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Photochemistry of Metal-Metal Bonded Complexes. II.[1] The Photochemistry of Rhenium and Manganese Carbonyl Complexes Containing a Metal-Metal Bond

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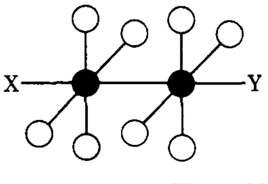
Abstract: The photochemistry of $Mn_2(CO)_{10}$, $Mn_2(CO)_9PPh_3$, $Mn_2(CO)_8(PPh_3)_2$, $Re_2(CO)_{10}$, and $MnRe(CO)_{10}$, I, II, III, IV, and V, respectively, is reported. Photolysis at 366 nm of I–V in CCl_4 yields the corresponding mononuclear metal carbonyl chloride with high (~0.5) quantum efficiencies and with stoichiometries consistent with symmetrical metal-metal bond cleavage. Photolysis of I, IV, or V in the presence of $\sim 10^{-3}$ *M* I_2 yields the expected $M(CO)_5I$ species with an essentially quantitative chemical yield and quantum yields comparable to those for reaction in pure CCl_4. Photolysis of I or IV in the presence of $PhCH_2Cl$ or Ph_3CCl gives good yields of bibenzyl or $Ph_3C\cdot$ radicals, respectively. Complexes I and IV are formed in ~1:1 yield upon flash photolysis of V; I and III are formed in ~1:1 yield upon flash photolysis of II in pure isooctane; and V is formed from the photolysis of a mixture of I and IV. Complex III is found to be the principal primary photoproduct upon 366-nm photolysis of I in isooctane solutions of 0.1 *M* PPh_3. All of the observed photochemistry can be interpreted as arising from homolytic metal-metal bond cleavage occurring from an excited state derived from a $\sigma_b \rightarrow \sigma^*$ one-electron transition associated with the metal-metal bond. Each of I–V exhibits a near-uv absorption corresponding to this transition.

Though structurally well characterized,[4,5] polynuclear metal carbonyls containing direct metal-metal bonds have received relatively little study with respect to reactions which could lead to clean rupture of the metal-metal interaction. Such reactions may have real importance in the characterization of paramagnetic organometallic complexes in that cleavage of the metal-metal bond can potentially lead to two paramagnetic centers. Even though paramagnetic metal carbonyls are rare, intermediates having an odd number of electrons may be important in both stoichiometric and catalytic reactions of metal carbonyls with organic substrates. The monomeric d^7, 17-electron C_{4v} $Co(CN)_5{}^{3-}$ complex having its unpaired electron in the $d_{z^2}(a_1)$ orbital[6] has rich chemistry including reaction with alkyl halides,[7] olefins,[8] and small molecules such as H_2, halogens, SO_2, etc.[9] The $Co(CN)_5{}^{3-}$ also catalyzes the hydrogenation of 1,3-dienes under very mild conditions.[10] The cleavage of the M–M bond in $M_2(CO)_{10}$ (M = Mn, Re) could yield a C_{4v}, d^7, 17-electron species having some reactivity patterns in common with $Co(CN)_5{}^{3-}$.

One of us recently communicated[1] the results of a quantitative study of the photolysis of $Re_2(CO)_{10}$ in CCl_4 which was found to proceed as in reaction 1. Other, more qualitative, reports[11-13] of the photochemistry of manganese and rhenium compounds containing metal-metal bonds are consistent with the notion that electronic excitation is followed by efficient chemical decay paths resulting in rupture of the metal-metal bond. We now report the results of the first quantitative studies of the photoreactivity of $Mn_2(CO)_{10}$, $Mn_2(CO)_9(PPh_3)$, and $Mn_2(CO)_8(PPh_3)_2$, I, II, and III, respectively. We include some new studies of $Re_2(CO)_{10}$

$$Re_2(CO)_{10} \xrightarrow[CCl_4]{313\text{ nm}\ \Phi = 0.6} 2Re(CO)_5Cl \qquad (1)$$



I, ● = Mn
○ = X = Y = CO
II, ● = Mn
○ = X = CO
Y = PPh_3
III, ● = Mn
○ = CO
X = Y = PPh_3
IV, ● = Re
○ = X = Y = CO

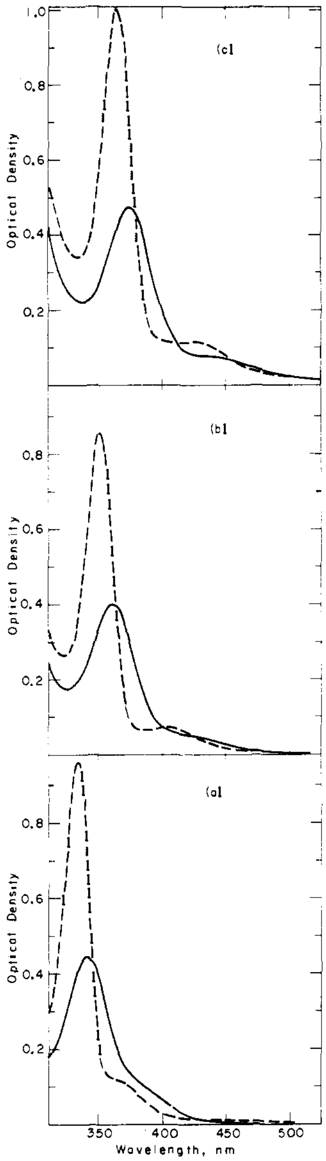


Figure 1. Comparison of 298 (——) and 77°K (- - - -) absorption spectra of (a) $Mn_2(CO)_{10}$, (b) $Mn_2(CO)_9PPh_3$, and (c) $Mn_2(CO)_8(PPh_3)_2$ in EPA. The spectra at 77°K are for the same solution as at 298°K but the low temperature spectra are not corrected for solvent contraction. Band maxima and molar extinction coefficients are given in Table I.

(IV) and we describe the photochemistry of the mixed Mn-Re complex $ReMn(CO)_{10}$ (V), which is isostructural with I and IV.

Results

a. Spectra. The band maxima and molar extinction coefficients are summarized in Table I for I-V. The electronic spectra of I-III have been measured in EPA solution at 298 and 77°K and are shown in Figure 1. The spectra are dominated by an intense ($\epsilon \approx 20{,}000$ l. mol^{-1} cm^{-1}) absorption maximizing in the near-uv. The band red shifts with increasing PPh_3 substitution being energetically ordered I > II > III. Each complex also exhibits a lower intensity ($\epsilon \approx 2000$ l. mol^{-1} cm^{-1}), absorption which falls at lower energy than the more intense near-uv absorption. This lowest energy absorption is only a shoulder at 298°K but is better resolved at 77°K. The absorptions tail sufficiently that even fairly modest concentrations of I-III yield yellow to orange solutions. Complex IV also has a very intense ($\epsilon \approx 16{,}000$ l. mol^{-1} cm^{-1}) near-uv absorption near 310 nm. There is no discernible low energy shoulder, even at 77°K as shown in Figure 2 and the absorption does not tail into the visible region. Absorption bands not observed in I-III do appear in

Table I. Electronic Spectral Band Maxima for Metal-Metal Bonded Compounds

Complex	Bands, nm (ϵ, l. mol^{-1} cm^{-1})[a]
I	~390 (sh), 342 (21,400)
II	~430 (sh), 360 (24,200)
III	~450 (sh), 373 (23,700)[b]
IV	~313 (15,500), 275 (12,800)
V	323 (13,700), ~263 (sh)

[a] Isooctane solution, 25° except where noted. [b] CH_2Cl_2 solution, 25°.

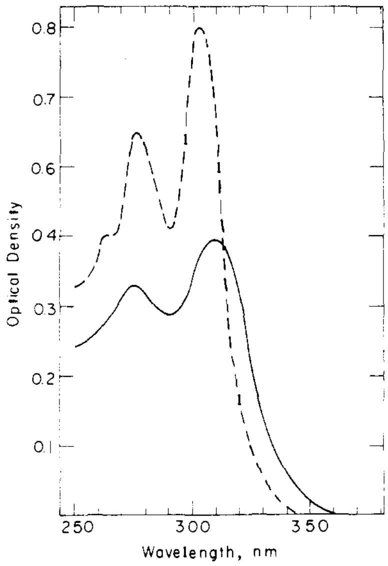


Figure 2. Comparison of 298 (——) and 77°K (- - - -) absorption spectra of $Re_2(CO)_{10}$ in EPA and as in Figure 1.

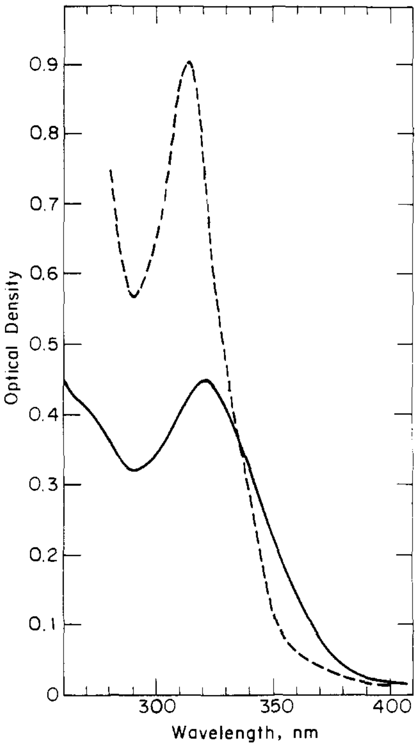


Figure 3. Comparison of 298 (——) and 77°K (- - - -) absorption spectra of $MnRe(CO)_{10}$ in EPA and as in Figure 1.

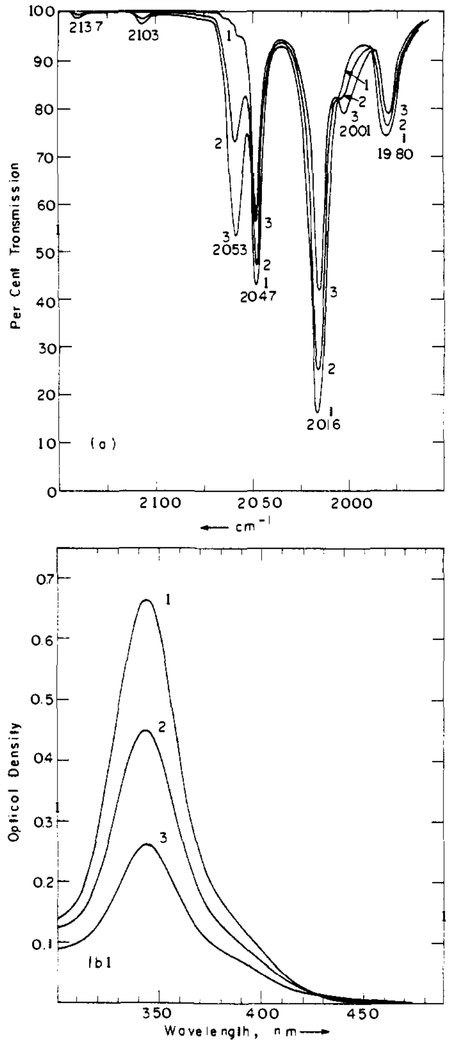


Figure 4. Ir (a) and uv-visible (b) spectral changes upon 366-nm photolysis of a 3.0 ml aliquot of $Mn_2(CO)_{10}$ in degassed CCl_4 solution. Ir bands 2047, 2016, and 1980 cm^{-1} are $Mn_2(CO)_{10}$, 2137, 2053, and 2001 cm^{-1} are $Mn(CO)_5Cl$, and the band at 2103 cm^{-1} is $[Mn(CO)_4Cl]_2$ formed from secondary photolysis and thermolysis of $Mn(CO)_5Cl$. Curve 1 in both (a) and (b) corresponds to the initial spectrum, and curves 2 and 3 are after 45 min and 90 min photolysis, respectively, at 1.7×10^{-7} einstein/min. The initial $Mn_2(CO)_{10}$ concentration was 2.89×10^{-3}, and ir spectra were obtained without dilution using 0.1-mm path length cells. Uv spectra were obtained subsequent to dilution 1:100 with CCl_4 using 1.00-cm cells.

IV on the high energy side of the intense 310-nm absorption. Complex V is a pale yellow solid giving weakly yellow solutions with an intense near-uv absorption maximum intermediate in energy between I and IV. There is no detectable low energy shoulder even at 77°K, but a shoulder does appear near 270 nm as found in IV. The absorption spectrum of V is shown in Figure 3.

The quantitative analysis of photoreactions of I–V has required the use of infrared absorption spectroscopy as well as electronic spectroscopy. We have determined the molar extinction coefficients of CO stretching bands for the complexes I–V as well as for several of their photoproducts and these along with CO stretching band maxima are given in Table II. The ir spectra are very sensitive to the nature of the solvent and this is specified in each case. The ir molar extinction coefficients in Table II are accurate to only ±15%.

b. Photochemistry. 1. Photolysis in the Presence of CCl_4. Near-uv and visible photolysis of I–V in degassed CCl_4 solutions has been carried out and the reactions proceed largely as indicated in (eq 1–5). Uv-visible and ir spectral changes upon photolysis of I in CCl_4 are shown in Figure 4, and ir spectral changes upon photolysis of II are shown in Figure 5. Disappearance quantum yields of the starting materials and appearance yields of $ClM(CO)_5$ and $ClM(CO)_4PPh_3$ are given in Table III. These known mononuclear complexes are formed in very high, if not quantitative, chemical yields and the initial quantum yields reveal that the total product formation quantum yields are about twice the disappearance yield of the starting material except for complex III. We have not measured the CCl_4 reac-

Table II. Ir Band Maxima and Molar Extinction Coefficients for Some Mn and Re Carbonyls[a]

Complex	Solvent	Bands, cm^{-1} (ϵ, l. mol^{-1} cm^{-1})
I	Isooctane (4% CH_2Cl_2 by volume)	2015 (34,400)
	Isooctane	2046 (13,900), 2015 (40,350), 1982 (7940)
	CCl_4	2050 (12,500), 2015 (26,500), 1970 (4500)
II	Isooctane	2093 (2300), 2013 (5800), 1998 (24,900), 1972 (2700), 1938 (4200)
	CCl_4	2091 (3170), 2010 (5200), 1998 (14,050), 1967 (1900), 1932 (3350)
III	Isooctane (4% CH_2Cl_2 by volume)	1955 (11,800)
	CCl_4	1955 (8800)
IV	Isooctane	2071 (8369), 2015 (42,400), 1972 (12,300)
V	Isooctane	2055 (8900), 2019 (36,500), 1977 (10,200)
	CCl_4	2055 (7700), 2018 (26,700), 1972 (6800)
$Mn(CO)_5Cl$	CCl_4	2060 (8100), 1999 (3900)
$Mn(CO)_5I$	Isooctane	2044 (23,300), 2003 (5400), 2125 (1400)
cis-$Mn(CO)_4ClPPh_3$	CCl_4	2095 (2350), 2030 (3060), 2010 (4230), 1958 (3510)
$Re(CO)_5I$	Isooctane	2145 (700), 2043 (21,800), 2017 (557), 1986 (6280)
$Re(CO)_5Cl$	CCl_4	2045 (16,000), 1982 (4300)

[a] 25°

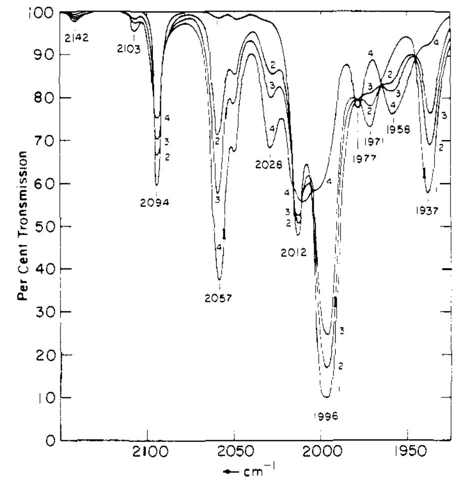


Figure 5. Ir spectral changes accompanying 366 nm (1.51×10^{-7} einstein/min) photolysis of a 3.0-ml aliquot of $Mn_2(CO)_9PPh_3$ (7.11×10^{-4} *M*) in degassed CCl_4 solution. Maxima in this figure at 2142 and 2057 cm^{-1} are $Mn(CO)_5Cl$, 2094, 2012, 1996, 1971, and 1937 cm^{-1} are $Mn_2(CO)_9PPh_3$, and 2028 and 1958 cm^{-1} are *cis*-$ClMn(CO)_4PPh_3$. The peak at 2103 cm^{-1} is ascribed to $[Mn(CO)_4Cl]_2$ formation by secondary reactions of $Mn(CO)_5Cl$. Curve 1 corresponds to zero irradiation time and curves 2, 3, and 4 are after 10, 15, and 30 min, respectively.

Table III. Quantum Yields for Reaction of Metal–Metal Bonded Compounds in CCl_4

Starting material	Product	Irradiation λ, nm	Φ_{dis} ±10%	Φ_{formn} ±10%	Φ_{formn}/Φ_{dis}
I	$Mn(CO)_5Cl$	366	0.41	0.72	1.76
	$Mn(CO)_5Cl$	313	0.48	1.02	2.13
II	$Mn(CO)_5Cl$	366	0.45	0.36	0.80
	$Ph_3PMn(CO)_4Cl$			0.40	0.89
III	$Ph_3PMn(CO)_4Cl$	366	0.70	0.48	0.69
IV[a]	$Re(CO)_5Cl$	313	0.60	1.20	2.0
V	$Re(CO)_5Cl$	366	0.42	0.43	1.02
	$Mn(CO)_5Cl$			0.46	1.10

[a] Reference 1.

Table IV. Reaction of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ with I_2[a]

Complex	Solvent	Φ_{dis} (M–M)	Φ_{dis} (I_2)	Φ_{formn}
$Re_2(CO)_{10}$	Isooctane	0.64	0.64	1.14[b]
	Isopentane	0.64	0.64	
	Nujol	0.30	0.30	
$Mn_2(CO)_{10}$	Isooctane	0.44	0.44	0.74[c]
	Isopentane	0.5_1	0.5_1	
	Nujol	0.30	0.30	
	Cyclohexane	0.4_4	0.4_4	
$MnRe(CO)_{10}$	Isooctane	0.45	0.55	0.38[b] 0.37[c]

[a] The metal–metal complex is typically 10^{-4} *M* and the I_2 is 10^{-3} to 10^{-4} *M*. [b] Formation quantum yield for $Re(CO)_5I$. [c] Formation quantum yield for $Mn(CO)_5I$.

$$Mn_2(CO)_{10} \xrightarrow[CCl_4]{h\nu} ClMn(CO)_5 \tag{2}$$

$$Mn_2(CO)_9(PPh_3) \xrightarrow[CCl_4]{h\nu} ClMn(CO)_5 + ClMn(CO)_4PPh_3 \tag{3}$$

$$Mn_2(CO)_8(PPh_3)_2 \xrightarrow[CCl_4]{h\nu} ClMn(CO)_4PPh_3 \tag{4}$$

$$ReMn(CO)_{10} \xrightarrow[CCl_4]{h\nu} ClMn(CO)_5 + ClRe(CO)_5 \tag{5}$$

tion product (cf. vida infra). Quantitative studies have been complicated by secondary thermal reactions of the mononuclear manganese carbonyls formed in the primary photoreaction. Fortunately, complexes I, II, IV, and V are inert at 25° *in the dark.* Complex III reacts with CCl_4 slowly at 25° in the dark to give some of the $ClMn(CO)_4PPh_3$ product and some decomposition. The major error, however, in the CCl_4 solvent system is likely the error in ir band molar extinction coefficients compounded by the difficulty in preparing extremely pure authentic samples of the products. We are most confident of the data for I, IV, and V which have been determined both by ir and uv-visible spectral changes. However, the noteworthy result for each of I–V is clear: electronic excitation of the M–M bonded molecule yields very efficient formation of mononuclear metal carbonyls containing one M–Cl bond.

2. Photolysis in the Presence of Ph_3CCl and $PhCH_2Cl$. Near-uv photolysis of I in the presence of 0.1 *M* $PhCH_2Cl$ in benzene continuously purged with N_2 leads to $PhCH_2$-CH_2Ph with a 68% chemical yield after essentially complete disappearance of I. Likewise, photolysis of IV under the same conditions gives a 70% yield of bibenzyl. Under these conditions the mononuclear metal carbonyl chloride is the major metal containing product.

Photolysis of any of I–V in degassed benzene solutions of Ph_3CCl yields the ESR detectable $Ph_3C\cdot$ free radical and the corresponding mononuclear metal carbonyl chloride. Photolysis of $M(CO)_5Cl$ (M = Mn, Re) under the same conditions gives no ESR detectable $Ph_3C\cdot$ radicals.

3. Photolysis in the Presence of Iodine Donors. Complexes II and III react thermally with I_2 in the dark but I, IV, and V are thermally inert to I_2 at 25°. Photolysis of I, IV, and V in degassed aliphatic hydrocarbon solutions of I_2 proceeds according to reaction 6. The disappearance of both

$$MM'(CO)_{10} \xrightarrow[\text{aliphatic hydrocarbon, } I_2(10^{-3}\text{–}10^{-4}\,M)]{366\text{ nm}} M(CO)_5I + M'(CO)_5I \tag{6}$$

the metal–metal bonded compound and the I_2 was measured, and the two reactants disappear with the same quantum yield. Uv–visible and ir spectral changes for the photoreaction of IV and I_2 are shown in Figure 6. Direct irradiation of the I_2 at 550 nm leads to no detectable reaction. Importantly, the initial reaction quantum yields for the disappearance are nearly the same as those for the yields obtained in CCl_4 solution even though the I_2 concentration is only ~10^{-3}–10^{-4} *M*. Quantum yields for several aliphatic hydrocarbon solvents are given in Table IV, and for I and IV a viscosity effect does obtain. The viscosity effect tends to rule out significant ground state interaction of the metal-metal bonded complex with I_2.

Photolysis at 313 nm of IV in 0.1 *M* CH_3I in deoxygenated isooctane solution results in $Re(CO)_5I$ as the only metal containing product. The ir and near-uv spectral changes accompanying this reaction are the same as those which occur upon photolysis of IV in the presence of I_2 (Figure 6) including the fact that an isosbestic point obtains at ~338 nm in the near-uv. These facts ensure that no $CH_3Re(CO)_5$ is formed.

4. Photolysis in Pure Isooctane. The photolysis of II in degassed isooctane proceeds as indicated in reaction 7. The

$$Mn_2(CO)_9PPh_3 \xrightarrow{h\nu} Mn_2(CO)_{10} + Mn_2(CO)_8(PPh_3)_2 \tag{7}$$

photolysis was carried out continuously at low light intensity at 366 nm or by flash photolysis and the important result in each case is that I and III are formed in nearly a 1:1 ratio. Typical experimental data are given in Table V. The chemical yield of the new products is not 100%, but as seen in Table V the chemical yields are quite substantial. Attempts to carry out reaction 7 at very low concentration of II (~10^{-5} *M*) leads to destruction of all metal-metal bonded compounds. Similar photochemical behavior has also been noted for I, III, IV, and V. Purging ~10^{-5} *M* solutions of I–IV with CO during photolysis minimizes decomposition, and for II and III the reaction ultimately yields I. Flash photolysis of approximately equimolar solutions of I and III yields a substantial amount of II, and the data are included in Table V.

The results above for apparent cross coupling of mononuclear metal carbonyl photofragments are somewhat equivocal since the coordination sphere does seem to be labile, and much net decomposition obtains. We have thus investigated the efficiency of both the formation of V from the photolysis of a mixture of I and IV and the photolysis of V itself. These photolyses were carried out under 1 atm of CO to attempt to minimize decomposition. The results are included in Table V and we find that flash photolysis of a 1:1 mixture of I and IV initially gives V with relatively little decomposition. Photolysis of V itself regenerates some I and IV in nearly a 1:1 ratio. The results for the photolysis of complexes such as I–V in isooctane show that metal-metal bond cleavage does obtain and that the cross coupling of photogenerated fragments does occur.

5. Photolysis of $Mn_2(CO)_{10}$ in the Presence of PPh_3. Photolysis of I in degassed isooctane solutions of PPh_3 yields III

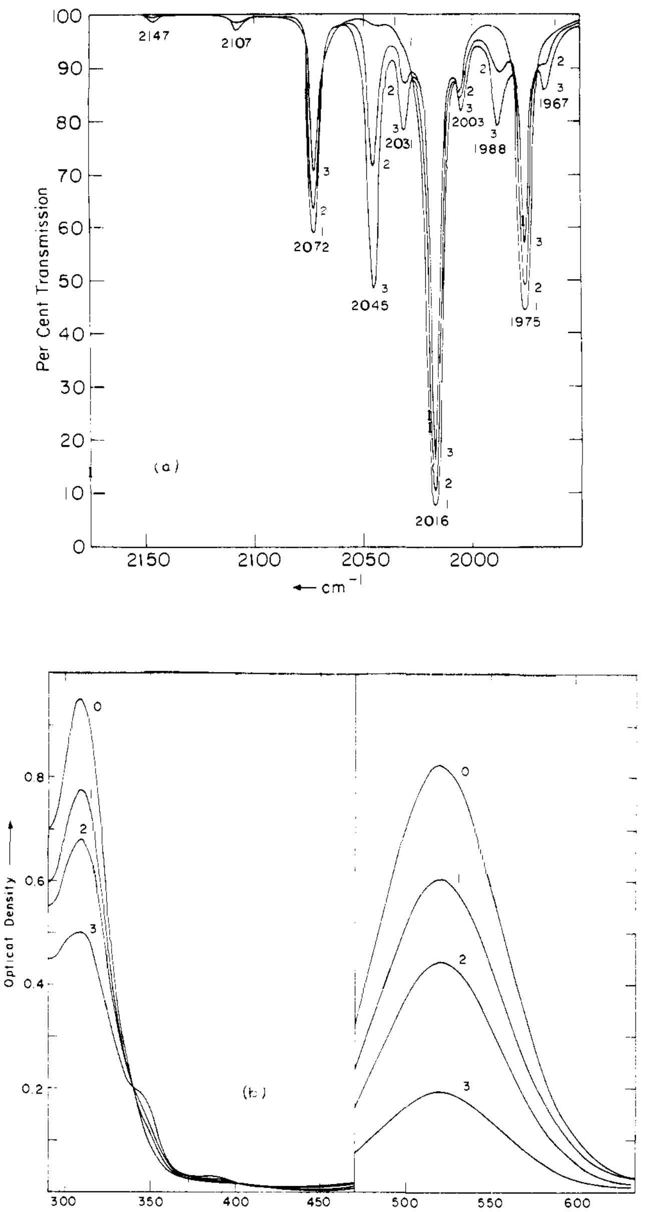


Figure 6. (a) Ir spectral changes accompanying 313-nm (1.64×10^{-8} einstein/min) photolysis of $Re_2(CO)_{10}$ (2.94×10^{-3} M) in the presence of 5×10^{-3} M I_2 in a degassed 3.0-ml isooctane solution. Peaks at 2072, 2016, and 1975 cm^{-1} are associated with $Re_2(CO)_{10}$, 2147, 2045, and 1988 cm^{-1} peaks are due to $Re(CO)_5I$, and 2107, 2031 and 2003 cm^{-1} peaks are due to $[Re(CO)_4I]_2$ formed from secondary photolysis of $Re(CO)_5I$. Curve 1 is the spectrum of the initial solution, and curves 2 and 3 are after 120 and 240 min of photolysis, respectively. (b) The uv and visible spectral changes accompanying 366-nm photolysis of $Re_2(CO)_{10}$ (1.4×10^{-3} M) in the presence of 1.0×10^{-3} M I_2 in a degassed 3.0 ml cyclohexane solution. The curves to the right show the decline in absorbance of I_2. The I_2 absorbances were measured in 1.00-cm path length cells with no dilution. The curves to the left show the spectral changes accompanying $Re_2(CO)_{10} \rightarrow Re(CO)_5I$ conversion and these spectra were measured subsequent to dilution by 1:25 with cyclohexane. The light intensity is $\sim 10^{-7}$ einstein/min and curves 0, 1, 2, and 3 correspond to zero, 30, 60, 90, and 120 min of photolysis, respectively.

as the principal primary photoproduct with a quantum yield of 0.31 at 366 nm. The formation of II is only a very minor component (<5%) of the reaction. The linear increase of III with irradiation time shown in Figure 7 confirms that this product is a primary photoproduct. This product accounts for essentially all of the Mn containing products based on I disappeared and III appeared by ir spectral measurements.

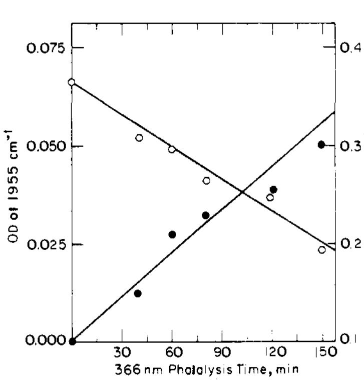


Figure 7. Plot of increase in optical density of the 1955-cm^{-1} absorption band of $Mn_2(CO)_8(PPh_3)_2$ (● and left scale) and decline of the 2015-cm^{-1} absorption band of $Mn_2(CO)_{10}$ (○ and right scale) against photolysis time of 3.0-ml degassed isooctane solutions of $Mn_2(CO)_{10}$ (1.1×10^{-3} M) in the presence of PPh_3 at 0.1 M. Photolysis is at 366 nm at 2.47×10^{-8} einstein/min.

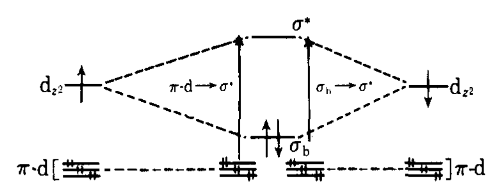
The quantum yield at 366 nm for this reaction is the same at 0 and 25°.

Discussion

The results support the general conclusions that near-uv photoexcitation of complexes I-V results in homolytic cleavage of the metal-metal bond as the principal primary photoreaction, and the nature of the lowest excited states in I-V is consistent with the observed photochemistry. The essential arguments supporting these conclusions are discussed below.

The lowest excited states for I-V are believed to feature one-electron population of an orbital which is σ-antibonding with respect to the metal-metal bond.[14] Assignment of the intense near-uv transition in I and IV as a $\sigma_b \rightarrow \sigma^*$ transition according to Scheme I was first made by Levenson, Caesar, and Gray[14] and has been adopted by several other groups[15-17] for these compounds and other simple analogs. The low intensity, lower energy absorption shoulder which appears in the Mn complexes I-III is associated with the π-d $\rightarrow \sigma^*$ one-electron transition,[14] while for IV and V we suspect that this band is buried under the $\sigma_b \rightarrow \sigma^*$.[14c] The higher energy bands at ~275 nm in IV and V can be ascribed to σ_b, π-d $\rightarrow \pi^*$ CO transitions.[14c] Both of the excited states achieved by the $\sigma_b \rightarrow \sigma^*$ and the π-d $\rightarrow \sigma^*$ transition should have a weaker metal-metal interaction than the ground electronic state. Formally, the $\sigma_b \rightarrow \sigma^*$ transition will diminish the M-M bond order from one to zero and the π-d $\rightarrow \sigma^*$ will reduce the M-M bond order from one to one-half according to Scheme I and the approximation that

Scheme I



the M-M bond is a two-electron bond.

The first convincing evidence that symmetrical M-M bond cleavage is a photoreaction comes from the previous qualitative reports of reactions 8-10.[11-13] Our results for the flash photolysis and continuous photolysis of $Mn_2(CO)_9PPh_3$ parallel these observations and the approximately 1:1 ratio of $Mn_2(CO)_{10}$ to $Mn_2(CO)_8(PPh_3)_2$ formed is evidence to the fact that the mononuclear intermediates generated couple in an essentially statistical fash-

Table V. Photoreactions of Metal–Metal Bonded Complexes in Pure Isooctane[a]

Starting mixture (mol)	Photolysis mode	Mol reacted	Product(s) (mol)	% yield of M–M bonded products
$Mn_2(CO)_9PPh_3$ (3.84×10^{-6})	4 flashes at 100 J[b]	5.76×10^{-7}	$Mn_2(CO)_{10}$ (9.05×10^{-8}) $Mn_2(CO)_8(PPh_3)_2$ (9.30×10^{-8})	31
	2 flash bulbs[c]	1.06×10^{-6}	$Mn_2(CO)_{10}$ (1.53×10^{-7}) $Mn_2(CO)_8(PPh_3)_2$ (1.20×10^{-7})	26
	2 flash bulbs[c]	1.06×10^{-6}	$Mn_2(CO)_{10}$ (1.00×10^{-7}) $Mn_2(CO)_8(PPh_3)_2$ (1.77×10^{-7})	26
	1 flash bulb[c]	1.28×10^{-6}	$Mn_2(CO)_{10}$ (1.00×10^{-7}) $Mn_2(CO)_8(PPh_3)_2$ (0.68×10^{-7})	13
$Mn_2(CO)_9PPh_3$ (3.76×10^{-6})	366 nm, 4 hr[d]	2.9×10^{-7}	$Mn_2(CO)_{10}$ (1.87×10^{-8}) $Mn_2(CO)_8(PPh_3)_2$ (4.64×10^{-8})	22
	366 nm, 12 hr[d]	7.0×10^{-7}	$Mn_2(CO)_{10}$ (4.67×10^{-8}) $Mn_2(CO)_8(PPh_3)_2$ (1.65×10^{-7})	30
	366 nm, 66 hr[d]	1.74×10^{-6}	$Mn_2(CO)_{10}$ (6.36×10^{-7}) $Mn_2(CO)_8(PPh_3)_2$ (7.25×10^{-7})	78
	366 nm, 118 hr[d]	3.0×10^{-6}	$Mn_2(CO)_{10}$ (3.92×10^{-7}), $Mn_2(CO)_8(PPh_3)_2$ (7.60×10^{-7})	38
$Mn_2(CO)_{10}$ (2.58×10^{-6}) $Mn_2(CO)_8(PPh_3)_2$ (1.81×10^{-6})	2 flash bulbs[c]	2.04×10^{-6} 1.21×10^{-6}	$Mn_2(CO)_9PPh_3$ (5.57×10^{-7})	17
$Mn_2(CO)_{10}$ (2.58×10^{-6}) + $Mn_2(CO)_8(PPh_3)_2$ (1.81×10^{-6})	5 flashes at 125 J[b]	8.50×10^{-7} 9.00×10^{-7}	$Mn_2(CO)_9PPh_3$ (6.43×10^{-7})	37
$Re_2(CO)_{10}$ (5.04×10^{-6}) $Mn_2(CO)_{10}$ (5.37×10^{-6})	10 flashes at 900 J[b,e]	1.18×10^{-6} 1.57×10^{-6}	$MnRe(CO)_{10}$ (2.16×10^{-6})	79
$Re_2(CO)_{10}$ (5.04×10^{-6}) $Mn_2(CO)_{10}$ (5.37×10^{-6})	15 flashes at 900 J[b,e]	1.54×10^{-6} 1.33×10^{-6}	$MnRe(CO)_{10}$ (2.70×10^{-6})	94
$Re_2(CO)_{10}$ (5.14×10^{-6}) $Mn_2(CO)_{10}$ (6.37×10^{-6})	300–380 nm,[d] 0.5 hr	2.14×10^{-6} 1.10×10^{-6}	$MnRe(CO)_{10}$ (2.09×10^{-6})	65
$Re_2(CO)_{10}$ (5.14×10^{-6}) $Mn_2(CO)_{10}$ (6.37×10^{-6})	300–380 nm,[d] 1.0 hr	3.10×10^{-6} 1.69×10^{-6}	$MnRe(CO)_{10}$ (4.28×10^{-6})	89
$ReMn(CO)_{10}$ (3.67×10^{-6})	12 flashes at 500 J[b,e]	6.74×10^{-7}	$Mn_2(CO)_{10}$ (1.42×10^{-7}) $Re_2(CO)_{10}$ (2.50×10^{-7})	58
$ReMn(CO)_{10}$ (3.84×10^{-6})	12 flashes at 500 J[b,e]	4.85×10^{-7}	$Mn_2(CO)_{10}$ (1.94×10^{-7}) $Re_2(CO)_{10}$ (2.14×10^{-7})	84

[a] Deoxygenated solutions at 25° in 3-ml aliquots in Pyrex ampules. [b] Flash photolyzed with the Xenon Corp. instrument at the indicated power. [c] Flash photolyzed with the indicated number of Sylvania Type 25B press size flash bulbs. [d] Continuous photolysis, $\sim 10^{-7}$ einstein/min. [e] Carried out under 1 atm of CO.

$$Mn_2(CO)_{10} + Re_2(CO)_{10} \xrightarrow[\text{hexane}]{h\nu} MnRe(CO)_{10} \qquad (8)$$

$$(OC)_5Mn{-}Mn(CO)_3(1,10\text{-phenanthroline}) \xrightarrow{h\nu} Mn_2(CO)_{10} + Mn_2(CO)_6(1,10\text{-phenanthroline})_2 \qquad (9)$$

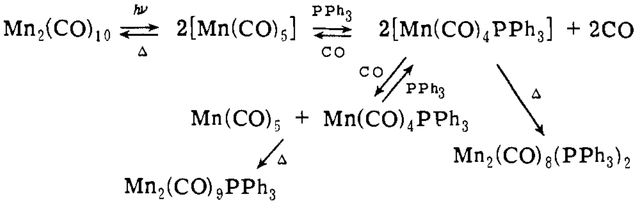
$$(OC)_5Mn{-}Re(CO)_3(1,10\text{-phenanthroline}) \xrightarrow{h\nu} Mn_2(CO)_{10} + Re_2(CO)_6(1,10\text{-phenanthroline})_2 \qquad (10)$$

ion. This result is consistent with, but does not unequivocally prove, homolytic cleavage of the metal-metal bond. However, the result is only consistent with symmetrical heterolytic cleavage if the two fragments are formed with both positive and negative charge in a 1:1 ratio; i.e., both $Mn(CO)_5^+$ and $Mn(CO)_5^-$ would have to be formed from $Mn_2(CO)_9PPh_3$ to ultimately yield $Mn_2(CO)_{10}$.

Our quantitative study of the cross coupling reaction of I and IV to yield V and the photolysis of V alone gives additional and more convincing evidence for the proposal that homolytic cleavage obtains subsequent to photoexcitation. In the presence of CO the photogenerated mononuclear metal carbonyls likely undergo CO exchange but this leads to no net decomposition and consequently we find much cleaner reaction chemistry. The initial chemical yield of V from I and IV is very high. Likewise the yields of I and IV upon flash photolysis of V are good and I and IV are formed in nearly a 1:1 ratio. The data for heteronuclear complex V, then, is in agreement with the unsymmetrically substituted homonuclear complex IV.

The low chemical yields for the cross coupling reactions carried out in the absence of CO suggest that the photogenerated intermediates are thermally coordinatively labile and decompose. This decomposition, the fact that III is the principal primary photoproduct from photolysis of I in the presence of PPh_3, and the fact that the quantum efficiency for the substitution is nearly equal to one-half the $Mn(CO)_5Cl$ formation quantum yield in CCl_4 solution convince us that a photosubstitution mechanism like that in Scheme II obtains for the formation of III. The primary formation of a disubstituted product as a primary photoproduct is unprecedented in photosubstitution chemistry except for the case of strongly chelating entering groups such as 1,10-phenanthroline. The substitution of CO by PPh_3 in $Mn(CO)_5$ may occur by a dissociative loss of CO, reaction 11, but the similarity in overall reaction quantum yield at 0 and 25° supports our modest preference for PPh_3 substitution via a six-

Scheme II



coordinate intermediate, reaction 12. Many metal carbonyls

$$Mn(CO)_5 \longrightarrow [Mn(CO)_4] + CO \xrightarrow{PPh_3} Mn(CO)_4PPh_3 \quad (11)$$

$$Mn(CO)_5 \overset{PPh_3}{\rightleftarrows} [Ph_3PMn(CO)_5] \rightleftarrows Ph_3PMn(CO)_4 + CO \quad (12)$$

undergo CO photosubstitution by dissociative loss of CO which in the case of I would yield some isomer of $Mn_2(CO)_9$. This coordinatively unsaturated intermediate would be expected to have some reactivity properties in common with $Cr(CO)_5$ photogenerated from $Cr(CO)_6$ which is degraded in CCl_4 solution. Thus, the essentially quantitative yield of $Mn(CO)_5Cl$ from I in CCl_4 provides a final fact tending to rule out the generation of $Mn_2(CO)_9$ as an important primary photoproduct of I.

The photoproducts and the stoichiometry from photolysis of I-V in the presence of low concentrations of I_2 or in the presence of chlorocarbons are further evidence that the important photoreaction of I-V is metal-metal bond cleavage. Only complex III shows deviant behavior in that relatively small yields of expected Mn-Mn cleavage products are obtained. The discrepancy may be due to PPh_3 photodissociation, but we still see sizable yields of cleavage products. These reactions parallel more qualitative studies of the photochemistry in the presence of halogen honors.[18] The lack of $M(CO)_5CH_2Ph$ formation upon photolysis of $M_2(CO)_{10}$ (M = Mn, Re) in the presence of $ClCH_2Ph$ and the appearance of $M(CO)_5Cl$ suggest that the two $M(CO)_5$ species have reacted independently of one another and that the two fragments are chemically the same. Further, photogenerated $M(CO)_5^-$ would be expected to give good yields of $M(CO)_5CH_2Ph$ *not* $M(CO)_5Cl$.[19] Likewise, $Re(CO)_5^-$ should yield $CH_3Re(CO)_5$ in the presence of CH_3I while we only find $Re(CO)_5I$ upon photolysis of IV in 0.1 *M* CH_3I solution. There is the possibility that any $M(CO)_5$(alkyl) formed could be photochemically decomposed to yield radical products, but generally the analyses reflect initial yields, and for $CH_3Re(CO)_5$ no light is absorbed at any wavelength used. The formation of bibenzyl in good yield when $ClCH_2Ph$ is the chlorine donor and the formation of $Ph_3C\cdot$ radicals when Ph_3CCl is the chlorine donor provide positive evidence supporting the homolytic metal-metal bond cleavage mechanism. The fact that $Co(CN)_5^{3-}$ yields both $Co(CN)_5R^{3-}$ and $Co(CN)_5X^{3-}$ upon reaction with RX (RX = alkylhalide) can be attributed to the relatively high concentration of $Co(CN)_5^{3-}$ used.[7] In our experiments the steady state concentration of metal radicals is small owing to the low light intensities. Thus, coupling of the metal radical with the organic radical has small probability.

Direct evidence for the $M(CO)_5$ radical intermediates is shaky. The claim[17] that $Mn(CO)_5$ radical has been detected by ESR in THF solution subsequent to irradiation of $Mn_2(CO)_{10}$ now appears unfounded[20] if only because it is too long lived. Additionally, paramagnetic species formed upon sublimation of $Mn_2(CO)_{10}$ on to a cold tip appear to be $\cdot OO\text{-}Mn(CO)_5$[21] and not $Mn(CO)_5$ as originally proposed.[22] The only convincing spectroscopic evidence for existence of the $M(CO)_5$ species comes from atom-ligand co-condensation and low temperature matrix isolation to yield $Re(CO)_5$ characterized only by vibrational spectroscopy.[23] The photochemistry reported here now allows a more reasonable quest for the direct spectroscopic observation in solution of the highly reactive radical intermediates proposed to account for the chemistry. Experiments directed toward this goal are in progress in these laboratories.

Summary

The photochemistry of the metal-metal bonded compounds I-V is consistent with a primary excited state decay path which leads to homolytic metal-metal bond cleavage with high quantum efficiency. The two lowest excited states in the metal-metal bonded compounds are expected to have a weaker metal-metal bond than in the ground state consistent with the observed chemistry. The mononuclear, paramagnetic (d^7) photofragments may undergo cage recombination or undergo cage escape and couple with a fragment generated from another metal-metal bonded species. The photogenerated metal radicals react with I_2 to yield M-I bonds or with chlorocarbons to generate M-Cl bonds and apparently the carbon radical in the case of $ClCH_2Ph$ and Ph_3CCl. The metal radicals are also coordinatively labile and undergo efficient thermal substitution at 25° by PPh_3.

Experimental Section

Materials. The $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Mn(CO)_5Cl$, and $Re(CO)_5Cl$ were obtained from Pressure Chemical Co. and were used after purification by column chromatography or sublimation. All solvents used were of a spectroscopic grade and were used without further purification. PPh_3 was recrystallized from Et_2O before use, and I_2, $PhCH_2Cl$, Ph_3CCl_3, and CCl_4 were used without further purification as reagent grade chemicals from Mallincrodt, Baker, Fisher, and Baker, respectively.

Spectra. All Uv-visible spectra were obtained using a Cary 17 uv-visible-near-ir spectrophotometer. All ir spectra were recorded using a Perkin-Elmer 521 grating infrared spectrometer. Low temperature uv-visible spectra were acquired in EPA solution with a quartz liquid nitrogen dewar fitted with quartz optical flats for windows. Quantitative ir measurements were made using matched 0. 1-mm or 1.0-mm path length NaCl cells obtained from Perkin-Elmer Corp.

Preparation of $Mn_2(CO)_9(PPh_3)$ and $Mn_2(CO)_8(PPh_3)_2$.[24] An N_2 purged 100-ml isooctane solution of 1 g (2.5 mmol) of $Mn_2(CO)_{10}$ and 2 g (7.6 mmole) of PPh_3 was photolyzed for 1 hr with a GE black lite (two 15-W bulbs with principal output 300-400 nm). After photolysis the solution was evaporated to dryness under reduced pressure and the remaining solid dissolved in a minimum amount of CH_2Cl_2. The various substituted products were separated from this solution by chromatography, in the dark, on grade 1 alumina. The unreacted $Mn_2(CO)_{10}$ was eluted with pure isooctane, the $Mn_2(CO)_9(PPh_3)$ was then eluted with a 10% solution of CH_2Cl_2 in isooctane, and the $Mn_2(CO)_8(PPh_3)_2$ was eluted with pure CH_2Cl_2. Both substituted derivatives were recrystallized from isooctane-CH_2Cl_2 mixtures. The yield based on $Mn_2(CO)_{10}$ disappearance is 60% for $Mn_2(CO)_8(PPh_3)_2$ and 10% for $Mn_2(CO)_9(PPh_3)$. These known compounds were identified by their characteristic ir spectra in the CO stretching region.[24]

Preparation of $Mn(CO)_5I$. A solution of 0.2 (0.5 mmol) g of $Mn_2(CO)_{10}$ and 0.2 (0.8 mmol) g of I_2 in 100 ml of isooctane was photolyzed with a GE black lite with constant N_2 purge, until the ir of the CO stretching region of the mixture showed all the $Mn_2(CO)_{10}$ had disappeared. The isooctane was removed under reduced pressure and the remaining solid was placed in a sublimer (40° and 0.05 mm). The excess I_2 sublimed followed by the $Mn(CO)_5I$ as a pure orange-red solid, yield 20% (0.06 g). The $Mn(CO)_5I$ is a known compound having ir bands (Table II) as reported in the literature.[25] The remaining residue in the sublimer was primarily the dihalo-bridged dimer $(Mn(CO)_4I)_2$ identified by its characteristic ir bands in the CO stretching region.[26]

Preparation of *cis*-$Mn(CO)_4(PPh_3)Cl$. A solution of 0.2 g (0.23 mmol) of $Mn_2(CO)_8(PPh_3)_2$ in 100 ml of CCl_4 was photolyzed with a GE black lite with constant N_2 purge, until the ir of the CO stretching region of the mixture showed all the $Mn_2(CO)_8(PPh_3)_2$ had disappeared. The CCl_4 was removed under reduced pressure and the product recrystalized from CH_2Cl_2-pentane, yield 33% (0.071 g). The compound was identified by its ir spectrum as compared to the known bromo analog.[27]

Preparation of $ReMn(CO)_{10}$. This complex was prepared by a modified version of that reported in the literature.[11] A ~100-ml isooctane solution of $Mn_2(CO)_{10}$ (0.90 mmol) and $Re_2(CO)_{10}$ (0.26 mmol) was photolyzed with 300-380-nm light while continuously purging with CO. The appearance of a characteristic CO stretching peak at ~2055 cm^{-1} evidences the generation of $MnRe(CO)_{10}$. The solution was photolyzed until all (>99%) of the $Re_2(CO)_{10}$ disappeared as determined by the decline in the $Re_2(CO)_{10}$ ir absorption at ~2070 cm^{-1}. At this point the solution was filtered to remove uncharacterized oxidation products from $M_2(CO)_{10}$ decomposition. The only remaining species in the filtrate are the $ReMn(CO)_{10}$ and the $Mn_2(CO)_{10}$. Essentially all (>98%) of the $Mn_2(CO)_{10}$ was removed by photolysis of the solution in air at 436 nm where $Mn_2(CO)_{10}$ absorption is substantial compared to $ReMn(CO)_{10}$. The oxidation products of $Mn_2(CO)_{10}$ are separated by filtration, and the filtrate is rotary evaporated to dryness yielding the $ReMn(CO)_{10}$ as a pale-yellow solid. Sublimation of the solid gave $ReMn(CO)_{10}$ (0.14 mmol) with the only impurities being $Mn_2(CO)_{10}$ (~2%) and $Re_2(CO)_{10}$ (~2%). This $ReMn(CO)_{10}$ has a melting range of 158–164° (lit. mp 167°),[28] uv_{max} 323 nm (lit. value is 324 nm),[15] and an ir spectra in the CO stretching region in accordance with the literature.[29]

Typical Photolysis Procedures. Solutions of the metal carbonyl and a substrate in 3-ml aliquots were placed in Pyrex test tubes (13 × 100 mm) with constrictions. These solutions were degassed in four freeze–pump–thaw cycles and then were hermetically sealed. Photolysis was performed with the use of merry-go-round[30] equipped with either 450- or 550-W Hanovia medium-pressure mercury sources, filtered with Corning glass filters and filter solutions to isolate the 313- or 366-nm mercury emissions. Ferrioxalate actinometry[31] was performed for each experiment to measure the light intensity. Analysis of the solutions was performed by uv–visible or ir spectroscopic measurements.

Flash Photolysis Experiments. All flash experiments were performed on degassed ampules of the metal carbonyl, with subsequent analysis by uv or ir spectroscopy or by separation of the products on activated alumina and then spectroscopic analysis. Sylvania press size flash bulbs (type 25B) were used after the blue protective covering was removed with repeated washings with acetone. The flash bulbs were mounted in a reflective housing of aluminum foil with the ampule mounted ⅛ in. from the bulb. The bulbs were flashed by connecting two 1.5-V batteries in series with the bulb. All other flash experiments were performed using a Xenon Corp. Model F-710 flash photolysis apparatus as the light source.

$PhCH_2Cl$ and Ph_3CCl Experiments. Degassed solutions of $PhCH_2Cl$ (10^{-1} *M*) and the metal carbonyl (2×10^{-3} *M*) in 100 ml of isooctane with octadecane (5×10^{-3} *M*) as an internal standard were photolyzed with the GE black lite, and the progress of the reaction was monitored by gas chromatography (Varian Series 1400 cm^3, with 3% SE-30 column at 200°) and ir. The gas chromatagraph was used to monitor the disappearance of the benzyl chloride and the appearance of the bibenzyl and the ir monitored the appearance of $M(CO)_5$-Cl and the disappearance of $M_2(CO)_{10}$. A solution of Ph_3CCl (10^{-1} *M*) and metal carbonyl (1×10^{-3} *M*) in either THF, benzene, or isooctane was degassed in 13 × 100 mm test tubes and a 4 mm o.d. quartz ESR tube. The solutions were irradiated in parallel for 2 min on the GE black lite and the test tubes were subsequently analyzed by ir for the metal carbonyl products, and the ESR tube was analyzed on a Varian E-9 ESR for the presence of the Ph_3C radical.

Solvent Dependence of the Reactions with I_2. Metal carbonyl (1×10^{-3} *M*) and I_2 (1×10^{-3} *M*) were dissolved in the appropriate solvents and 3-ml aliquots of the solutions degassed in 13 × 100 mm test tubes. The tubes were photolyzed using the 366 or 313-nm merry-go-round and the tubes were analyzed by uv spectral changes for I_2 and $M_2(CO)_{10}$ disappearance.

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