Attempts to oxidize this Mo^{III}, Mo^{III} unit have been described. By using potassium azide, only half the molybdenum atoms can be oxidized to give a Mo^{III}, Mo^{IV} species that has a tetranuclear structure consisting of two $Mo_2(\mu\text{-}O)(\mu\text{-}OH)$EDTA units linked by bridging oxide ions.[16] It also appears that dinuclear Mo^{IV}, Mo^{IV} compounds can be obtained but there is no proof of structure yet available for these.[17]

The trinuclear species[2,7] we have been isolating from the Ardon and Pernick solution, including the EDTA compound reported here, do not seem related to the bi- or tetranuclear species that have been found or postulated by Sykes and his co-workers. Clearly, the solution chemistry of Mo^{IV} still holds challenges for research.

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Supplementary Material Available: A list of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

References and Notes

(1) (a) Texas A&M University; (b) Visiting Professor, Texas A&M University, 1977–1978; (c) Technion-Israel Institute of Technology, Haifa, Israel.
(2) A. Bino, F. A. Cotton, and Z. Dori, *J. Am. Chem. Soc.*, **100**, 5252 (1978).
(3) A. Bino, F. A. Cotton, Z. Dori, S. Koch, H. Küppers, M. Millar, and J. C. Sekutowski, *Inorg. Chem.*, **17**, 3245 (1978).
(4) A. Bino, F. A. Cotton, Z. Dori, and R. Najjar, unpublished work on $Mo_3O_2^-$-containing compounds analogous to the W_3O_2 compounds described in ref 3.
(5) W. H. McCarroll, L. Katz, and R. Ward, *J. Am. Chem. Soc.*, **79**, 5410 (1957).
(6) F. A. Cotton, *Inorg. Chem.*, **3**, 1217 (1964).
(7) A. Bino, F. A. Cotton, and Z. Dori, *Inorg. Chim. Acta*, **33**, L133 (1979).
(8) (a) M. Ardon and A. Pernick, *J. Am. Chem. Soc.*, **95**, 6871 (1973); (b) M. Ardon, A. Bino, and G. Yahav, *ibid.*, **98**, 2338 (1976).
(9) (a) B. Spivak and Z. Dori, *J. Chem. Soc., Dalton Trans.*, **1173** (1973); (b) L. V. Haynes and D. T. Sawyer, *Inorg. Chem.*, **6**, 2146 (1967); (c) G. K. Kneale, A. J. Geddes, Y. Sasaki, T. Shibahara, and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 356 (1975).
(10) F. A. Cotton, B. A. Frenz, G. Deganello, and A. Shaver, *J. Organomet. Chem.*, **50**, 227 (1973); R. D. Adams, D. M. Collins, and F. A. Cotton, *J. Am. Chem. Soc.*, **96**, 749 (1974).
(11) All crystallographic computing was done on a PDP11/45 computer at the Molecular Structure Corp., College Station, Texas, using the Enraf-Nonius structure determination package.
(12) J. J. Park, M. D. Glick, and J. L. Hoard, *J. Am. Chem. Soc.*, **91**, 301 (1969).
(13) J. Kloubek and J. Podlahá, *J. Inorg. Nucl. Chem.*, **33**, 2981 (1971).
(14) T. Shibahara and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 95 (1978).
(15) G. G. Kneale and A. J. Geddes, *Acta Crystallogr., Sect. B*, **31**, 1233 (1975).
(16) T. Shibahara, B. Sheldrick, and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 523 (1976).
(17) T. Shibahara and A. G. Sykes, *J. Chem. Soc., Dalton Trans.*, 100 (1978).

Photoinduced Fragmentation of $H_3Re_3(CO)_{12}$ and $H_3Mn_3(CO)_{12}$

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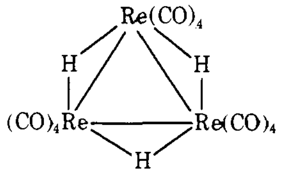
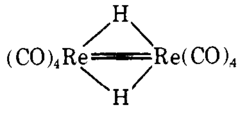
Abstract: Ultraviolet irradiation of $H_3Re_3(CO)_{12}$ in degassed solution leads to quantitative formation of $H_2Re_2(CO)_8$. Quantum yields measured at 313 and 366 nm are of the order of 0.1. Photolysis in the presence of CO also gives fragmentation and formation of $HRe(CO)_5$ and $H_2Re_2(CO)_8$, but the latter thermally reacts with CO to form $HRe(CO)_5$ and $Re_2(CO)_{10}$. The quantum yield of disappearance of $H_3Re_3(CO)_{12}$ in the presence of CO is 0.02. Photolysis of the analogous $H_3Mn_3(CO)_{12}$ cluster produces $HMn(CO)_5$, $Mn_2(CO)_{10}$, and an unidentified brown precipitate. Experiments directed toward elucidating the mechanism of these photoreactions are discussed.

The photochemistry of metal carbonyl complexes has been extensively investigated both for its mechanistic and synthetic value.[1,2] The majority of studies have focused on monomeric and dimeric complexes but relatively few reports describing the photochemistry of metal carbonyl clusters have appeared.[3-19] As with dimeric metal carbonyls, the dominant reaction mode of trimeric clusters appears to be metal–metal bond cleavage and subsequent fragmentation. $Ru_3(CO)_{12}$, for example, has been shown to yield monomeric $Ru(CO)_4L$ and $Ru(CO)_3L_2$ compounds upon photolysis in the presence of the appropriate donor ligand L,[3-6] and several $Os(CO)_3L_2$ complexes have been prepared via photolysis of $Os_3(CO)_{12}$.[7-9] Irradiation of the $RCCo_3(CO)_9$ (R = H, CH_3) clusters under an H_2 atmosphere has likewise been shown to give fragmentation and subsequent formation of $Co_4(CO)_{12}$ and CH_4 (R = H), C_2H_4, and C_2H_6 (R = CH_3).[10]

In all the cluster photoreactions reported to date, smooth conversion to tractable products occurs only in the presence of suitable substrates such as CO, H_2, and PR_3, which can capture the photoproduced intermediates.[20] In contrast, we find that photolysis of the trimeric cluster $H_3Re_3(CO)_{12}$[21,22] gives quantitative conversion to $H_2Re_2(CO)_8$,[23] eq 1, even in degassed solutions in the absence of substrate.[24] The smooth trimer to dimer conversion observed for $H_3Re_3(CO)_{12}$ suggested that this system was well suited for detailed mechanistic studies, and we describe the results of those experiments herein. The analogous $H_3Mn_3(CO)_{12}$[25,26] cluster also undergoes ready photofragmentation in degassed solution, but in this case a mixture of $HMn(CO)_5$, $Mn_2(CO)_{10}$, and an unidentified brown solid is formed.

$$2H_3Re_3(CO)_{12} \xrightarrow{h\nu} 3H_2Re_2(CO)_8 \qquad (1)$$





Experimental Section

$H_3Re_3(CO)_{12}$,[21] $H_2Re_2(CO)_8$,[23] and $H_3Mn_3(CO)_{12}$[25] were synthesized by published procedures. $H_3Re_3(CO)_{12}$ was recrystallized from hexane and $H_2Re_2(CO)_8$ from hexane/CH_2Cl_2 at −20 °C.

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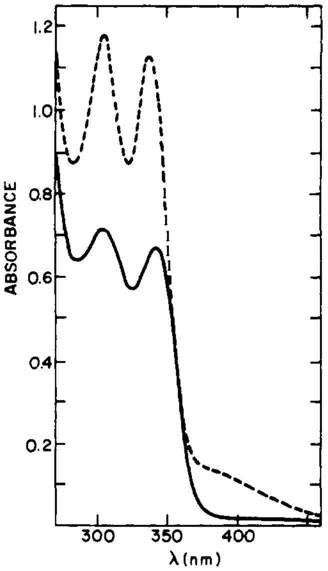


Figure 1. Electronic absorption spectra of $H_3Re_3(CO)_{12}$ at 300 (—) and 77 K (---) measured in methylcyclohexane-pentane (7:4) solution. The 77 K spectrum is corrected for a 20% solvent contraction upon cooling.

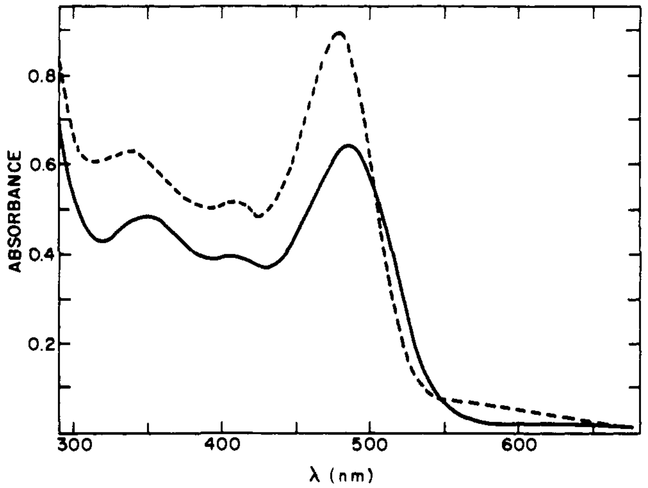


Figure 2. Electronic absorption spectra of $H_3Mn_3(CO)_{12}$ at 300 (—) and 77 K (---) measured in methylcyclohexane-pentane (7:4) solution. The 77 K spectrum is corrected for a 20% solvent contraction upon cooling.

$H_3Mn_3(CO)_{12}$ was freshly sublimed before use. Chemically pure (CP) carbon monoxide (Matheson) was used directly as received. Gas chromatographic analysis of this CO showed it to contain ~80 ppm oxygen. Passing the CO through a BASF BTS Katalysator column at 70 °C failed to lower the O_2 content below this value. All solvents were dried by standard procedures[27] and transferred under N_2 or by vacuum distillation.

General Irradiation Procedures. Photolyses were conducted with a 450-W medium-pressure Hg lamp (Hanovia) equipped with the appropriate Corning Glass narrow band-pass and sharp cutoff filters (435 nm, 5-74; 366 nm, 7-83; $\lambda > 510$ nm, 3-68). Isolation of the 313-nm Hg line was achieved by filtering the light through a Corning 7-54 filter and a 1-cm path length solution prepared by dissolving 45.08 g of K_2CO_3 and 2.37 g of K_2CrO_4 in 4500 mL of water. Light intensities were determined by ferrioxalate actinometry.[28] Reactions which were monitored in the UV-visible spectral region were conducted in degassable quartz cells similar to that described by Shriver.[29] Reactions which were followed in the infrared spectral region were conducted in a three-neck flask directly attached to a vacuum line. Samples were withdrawn with an N_2-flushed syringe and transferred to IR cells which were fitted with serum caps and flushed with N_2. Flash photolysis experiments were conducted with an apparatus made available to us by F. Lampe of this department and for which construction details have been described.[30]

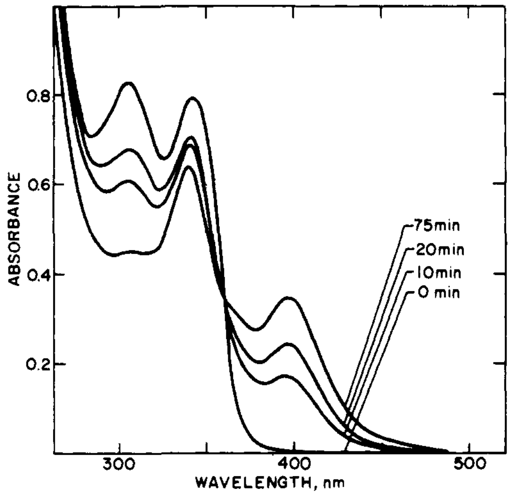


Figure 3. Electronic absorption spectral changes resulting from 366-nm photolysis of a degassed isooctane solution of $H_3Re_3(CO)_{12}$.

Table I. Electronic Absorption Spectral Data

compd	300 K[a] λ_{max}, nm (ϵ_{max}, L mol^{-1} cm^{-1})	77 K[b] λ_{max}, nm (ϵ_{max}, L mol^{-1} cm^{-1})
$H_3Re_3(CO)_{12}$	342 (6300)	335 (10 500)
	303 (6500)	305 (10 700)
	255 (9300)	
$H_3Mn_3(CO)_{12}$	487 (4160)	480 (5700)
	407 (2100)	410 (2700)
	352 (2600)	340 (3400)
	270 (6300)	
$H_2Re_2(CO)_8$	392 (2420)	
	360 sh	
	340 (3890)	
	310 sh	
	250 (6800)	
$HRe(CO)_5$	300 sh	
	272 (2620)	

[a] Isooctane solution. [b] Methylcyclohexane-pentane (7:4) glass. ϵ's given have been corrected for the 20% solvent contraction upon cooling.

Results

Electronic Absorption Spectra. Electronic absorption spectral data for $H_3Mn_3(CO)_{12}$, $H_3Re_3(CO)_{12}$, $H_2Re_2(CO)_8$, and $HRe(CO)_5$ are set out in Table I. The electronic absorption spectra of $H_3Re_3(CO)_{12}$ and $H_3Mn_3(CO)_{12}$ at 300 and 77 K are shown in Figures 1 and 2, respectively. At 300 K, $H_3Re_3(CO)_{12}$ exhibits two well-defined absorption bands at 342 and 303 nm. Upon cooling to 77 K, these bands sharpen and the 342-nm band blue shifts to 335 nm whereas the 303-nm band red shifts slightly to 305 nm. The $H_3Mn_3(CO)_{12}$ bands at 487, 407, and 352 nm also sharpen upon cooling and shift as shown in Figure 2.

Photolysis of $H_3Re_3(CO)_{12}$ in Degassed Solution. Irradiation of a thoroughly degassed isooctane solution of $H_3Re_3(CO)_{12}$ with 366 nm gives the electronic absorption spectral changes shown in Figure 3. As the irradiation proceeds the color of the solution changes from colorless to bright yellow, and a new absorption band appears and grows in at 392 nm. The final spectrum shown in Figure 3 is virtually identical with that of $H_2Re_2(CO)_8$ (Table I), a compound first prepared and characterized by Graham and co-workers.[31] The formation of $H_2Re_2(CO)_8$ was further verified by the infrared spectrum of the photolyzed solution which showed bands at 2093, 2020, 2000, and 1979 cm^{-1} attributable to $H_2Re_2(CO)_8$.[31] A very

Table II. Quantum Yield Data

cluster	exptl conditions	irradiation wavelength, nm	Φ^a
$H_3Re_3(CO)_{12}$	degassed soln	366	0.10 ± 0.02
	degassed soln	313	0.12 ± 0.01
	degassed soln with 7% T neutral density filter	366	0.15 ± 0.02
	CO atm	366	0.021 ± 0.002
	CO atm	313	0.013 ± 0.002
	O_2 atm	366	0.12 ± 0.02[b]
$H_3Mn_3(CO)_{12}$	degassed soln	366	0.02 ± 0.01
	degassed soln	435	0.006 ± 0.002
	CO atm	366	0.007 ± 0.007

[a] Unless otherwise indicated, the quantum yields are for disappearance of the initial cluster. [b] Quantum yield for formation of $H_2Re_2(CO)_8$.

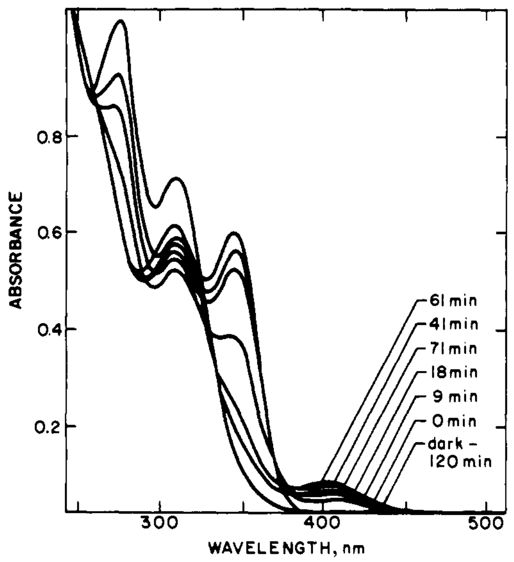


Figure 4. Electronic absorption spectral changes resulting from 366-nm irradiation of an isooctane solution of $H_3Re_3(CO)_{12}$ under an atmosphere of carbon monoxide.

weak band at 2070 cm^{-1} was also observed and indicated the presence of a trace amount of $Re_2(CO)_{10}$.[32] The principal photoreaction is that indicated in the equation

$$2H_3Re_3(CO)_{12} \xrightarrow{h\nu} 3H_2Re_2(CO)_8 \quad (2)$$

Quantum yield data for the clusters examined under various conditions are set out in Table II. The 313- and 366-nm quantum yields of disappearance of $H_3Re_3(CO)_{12}$ in degassed solutions are 0.12 ± 0.01 and 0.10 ± 0.02, respectively, and indicate that there is no significant wavelength effect within this spectral region. The effect of varying the light intensity on the quantum yield was determined by irradiating samples with a 7%-transmittance neutral density filter placed in the light beam. The light intensity decreased from 2.86×10^{-7} to 0.20×10^{-7} einstein/min but the quantum yield remained essentially constant: 0.10 ± 0.02 vs. 0.15 ± 0.02. Although $H_3Re_3(CO)_{12}$ is air stable in the solid state and in solution, photolysis under an O_2 atmosphere gave formation of $H_2Re_2(CO)_8$ and an uncharacterized white precipitate. The 366-nm quantum yield of formation of $H_2Re_2(CO)_8$ under these conditions was 0.12.

Irradiation of $H_3Re_3(CO)_{12}$ in the Presence of Carbon Monoxide. The electronic absorption spectral changes which result upon photolysis of an isooctane solution of $H_3Re_3(CO)_{12}$ under an atmosphere of CO are shown in Figure 4. They are much more complex than those obtained upon irradiation of degassed solutions, Figure 3, but the appearance of the band at 392 nm does indicate that $H_2Re_2(CO)_8$ is formed. During the photolysis the absorbance at 392 nm initially increases to a maximum, remains relatively constant until all the $H_3Re_3(CO)_{12}$ is depleted, and then completely disappears. This suggests that $H_2Re_2(CO)_8$ is continuously being produced and depleted and that in the intermediate stages of the photolysis it is in a steady-state concentration. When the irradiation was stopped with the 392-nm band at its maximum and the sample then placed in the dark, the 392-nm absorbance decreased to zero, indicating that $H_2Re_2(CO)_8$ reacts thermally with carbon monoxide. This was subsequently verified by allowing pure $H_2Re_2(CO)_8$ to react with CO in the dark (see below). The steady-state $H_2Re_2(CO)_8$ concentration increased upon increasing the light intensity or the initial $H_3Re_3(CO)_{12}$ concentration.

After completion of the reaction, the electronic absorption spectrum exhibited maxima at 272 and 308 nm. Solvent and volatile organometallics were distilled from the irradiated solution under vacuum. The electronic absorption and infrared spectra of the distillate clearly showed the presence of $HRe(CO)_5$ (λ_{max} 272 nm;[33] ν_{CO} 2015 s, 2005 m cm^{-1} [34]). Analysis of the white residue remaining after distillation showed it to be pure $Re_2(CO)_{10}$ (λ_{max} 310 and 278 nm;[35] ν_{CO} 2070 m, 2014 vs, 2003 w, 1976 m, 1959 vw, 1942 vw cm^{-1} [32]). The overall reaction in the presence of carbon monoxide is that indicated in the equation

$$H_3Re_3(CO)_{12} + CO \xrightarrow{h\nu} HRe(CO)_5 + Re_2(CO)_{10} \quad (3)$$

Presumably H_2 is also produced during the photolysis. The $HRe(CO)_5/Re_2(CO)_{10}$ ratio was observed to increase with increasing light intensity and with the initial $H_3Re_3(CO)_{12}$ concentration. The quantum yield of disappearance of $H_3Re_3(CO)_{12}$ is significantly reduced from its value of 0.12 in degassed solution to 0.02 in the presence of carbon monoxide and shows little if any wavelength dependence, Table II. It is important to note that $H_3Re_3(CO)_{12}$ does not react thermally with carbon monoxide at room temperature.

Photolysis of $H_3Re_3(CO)_{12}$ in the Presence of Diphenylacetylene. $H_3Re_3(CO)_{12}$ does not react at room temperature with diphenylacetylene (DPA). However, a rapid reaction occurred upon 366-nm irradiation of an isooctane solution of $H_3Re_3(CO)_{12}$ and DPA to give an exceedingly complex mixture of products. Distillation of the solvent and volatile organometallics from the irradiated solution left a yellow-orange residue. The infrared spectrum of the distillate showed it to contain a significant amount of $HRe(CO)_5$. The residue was washed with hexane to give a red-orange solution and a yellow, insoluble material. Chromatography of the hexane solution yielded eight fractions, only two of which were subsequently shown to contain single pure compounds. Mass spectra of the material isolated as red and yellow crystalline solids were consistent with the formulations $H_2Re_2(CO)_7(DPA)_2$[36] and $H_2Re_2(CO)_5(DPA)_3$.[37] The latter species was only slightly soluble in hexane and was shown to be the major constituent of the yellow residue remaining after the hexane extraction. Further characterization of these compounds is in progress. Other compounds which were positively identified by mass spectrometry were $HRe_3(CO)_{14}$[38] and $Re_2(CO)_{10}$. No $H_2Re_2(CO)_8$ was detected in any of the isolated fractions and it was later shown that $H_2Re_2(CO)_8$ does not react with DPA under thermal or photochemical conditions. Hence the products described above must arise from photochemically produced intermediates.

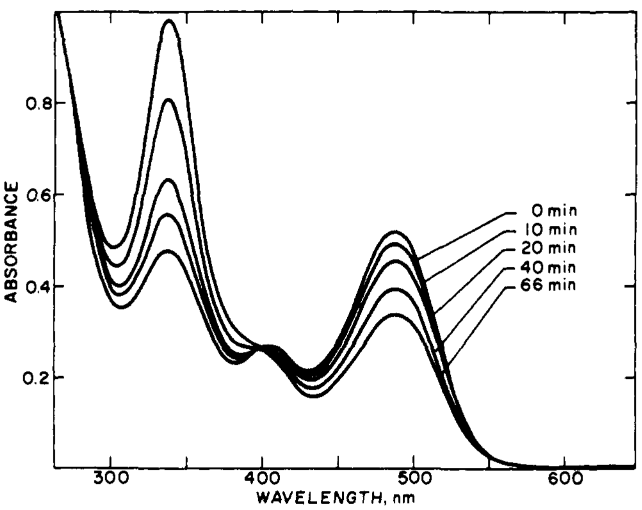


Figure 5. Electronic absorption spectral changes resulting from 366-nm irradiation of a degassed isooctane solution of $H_3Mn_3(CO)_{12}$.

Reaction of $H_2Re_2(CO)_8$ with Carbon Monoxide. $H_2Re_2(CO)_8$ was observed to thermally react with CO to produce $HRe(CO)_5$, $Re_2(CO)_{10}$, and presumably H_2:[39]

$$H_2Re_2(CO)_8 + CO \rightarrow HRe(CO)_5 + Re_2(CO)_{10} + H_2 \tag{4}$$

When the reaction was monitored by following the changes in the electronic absorption spectrum, an induction period was clearly apparent and this was followed by exponential decay of the $H_2Re_2(CO)_8$ absorbance. It was also observed that the rate of the reaction slowed appreciably when air was admitted to the sample. Furthermore, the $HRe(CO)_5/Re_2(CO)_{10}$ product ratio was highly sensitive to the reaction conditions. This ratio decreased as the initial $H_2Re_2(CO)_8$ concentration increased whereas the ratio increased when samples were irradiated during the reaction. These various results strongly implicate a radical reaction pathway, perhaps similar to those studied by Byers and Brown,[40] and this reaction is currently being investigated in our laboratory.

Photolysis of $H_3Mn_3(CO)_{12}$. Irradiation of $H_3Mn_3(CO)_{12}$ in isooctane solution with 366 nm gave the electronic absorption spectral changes shown in Figure 5. Infrared spectroscopy indicated the formation of $HMn(CO)_5$ (ν_{CO} 2015, 2007 cm^{-1} [34]) and $Mn_2(CO)_{10}$ (ν_{CO} 2046, 2015, 1984 cm^{-1} [41]) in about equal amount, and an insoluble brown precipitate deposited in the latter stages of the photolysis:

$$H_3Mn_3(CO)_{12} \xrightarrow{h\nu} HMn(CO)_5 + Mn_2(CO)_{10} + \text{brown solid}$$

Photolysis under a carbon monoxide atmosphere also gave formation of $HMn(CO)_5$ and $Mn_2(CO)_{10}$ in approximately equal amount but no precipitate was observed under these conditions. The quantum yields obtained under the various conditions are summarized in Table II. There is no significant wavelength or CO effect.

Discussion

Electronic Absorption Spectra. The position and intensities of the low-energy bands in the electronic absorption spectra of $H_3Re_3(CO)_{12}$ and $H_3Mn_3(CO)_{12}$, Figures 1 and 2 and Table I, suggest that they are a consequence of the metal-metal bonding within the clusters. Specifically, metal to ligand charge transfer (MLCT) transitions are ruled out since previous studies[42] have shown that MLCT transitions in the corresponding monomeric $HM(CO)_5$ complexes occur at λ <250 nm. The spectra of the $H_3M_3(CO)_{12}$ trimers are qualitatively similar to the spectra of the isoelectronic $M_3(CO)_{12}$ (M = Fe, Ru, Os) trimers,[43] showing bands in the same spectral region and the characteristic blue shift in the low-energy bands in moving from first- to third-row metals.

Gray and co-workers[43] have studied the electronic structure of the $M_3(CO)_{12}$ trimers and have assigned their spectra with the aid of molecular orbital calculations, magnetic circular dichroism spectra, and polarized electronic absorption spectra. In each case, the two lowest energy bands were attributed to transitions localized within the metal triangle and were specifically assigned to bonding to antibonding ($\sigma \rightarrow \sigma^*$) and antibonding to antibonding ($\sigma^{*\prime} \rightarrow \sigma^*$) transitions. A key observation in the assignment of these bands is that upon cooling to 77 K the band position of the $\sigma^{*\prime} \rightarrow \sigma^*$ transition red shifted while that of the $\sigma \rightarrow \sigma^*$ transition blue shifted from their 300 K positions. A blue shift upon cooling is also characteristic of the $\sigma \rightarrow \sigma^*$ bands in dimeric species such as $Re_2(CO)_{10}$.[35,44]

Comparison of the 300 and 77 K spectra of $H_3Mn_3(CO)_{12}$ and $H_3Re_3(CO)_{12}$, Figures 1 and 2, shows that in each case the maximum of the lowest energy band also blue shifts upon cooling. This parallels the behavior of the $\sigma \rightarrow \sigma^*$ transitions in the $M_3(CO)_{12}$ clusters and suggests an analogous assignment.

This type of transition has been identified in the spectra of the dimeric complexes $M_2(CO)_{10}$ (M = Tc, Mn, Re) and $[(\eta^5\text{-}C_5H_5)M(CO)_3]_2$ (M = Mo, W) and the photochemistry of these complexes has been extensively investigated.[1b,44,45] The majority of the experimental evidence indicates that irradiation into the $\sigma \rightarrow \sigma^*$ absorption band leads to homolytic cleavage of the metal-metal bond. In a recent definitive study, Kidd and Brown[46] showed that irradiation of $Mn_2(CO)_{10}$ leads to the formation of $\cdot Mn(CO)_5$ as the only primary photoproduct. One would thus anticipate that irradiation into the $\sigma \rightarrow \sigma^*$ transitions of the $H_3M_3(CO)_{12}$ trimers would also lead to metal-metal bond cleavage and subsequent fragmentation. Similar conclusions have been drawn by Wrighton and co-workers[6] for the $M_3(CO)_{12}$ (M = Fe, Ru, Os) trimers.

Photochemistry. Irradiation of degassed solutions of $H_3Re_3(CO)_{12}$ and $H_3Mn_3(CO)_{12}$ does indeed lead to fragmentation. $H_3Re_3(CO)_{12}$ produces $H_2Re_2(CO)_8$ quantitatively upon photolysis whereas $H_3Mn_3(CO)_{12}$ yields $HMn(CO)_5$ and $Mn_2(CO)_{10}$ but with no evidence for the unknown $H_2Mn_2(CO)_8$ dimer. The mechanism by which clusters such as these undergo fragmentation is of obvious interest but has not been previously discussed. The clean trimer → dimer conversion found for $H_3Re_3(CO)_{12}$ suggested that this system would be ideally suited for a mechanistic study. Unfortunately, the experiments described herein and discussed below do not allow us to delineate the exact mechanism but only narrow the various possibilities.

The quantum yield of disappearance of $H_3Re_3(CO)_{12}$ is independent of the intensity of the irradiation source, indicating that the trimer → dimer conversion occurs as the result of absorption of a single photon. The four primary single-

cleavage of three Re–Re bonds

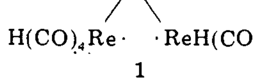
$$H_3Re_3(CO)_{12} \xrightarrow{h\nu} 3HRe(CO)_4 \tag{5}$$

cleavage of two Re–Re bonds

$$H_3Re_3(CO)_{12} \xrightarrow{h\nu} H_2Re_2(CO)_8 + HRe(CO)_4 \tag{6}$$

cleavage of one Re–Re bond

$H_3Re_3(CO)_{12} \xrightarrow{h\nu}$



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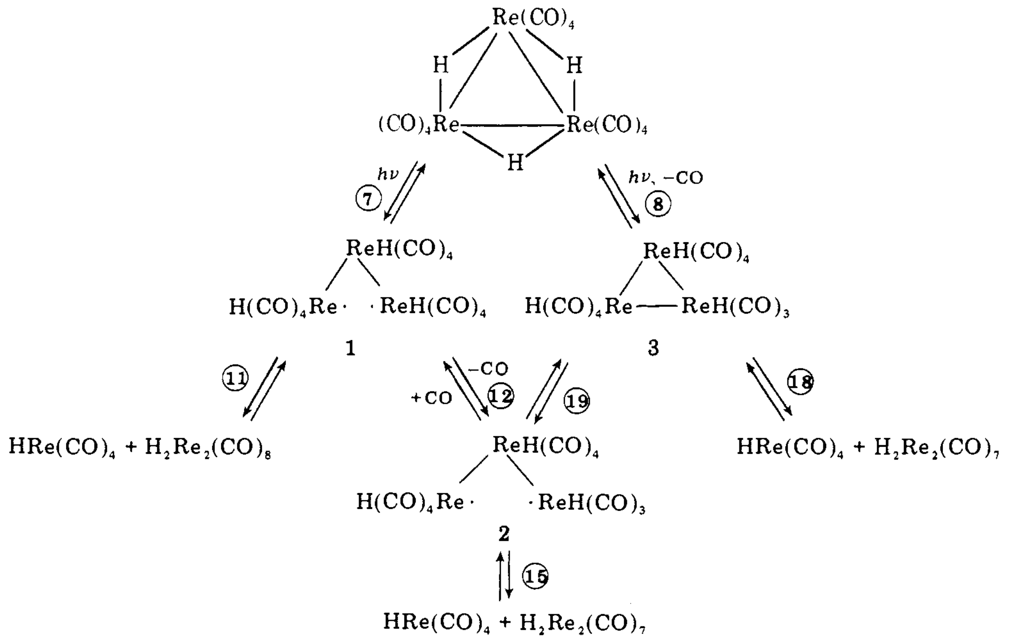
(7)

Scheme I[a]



[a] Circled numbers refer to equations in the text.

expulsion of CO

$$H_3Re_3(CO)_{12} \xrightarrow{h\nu} \underset{\mathbf{3}}{H_3Re_3(CO)_{11}} + CO \qquad (8)$$

photon processes which can be postulated are summarized in eq 5-8. Each of these will be discussed in turn.

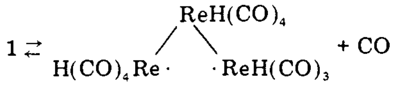
Absorption of a photon could directly lead to cleavage of all three Re-Re bonds and formation of $3HRe(CO)_4$ fragments, eq 5. Alternatively, two Re-Re bonds could be broken simultaneously, eq 6, to produce $H_2Re_2(CO)_8$ and $HRe(CO)_4$. In degassed solution, the $HRe(CO)_4$ fragments would presumably dimerize to yield $H_2Re_2(CO)_8$[40a] and thereby give quantitative trimer → dimer conversion. Both of these mechanisms can be ruled out on the basis of the data obtained upon irradiation in the presence of CO. The quantum yield of disappearance of $H_3Re_3(CO)_{12}$ under a CO atmosphere is only one-sixth that measured under degassed conditions. Neither of the mechanisms shown in eq 5 and 6 provides a means for this CO inhibition. Indeed, if these mechanisms were operative, CO would be expected to increase the quantum yield by scavenging the $HRe(CO)_4$ to form $HRe(CO)_5$ and thus prevent any back reaction. Furthermore, the observation of the production of $H_2Re_2(CO)_8$ during irradiation under a CO atmosphere is inconsistent with the direct formation of $3HRe(CO)_4$ fragments, eq 5, since these would be expected to combine with the CO present in large excess to give only $HRe(CO)_5$. The direct production of $H_2Re_2(CO)_8$ as in eq 6 can also be ruled out on the basis of the $H_3Re_3(CO)_{12}$ photolysis in the presence of DPA in which no $H_2Re_2(CO)_8$ was observed. Further, since $H_2Re_2(CO)_8$ is itself inert to DPA under these conditions, it cannot be directly formed as a primary photoproduct.

We are thus left with photoinduced cleavage of a single Re-Re bond, eq 7, or photoinduced CO loss, eq 8, or a combination of both as reasonable alternatives. Cleavage of a single Re-Re bond would produce the diradical **1** as the primary photoproduct. This species could decay by re-forming the Re-Re bond to regenerate $H_3Re_3(CO)_{12}$, eq 9, by cleavage of two Re-Re bonds to produce three molecules of $HRe(CO)_4$, eq 10, by cleavage of a single Re-Re bond to give $H_2Re_2(CO)_8$ and $HRe(CO)_4$, eq 11, or by dissociation of CO to give the open cluster $H_3Re_3(CO)_{11}$, **2**, eq 12. Cleavage to produce three $HRe(CO)_4$ molecules, eq 10, is eliminated by the results obtained upon photolysis under a CO atmosphere (see above). The observation that no $H_2Re_2(CO)_8$ was produced when $H_3Re_3(CO)_{12}$ was irradiated in the presence of DPA would seem to rule out direct formation of $H_2Re_2(CO)_8$ as in eq 11, but it may be possible for DPA to interact directly with the diradical intermediate **1** and thus change the process by which this species decays.

$$\mathbf{1} \rightarrow H_3Re_3(CO)_{12} \qquad (9)$$

$$\mathbf{1} \rightarrow 3HRe(CO)_4 \qquad (10)$$

$$\mathbf{1} \rightarrow H_2Re_2(CO)_8 + HRe(CO)_4 \qquad (11)$$



$$\mathbf{1} \rightleftarrows \underset{\mathbf{2}}{H(CO)_4Re\cdot\ \ ReH(CO)_4\ \ \cdot ReH(CO)_3} + CO \qquad (12)$$

If **1** is formed in the primary photochemical event, the experimental evidence suggests that it leads to the above products via conversion to **2**, eq 12. Although there are no documented examples of dissociation of CO from a polynuclear radical as in eq 12, it is known that CO can rapidly dissociate from monomeric organometallic radicals.[40] Specifically, as it relates to the $H_3Re_3(CO)_{12}$ system, Byers and Brown have shown that dissociation of CO from $\cdot Re(CO)_5$ occurs more rapidly than CO dissociation from $HRe(CO)_5$.[40a] The observed CO inhibition of the quantum yield of disappearance of $H_3Re_3(CO)_{12}$ would be explained by CO recombining with the open $H_3Re_3(CO)_{11}$ intermediate **2** to re-form **1**.

If intermediate **2** were formed in the photoprocess it could subsequently decay via one of the reactions shown in eq 13-15.

$$\mathbf{2} \rightarrow H_2Re_2(CO)_8 + HRe(CO)_3 \qquad (13)$$

$$\mathbf{2} \rightarrow 2HRe(CO)_4 + HRe(CO)_3 \qquad (14)$$

$$\mathbf{2} \rightarrow H_2Re_2(CO)_7 + HRe(CO)_4 \qquad (15)$$

Formation of the 14-valence-electron $HRe(CO)_3$ species as in eq 13 and 14 seems highly unlikely. Likewise, the observation of the production of $H_2Re_2(CO)_8$ during irradiation of

$H_3Re_3(CO)_{12}$ under a CO atmosphere would also eliminate reaction 14. We thus suggest that, if intermediate **2** is formed in the reaction, it would decay via eq 15 to produce $H_2Re_2(CO)_7$ and $HRe(CO)_4$. In degassed solution, $H_2Re_2(CO)_7$ would react with the dissociated CO to give $H_2Re_2(CO)_8$, while the $HRe(CO)_4$ formed would dimerize to give an overall quantitative conversion of $H_3Re_3(CO)_{12}$ into $H_2Re_2(CO)_8$. Under a CO atmosphere, both $HRe(CO)_5$ and $H_2Re_2(CO)_8$ would initially result as required by the experimental data. Likewise, in the presence of DPA, the photogenerated $H_2Re_2(CO)_7$ species could react to give the observed $H_2Re_2(CO)_7(DPA)_2$ product.

The other alternative for the primary photochemical event is direct photoinduced loss of a carbonyl ligand, eq 8. The unsaturated but closed cluster $H_3Re_3(CO)_{11}$ (**3**), which would result from CO loss, could then decay by breaking one, two, or three metal-metal bonds as in eq 16–19.

$$\mathbf{3} \rightarrow 2HRe(CO)_4 + HRe(CO)_3 \tag{16}$$

$$\mathbf{3} \rightarrow H_2Re_2(CO)_8 + HRe(CO)_3 \tag{17}$$

$$\mathbf{3} \rightarrow H_2Re_2(CO)_7 + HRe(CO)_4 \tag{18}$$

$$\mathbf{3} \rightarrow \mathbf{2} \tag{19}$$

Since the primary photoprocess in this mechanism involves CO loss, the CO inhibition of the disappearance of $H_3Re_3(CO)_{12}$ is readily explained. The observation that $H_2Re_2(CO)_8$ is formed during photolysis under a CO atmosphere eliminates cleavage of all three metal-metals, eq 16, and formation of $HRe(CO)_3$, eq 17, appears unlikely. Our experimental evidence cannot differentiate between cleavage of two Re-Re bonds, eq 18, and cleavage of one Re-Re bond, eq 19. The latter process would generate the same open $H_3Re_3(CO)_{11}$ intermediate **2** that would be formed via the intermediate **1**, eq 12.

The experimental data thus narrows the mechanistic possibilities to those shown in Scheme I. Although reaction 11 cannot be explicitly ruled out, it appears unlikely as a result of the photolysis experiments in the presence of DPA. Unfortunately, we have not been able to distinguish between Re-Re bond cleavage, eq 7, and loss of CO, eq 8, in the primary photochemical event, although the radical labilization studies of Byers and Brown[40] and the precedent established by the photochemical studies of metal-metal dimers[1b,44,45] strongly favor direct Re-Re bond cleavage.[47] It is further conceivable that a single photon could lead to both Re-Re bond rupture and expulsion of CO in a single step leading directly from $H_3Re_3(CO)_{12}$ to **2**.

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References and Notes

(1) (a) M. S. Wrighton, *Chem. Rev.*, **74**, 401 (1974); (b) G. L. Geoffroy and M. S. Wrighton, "Organometallic Photochemistry", Academic Press, New York, 1979.
(2) Arnd Volger in "Concepts of Inorganic Photochemistry", A. W. Adamson and P. D. Fleischauer, Eds., Wiley, New York, 1975.
(3) (a) B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Organomet. Chem.*, **67**, C75 (1974); (b) B. F. G. Johnson, J. Lewis, and M. V. Twigg, *J. Chem. Soc., Dalton Trans.*, 1876 (1975).
(4) F. A. Cotton and D. L. Hunter, *J. Am. Chem. Soc.*, **98**, 1413 (1976).
(5) L. Kruczynski, J. L. Martin, and J. Takats, *J. Organomet. Chem.*, **80**, C9 (1974).
(6) (a) R. G. Austin, R. S. Paonessa, P. J. Giordano, and M. S. Wrighton, *Adv. Chem. Ser.*, **No. 168**, 189 (1978); (b) J. L. Graff, R. D. Sanner, and M. S. Wrighton, *J. Am. Chem. Soc.*, **101**, 273 (1979).
(7) M. I. Bruce, M. Cooke, M. Green, and D. J. Westlake, *J. Chem. Soc. A*, 987 (1969).
(8) F. A. Cotton, A. J. Deeming, P. L. Josty, S. S. Ullah, A. J. P. Domingos, B. F. G. Johnson, and J. Lewis, *J. Am. Chem. Soc.*, **93**, 4624 (1971).
(9) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 3147 (1970).
(10) (a) G. L. Geoffroy and R. A. Epstein, *Inorg. Chem.*, **16**, 2795 (1977); (b) *Adv. Chem. Ser.*, **No. 168**, 132 (1978).
(11) I. Fischer, R. Wagner, and E. A. Koerner von Gustorf, *J. Organomet. Chem.*, **112**, 155 (1976).
(12) B. F. G. Johnson, J. W. Kelland, J. Lewis, and S. K. Rehani, *J. Organomet. Chem.*, **113**, C42 (1976).
(13) P. F. Heveldt, B. F. G. Johnson, J. Lewis, P. R. Raithby, and G. M. Sheldrick, *J. Chem. Soc., Chem. Commun.*, 340 (1978).
(14) C. R. Bock and M. S. Wrighton, *Inorg. Chem.*, **16**, 1309 (1977).
(15) (a) S. A. R. Knox and F. G. A. Stone, *J. Chem. Soc. A*, 2559 (1969); (b) *ibid.*, 2874 (1971).
(16) A. Brooks, S. A. R. Knox, and F. G. A. Stone, *J. Chem. Soc. A*, 3469 (1971).
(17) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *J. Am. Chem. Soc.*, **90**, 3293 (1968).
(18) W. R. Cullen and D. A. Harbourne, *Inorg. Chem.*, **9**, 1839 (1970).
(19) W. R. Cullen, D. A. Harbourne, B. V. Liengme, and J. R. Sams, *Inorg. Chem.*, **9**, 702 (1970).
(20) An apparent exception is $Fe_4(\eta^5\text{-}C_5H_5)_4(CO)_4$, which can be smoothly photooxidized to $[Fe_4(\eta^5\text{-}C_5H_5)_4(CO)_4]^+$, but this reaction only occurs in the presence of electron-accepting solvents such as CCl_4.[14]
(21) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4841 (1964).
(22) M. R. Churchill, P. H. Bird, H. D. Kaesz, R. Bau, and B. Fontal, *J. Am. Chem. Soc.*, **90**, 7135 (1968).
(23) M. A. Andrews, S. W. Kirtley, and H. D. Kaesz, *Inorg. Chem.*, **16**, 1556 (1977).
(24) Kaesz and co-workers have also observed this photoreaction: H. D. Kaesz, private communication.
(25) B. F. G. Johnson, R. D. Johnston, J. Lewis, and B. H. Robinson, *J. Organomet. Chem.*, **10**, 105 (1967).
(26) S. W. Kirtley, J. P. Olsen, and R. Bau, *J. Am. Chem. Soc.*, **95**, 4532 (1973).
(27) W. L. Jolly, "The Synthesis and Characterization of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1970.
(28) C. G. Hatchard and C. A. Parker, *Proc. R. Soc. London, Ser. A*, **235**, 518 (1956).
(29) D. F. Shriver, "The Manipulation of Air-Sensitive Compounds", McGraw-Hill, New York, 1969.
(30) J. W. Majerik, Ph.D. Thesis, The Pennsylvania State University, 1969.
(31) M. J. Bennett, W. A. G. Graham, J. K. Hoyano, and W. L. Hutcheon, *J. Am. Chem. Soc.*, **94**, 6232 (1972).
(32) N. Flitcroft, D. K. Huggins, and H. D. Kaesz, *Inorg. Chem.*, **3**, 1123 (1964).
(33) G. B. Blakney and W. F. Allen, *Inorg. Chem.*, **10**, 2763 (1971).
(34) P. S. Braterman, R. W. Harrill, and H. D. Kaesz, *J. Am. Chem. Soc.*, **89**, 2851 (1967).
(35) R. A. Levenson and H. B. Gray, *J. Am. Chem. Soc.*, **97**, 6042 (1975).
(36) ν_{CO}, hexane solution: 2088 m, 2036 s, 2015 s, 1994 s, 1981 vs, 1963 w, 1950 m cm^{-1}
(37) ν_{CO}, hexane solution: 2049 s, 2021 s, 1968 m, br, 1948 w, 1932 m cm^{-1}.
(38) W. D. Fellman and H. D. Kaesz, *Inorg. Nucl. Chem. Lett.*, **2**, 63 (1966).
(39) The IR spectra of the distillate from this reaction showed bands at 2015 s and 2005 m cm^{-1} attributable to $HRe(CO)_5$.[32] The white residue remaining after distillation showed bands at 2070 m, 2014 vs, 2003 w, 1976 m, 1959 vw, and 1942 vw cm^{-1} characteristic of $Re_2(CO)_{10}$.[30]
(40) (a) B. H. Byers and T. L. Brown, *J. Am. Chem. Soc.*, **99**, 2527 (1977); (b) *ibid.*, **97**, 947 (1975); (c) *ibid.*, **97**, 3260 (1975).
(41) G. Bor, *Chem. Commun.*, 641 (1969).
(42) R. A. N. McLean, *J. Chem. Soc., Dalton Trans.*, 1568 (1974).
(43) D. R. Tyler, R. A. Levenson, and H. B. Gray, *J. Am. Chem. Soc.*, **100**, 7888 (1978).
(44) M. S. Wrighton and D. S. Ginley, *J. Am. Chem. Soc.*, **97**, 2065 (1975).
(45) M. S. Wrighton, *Top. Curr. Chem.*, **65**, 37 (1976).
(46) D. R. Kidd and T. L. Brown, *J. Am. Chem. Soc.*, **100**, 4095 (1978).
(47) Flash photolysis experiments were conducted in an attempt to resolve this mechanistic question (R. Epstein, Ph.D. Thesis, The Pennsylvania State University, 1978). Although several transients were observed, we were unable to confidently assign them to specific intermediates on the basis of their decay and spectral characteristics.