very large excess of the reactants (CH$_2$Cl$_2$, 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)$_2$Re(μ-CO)Mn(CO)$_3$(α-dimine) 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:

\[
\begin{align*}
\text{(CO)$_2$ReMn(CO)$_3$(α-dimine)} & \xrightarrow{h\nu} \text{(CO)$_2$ReMn(CO)$_3$(α-dimine)} \\
& \xrightarrow{-\text{CO}} \text{(CO)$_2$Re(μ-CO)Mn(CO)$_3$(α-dimine)}
\end{align*}
\]

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

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$^\text{A}$. 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
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. $+21 \text{ cm}^3 \text{ mol}^{-1}$ for HRu$_3$(CO)$_3$[135,132,37], Cr(CO)$_6$ (7.0 - 9.3 cm$^3$ mol$^{-1}$), Mo(CO)$_6$ (14.0 cm$^3$ mol$^{-1}$), W(CO)$_6$(bpy) (5.7 cm$^3$ mol$^{-1}$), and Cr(CO)$_5$ (9.6 - 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 the 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)$_3$ReMn(CO)$_2$- (a-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 photoprodut, (CO)$_2$Re(μ-CO)Mn(CO)$_2$- (a-diimine), undergoes reactions with PPh$_3$ as well as with CH$_2$Cl$_2$, CCl$_4$, and PhenQ, as shown in Scheme 1. This assumption was confirmed at low temperatures by the direct observation that the photoproduced (CO)$_2$Re(μ-CO)Mn(CO)$_2$(bpy) reacts thermally with PPh$_3$ and CCl$_4$ to afford (CO)$_2$ReMn(CO)$_2$(PPh$_3$) and Cl-containing products, Re(CO)$_3$Cl and Mn(CO)$_2$(bpy)/Cl, respectively.

The high reactivity of the (CO)$_2$Re(μ-CO)Mn(CO)$_2$- (a-diimine) primary photoprocess toward CH$_2$Cl$_2$ and CCl$_4$ is rather surprising. The propensity of analogous coordinatively unsaturated binuclear metal carbonyl complexes and oxidative additions has already been demonstrated. Thus, the (CO)$_2$M(μ-CO)M(CO)$_2$ (M = Mn, Re) complexes react with α-quinones (17) to form Mn(CO)$_2$(α-quinone) radical species. Semibridged (μ-Mn(μ-CO)M(CO)$_2$ produced by irradiation of Mn$_2$(CO)$_3$ in alkane glass yielded (48) only a negligible amount of Mn(CO)$_2$Cl 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)$_3$ was also obtained from a detailed quantum yield study (55) carried out at room temperature. The kinetics of oxidative addition of Bu$_3$SnH and Et$_3$SiH to photocatalytically generated L(CO)$_2$(μ-CO)Mn(μ-CO)Mn(CO)$_2$L species (L = CO, PMe$_3$, PBu$_3$, PPri$_3$) was also studied in detail (47). 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 mononeric compounds containing oxidized metal atoms, M$_2$ are ultimately formed. Mn(CO)$_3$Cl is thus produced in the reaction with CCl$_4$, whereas oxidative addition of Bu$_3$SnH leads to HMn(CO)$_4$L and Bu$_3$SnMn(CO)$_3$L. For dinuclear carbonyl complexes containing diimine ligands, an efficient reaction of bridged (μ-Mn(μ-CO)Mn(CO)$_2$(bpy)), photoproduced from Mn$_2$(CO)$_3$(bpy), with CCl$_4$, CH$_2$Cl$_2$, and PhenQ was demonstrated (18). Unbridged Ph$_3$SnMn(CO)$_2$(a-diimine) complexes, which are formed by a CO photodissociation from Ph$_3$SnMn(CO)$_2$(a-diimine), add oxidatively PhenQ (18). However, their reactions with CCl$_4$ and CH$_2$Cl$_2$ are very inefficient (9), apparently because of the great strength of the Sn–Mn bond. The CO-loss products of 1a-e, i.e. (CO)$_2$Re(μ-CO)Mn(CO)$_2$- (a-diimine) complexes, are the first dinuclear carbonyl species that abstract the Cl atom efficiently from CH$_2$Cl$_2$ despite the presence of a strong Re–Mn bond. This (semi)bridged intermediate also readily reacts with potential ligands L to produce (CO)$_2$ReMn(CO)$_2$(L)(a-diimine). For L being a strong ligand (PPh$_3$, PBu$_3$), this substitution product is stable. However, if L is a redox-active species like PhenQ, CH$_2$Cl$_2$, 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$_2$Cl$_2$ with complexes 1a-e than with Ph$_3$SnMn(CO)$_3$(bpy), whose primary photoprocess, Ph$_3$SnMn(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)$_2$Re(μ-CO)- Mn(CO)$_2$(a-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 (35), unless accompanied by mechanistic studies.

The (CO)$_2$ReMn(CO)$_2$(a-diimine) complexes are exceptional among dinuclear transition-metal carbonyls, as they undergo efficient ($\phi \geq 0.5$) 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. However, such a MLCT reactivity is usually low and characterized by a pronounced excitation-wavelength dependence of photochemical quantum yields (38,39), 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)$_2$(a-diimine) fragment of the L$_2$M'Mn(CO)$_3$(a-diimine) complexes. Analogous L$_2$M'(Re(CO)$_2$(a-diimine) complexes do not undergo photochemical CO dissociation. The reactive Mn(CO)$_2$(a-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$^5$-d$^6$ (LF) state (d$^5$ being a d orbital antibonding with respect to the Mn–CO bond). Rapid non-
Photochemistry of Metal–Metal-Bonded Complexes

The photochemistry of dinuclear carbonyls which do undergo efficient M'-M-bond homolysis, e.g. \((\text{CO})_5\text{MRe(CO)}_3(\alpha\text{-diimine})\) \((M = \text{Mn, Re})\), is usually interpreted by population of the spectroscopically silent \(\sigma\rightarrow\pi^*\) excited state that corresponds to the electron excitation from the \(\sigma\) bonding orbital to the diimine \(\pi^*\) orbital. As shown by the UPS spectra, the \(\sigma\) 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 \(\sigma\rightarrow\pi^*\) MLCT states is quite conceivable, as it involves only an electronic transition from the \(\sigma\) orbital to a lower-lying half-occupied \(\sigma^*\) orbital. The \(\sigma\rightarrow\sigma^*\) state lies much higher because of the large ligand-field splitting of Re(1) \(d\) orbitals. Thus, the Re-Mn 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 \((\text{CO})_5\text{MRe(CO)}_3(\alpha\text{-diimine})\). However, for complexes 1 that contain the Mn\((\alpha\text{-diimine})\) fragment, the separation between the manganese \(d\) and \(d^*\) orbitals is so small that the \(\sigma\rightarrow\sigma^*\) state becomes the lowest-lying state. Consequently, the Re-Mn bond does not photodissociate and, instead, CO dissociation from the \(\sigma\rightarrow\sigma^*\) (LF) excited states. The last is sufficiently low-lying in complexes containing the Mn\((\alpha\text{-diimine})\) fragment. Only the \(\text{LnM'Mn(CO)}_3(\alpha\text{-diimine})\) complexes thus undergo efficient CO dissociation as primary photoprocess.

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