slow evaporation of an aqueous solution at room temperature. A systematic search in reciprocal space using an Enraf-Nonius four-circle CAD-4 automatic diffractometer controlled by a PDP 8a computer showed that crystals of **2** belong to the monoclinic system and that the space group is *C*2, *Cm*, or *C*2/*m*. The lattice parameters and the data collection were obtained as described for compound **1**. Crystal data and details of the data collection are summarized in Table IV. The resolution of this structure was carried out in the same way as was done for **1**. The final least-squares cycle converged to values of R and R_w on F^2 of 0.040 and 0.060, respectively, for the 99 variables and 1216 data. The standard error in an observation of unit weight is 1.37 e^2. The highest density in the final difference Fourier map is <0.10 e Å^{-3}. Final xyz, β_{ij} non-hydrogen parameters are listed in Table VI. Table VIII[30] lists the values of hkl, $10|F_o|$ vs. $10|F_c|$.

Magnetic Measurements

The magnetic susceptibility measurements were carried out with a Faraday-type magnetometer equipped with a continuous-flow cryostat in the temperature range 3.8–300 K. The polycrystalline powder samples weighed about 7 mg. The applied magnetic fields were in the range 0.3–0.6 T. The independence of the susceptibility against the magnetic field was checked at both room temperature and 20 K. Mercury tetrakis(thiocyanato)cobaltate(II) was used as a susceptibility standard. The uncertainty on the temperature T is estimated as 0.1 K. The uncertainty on the molar magnetic susceptibility χ_M is more difficult to appreciate. If the uncertainty on the measurement itself is less than 2% as shown by the reproductibility of the magnetic curves carried out on different samples of the same compound, the uncertainty on the temperature-independent susceptibility, including diamagnetism and TIP, is probably rather high. The magnetic data were corrected for that, and these corrections were estimated as -290×10^{-6} cm^3 mol^{-1} for **1** and -250×10^{-6} cm^3 mol^{-1} for **2**. If an uncertainty of 50×10^{-6} cm^3 is assumed for these values, the uncertainty on $\chi_M T$ is as large as 0.03 cm^3 mol^{-1} K. It will be important to keep in mind this $\Delta\chi_M T$ value when interpreting the magnetic data.

EPR Measurements

The EPR study was carried out on a crystal of $\mathbf{1}\cdot H_2O$ and on a powder sample of **2** in the 4.2–300 K temperature range with a Bruker ER 200 spectrometer equipped with a continuous-flow cryostat and working in the X-band. A 100-KHz field modulation was used, and the magnetic fields were measured by a Hall probe.

Registry No. $\mathbf{1}\cdot H_2O$, 83095-47-0; **2**, 83095-48-1; **3**, 71072-85-0; **5**, 43090-52-4; **6b**, 83076-80-6; **7**, 56187-04-3; **8**, 83076-78-2; **9**, 83076-79-3; 2-(2-chloroethoxy)ethanol, 628-89-7; *p*-toluenesulfonyl chloride, 98-59-9.

Supplementary Material Available: Tables VII and VIII, listing the values of hkl, $10|F_o|$ vs. $10|F_c|$ for $\mathbf{1}\cdot H_2O$ and **2**, respectively; Figures 12 and 13, showing the packing in the unit cell for **1** and **2**, respectively (21 pages). Ordering information is given on any current masthead page.

Photochemical Reaction of Dirhenium Decacarbonyl with Water[1]

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Abstract: The photochemical reaction of $Re_2(CO)_{10}$ with H_2O in THF and other solvents has been studied, with use of radiation of varying wavelength. The initial reaction leads to $Re_2(CO)_9(OH_2)$, formed upon irradiation at 313 nm. This product is shown to form via a primary photochemical homolysis of the Re–Re bond, followed by thermal substitution of the $Re(CO)_5\cdot$ radical by H_2O, and then re-formation of the metal–metal bond to give $Re_2(CO)_9(OH_2)$. Although $Re_2(CO)_9(OH_2)$ is relatively stable toward 313-nm irradiation, it decomposes rapidly under 366-nm irradiation to form $HRe(CO)_5$ and $Re_4(CO)_{12}(OH)_4$. The decomposition pathway is thought to involve $Re_2(CO)_8(OH_2)_2$, an unstable intermediate. The presence of this intermediate is substantiated in part by the observation that thermal reaction of $Re_2(CO)_8(CH_3CN)_2$ with H_2O in THF leads to formation of $Re_4(CO)_{12}(OH)_4$. The decomposition of $Re_2(CO)_8(OH_2)_2$ is proposed to proceed via initial loss of H_2O and oxidative addition of an O–H bond to form (μ-hydrido)(μ-hydroxo)dirhenium octacarbonyl, $HRe_2(CO)_8(OH)$, which undergoes decomposition to form the observed products.

Introduction

Herberhold and Süss have reported[2,3] that photolysis of $Re_2(CO)_{10}$ in wet ether solution results in quantitative conversion to the tetranuclear hydroxo compound $Re_4(CO)_{12}(OH)_4$, with evolution of H_2 (eq 1). The only intermediate observed during the

$$2Re_2(CO)_{10} + 4H_2O \rightarrow Re_4(CO)_{12}(OH)_4 + 2H_2 + 8CO \quad (1)$$

reaction was $H_3Re_3(CO)_{12}$. This reaction, which results in partial water splitting, is of synthetic and mechanistic interest, particularly since few stable transition-metal hydroxocarbonyl compounds are known. The pathway leading to formation of the product is not evident, and the failure to observe several rhenium carbonyl compounds that might be expected as intermediates is not readily accounted for. Accordingly, we have reinvestigated this reaction in some detail, paying attention to the dependence of the reaction on irradiation wavelength. Our results show that the reaction follows an unexpected route; the use of varying wavelengths of irradiation has made it possible to isolate intermediates along the pathway to the final product.

Experimental Section

Reagents. Dirhenium decacarbonyl, $Re_2(CO)_{10}$, and triosmium dodecacarbonyl, $Os_3(CO)_{12}$, were purchased from Pressure Chemical Co. and Strem Chemical Co., respectively, and used without further purification.

Deionized water was purified by passing through a mixed bed of IR-20 and A-101D ion-exchange resins (Dearborn Chemical). The water was degassed prior to use by boiling.

Linde CP carbon monoxide, CO, was passed through activated manganese(II) oxide and 3A molecular sieves to reduce levels of O_2 and H_2O, respectively.

Trimethylamine *N*-oxide dihydrate, $Me_3NO\cdot 2H_2O$, was obtained from Aldrich Chemical Co. (98%) and used without further purification.

Hydridorhenium pentacarbonyl, $HRe(CO)_5$, was prepared by acidification of $NaRe(CO)_5$.[4]

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Triphenylphosphine, PPh_3 (99%, Aldrich Chemical Co.), was recrystallized twice from EtOH and stored under N_2.

Acetonitrile, CH_3CN (Mallinckrodt AR), was dried over 3A molecular sieves.

CP grade hydrogen, H_2, was obtained from Linde and used directly.

Solvent Purification. Syntheses under thermal reaction conditions were conducted in analytical grade solvents dried over 3A and 4A molecular sieves. Solvents used for chromatography, recrystallization, or extraction were commercially available analytical or bulk grade solvents. The purification procedures for solvents used in the photochemical reactions were as follows.

Tetrahydrofuran, THF. Aldrich 99%+ THF was purified by two distillations from sodium–benzophenone ketyl under argon and used immediately thereafter.[5] The ^1H NMR spectrum of the purified solvent showed no signs of oxidized organic products commonly found when THF is exposed to air.[6] GC analysis indicates that freshly distilled THF contains approximately 100 ppm or less of H_2O (vide infra).

Heptane. Phillips bulk heptane was extensively treated with concentrated H_2SO_4, neutralized with aqueous $NaHCO_3$, dried over $MgSO_4$, and distilled from sodium–benzophenone ketyl.

Toluene. Mallinckrodt analytical reagent grade toluene was treated with concentrated H_2SO_4, rinsed with aqueous $NaHCO_3$, dried over $CaCl_2$, passed through activated silica, and distilled from 4A molecular sieves.

Acetonitrile. Mallinckrodt analytical reagent grade CH_3CN was predried with $CaCl_2$, distilled from P_2O_5 onto K_2CO_3, and redistilled from CaH_2.

Diethyl Ether. Baker reagent grade Et_2O was distilled directly from CaH_2.

Inert-Atmosphere Techniques. While in some cases the products of the photochemical reactions are fairly air stable, the reactions themselves are quite sensitive to traces of O_2. All samples for photolysis and for the synthesis and purification of air-sensitive materials were prepared either in Schlenk apparatus under protection of argon or in an inert-atmosphere glovebox.[7]

Evolution of H_2 in photochemical reactions was measured by GLC. To a quartz tube fitted with a Teflon stopcock and rubber septum was added a small amount of mercury followed by injection of a sample of the solution to be photolyzed under argon. When the tube is inverted, the mercury acts as a gas seal. The sample is photolyzed and then frozen in liquid N_2. The gas above the solution is either sampled directly or first quantitatively transferred with a Toepler pump into a larger flask of argon at atmospheric pressure. A direct or diluted gas sample is injected into a 2-m length, 6.3-mm diameter column of Porapak Q (50–80 mesh) at 30 °C with argon as the carrier gas. Under the reaction conditions employed, an approximately 2% yield of H_2 from the photochemical reactions can be detected.

Lamps and Filters. All photochemical experiments using 313-nm light (including quantum yield measurements, synthesis, and reactions monitored by IR or NMR spectroscopy) were conducted with a Hanovia 200-W medium-pressure mercury vapor arc lamp (Ace Glass #6515-32) inside a jacketed quartz immersion well. The immersion well fits into a Pyrex solution jacket manifold, which consists of two concentric filter solution compartments. Filter solutions used to segregate the 313-nm irradiation are similar to those described by Bowen.[8] Absorbances of the filter solutions were monitored periodically for changes in their transmission characteristics. Analysis of the distribution of wavelengths impinging on the sample[9,10] indicates that 85% of the useful photon flux is of 313-nm wavelength. The 313-nm photon flux is approximately 10^{-7} einstein/(cm^2 s).

Sunlamp Photolyses. Photochemical syntheses and reactions utilizing irradiation from a General Electric 275-W sunlamp were carried out under an argon atmosphere in Pyrex Schlenk vessels. The walls of the flask (approximately 1 mm thick) act as a cutoff filter for $\lambda < 297$ nm. Photons of $\lambda > 436$ nm are not absorbed appreciably. All wavelengths from 297 to 366 nm are totally absorbed by the solutions. The extent of absorption of 406- and 436-nm photons depends on the compounds being irradiated and their concentrations. In all cases the absorbed sunlamp radiation will be principally of wavelengths longer than 313 nm; the major component is 366 nm. With typical sample volumes and areas, the total absorbed photon flux is about 10^{-4}–10^{-5} einstein/(L s).

Photolyses monitored by ^1H NMR were performed in the NMR tube shielded from the lamp by a piece of Pyrex. The evolved gases were allowed to escape through a bubbler attached to the tube by a needle and septum.

500-nm Irradiation. Monochromatic 500-nm radiation was provided by a 300-W high-pressure xenon arc lamp (PEK X-300), in a Schoeffel LH 151 N lamp housing in conjunction with a 500-nm interference filter (band width at half-height 12 nm). The absorbed photon flux for samples irradiated with 500-nm light is estimated to be roughly 10^{-8} einstein/(L s).

Quantum Yield Measurements. The disappearance quantum yields for $Re_2(CO)_{10}$ upon irradiation with 313-nm light were measured in wet solvents under a variety of conditions. The samples for these determinations were prepared by freshly distilling solvent under argon into an oven-dried Schlenk flask containing $Re_2(CO)_{10}$. Depending on the H_2O concentration desired, a measured amount of degassed, deionized water was syringed into the $Re_2(CO)_{10}$ solution. The concentration of $Re_2(CO)_{10}$ used in all cases is $(2.0 \pm 0.2) \times 10^{-3}$ M, providing a totally absorbing solution at 313 nm. Traces of O_2 or other volatile impurities were reduced by one freeze–pump–thaw cycle. This procedure is expected to leave nearly pure argon as the residual gas above the solution.

Samples photolyzed with a carbon monoxide atmosphere were prepared by bubbling Linde CP grade CO (purified by passage through activated manganese oxide and 3A molecular sieves) through the argon-saturated solutions without evacuation. The concentration of CO in THF at 20 °C is estimated to be 1×10^{-2} M.[12]

Some samples were photolyzed at 313 nm in a merry-go-round apparatus. The light intensity reaching the sample may be varied by wrapping the outside of the filter solution manifold with nylon screening. The samples were photolyzed for a time sufficient to provide $7 \pm 2\%$ conversion of $Re_2(CO)_{10}$, depending on the light intensity employed (6.64×10^{-8} or 7.18×10^{-7} einstein/(L s)).

Following photolysis, the decrease in absorbance due to $Re_2(CO)_{10}$ at 2070 cm^{-1} in relation to absorbance of the nonirradiated reference samples was measured.

The photon flux impinging on the sample was measured with use of potassium ferrioxalate actinometry.[13,14]

With a knowledge of the change in $Re_2(CO)_{10}$ concentration and the absorbed light intensity, along with the irradiation time, the disappearance quantum yield of $Re_2(CO)_{10}$, Φ_d, can be calculated (supplementary material). The inner filter correction to Φ_d due to absorption by product can be shown to be on the order of only 3%. Therefore, uncorrected values of Φ_d are reported.

A GLC method was employed to measure the H_2O concentration in nonphotolyzed reference solution samples in cases where it was expected to be quite low (wet toluene solutions of THF solutions to which no extra water had been added). The water content of solutions prepared for quantum yield measurements with dry THF was found to be typically 100 ± 50 ppm or approximately 6×10^{-3} M. Only a rough quantitative estimate is obtained; precision is lost due to unavoidable moisture contamination during sample handling.

Preparation of Compounds. Tetrakis[(μ_3-hydroxo)rhenium tricarbonyl], $Re_4(CO)_{12}(OH)_4$. Following the preparation given by Herberhold and Süss, $Re_2(CO)_{10}$ (1.00 g, 1.53 mmol) and 1.5 mL of H_2O were dissolved in 25 mL of THF under argon in a Pyrex Schlenk flask. The solution was irradiated with a GE 275-W sunlamp for 1 week. Over this period the solution turned from colorless to yellow, then to orange, and then to a faint red or to colorless again. The solvent was removed under vacuum, and the solutes were chromatographed on silica with petroleum ether (bp 60–68 °C)/acetone as eluent, with increasing portions of acetone. The first compounds eluted were traces of hydrides and unreacted $Re_2(CO)_{10}$, followed by $Re_4(CO)_{12}(OH)_4$. $Re_4(CO)_{12}(OH)_4$ was then recrystallized twice from 1/2 Et_2O/petroleum ether and dried at 80 °C under vacuum for 24 h; yield 625 mg (0.54 mmol), 71%. The ^1H NMR spectrum and elemental analysis indicate that some THF, which is difficult to completely remove, remains adducted to $Re_4(CO)_{12}(OH)_4$.[3]

IR (ν(CO), THF): 2025 (s), 1918 (vs) cm^{-1}. Lit.[2] IR (THF): 2021 (s), 1919 (vs) cm^{-1}. Electron impact mass spectrum, m/e (relative intensity): parent ions at 1144 (9), 1145 (36), 1148 (93), 1150 (100), and 1152 (50). Masses of the daughter ions correspond to competitive loss

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of OH and CO. ^{1}H NMR (singlet that shifts downfield with higher concentrations of H_2O in the solvent): in dry acetone-d_6, τ 3.34. Lit.,[2,3] 3.88; in dry THF-d_8, 3.00.

Tris(acetonitrile)rhenium(I) tricarbonyl tetrafluoroborate, $Re(CO)_3(CH_3CN)_3{}^+BF_4{}^-$, was prepared by following a preparation by Darensbourg et al.[15]

IR (ν(CO), CH_3CN): 2053 (s), 1952 (vs) cm^{-1}. Lit.[15] IR (CH_3Cl): 2045 (s), 1956 (s, br) cm^{-1}.

(1,10-Phenanthroline)dirhenium octacarbonyl, $Re_2(CO)_8$(phen), was prepared by following a preparation by Morse and Wrighton.[16] All preparations were carried out in the dark with a red safety lamp.

IR (ν(CO), THF): 2073 (w–m), 1992 (s), 1959 (s), 1888 (m), 1861 (m) cm^{-1}. Lit.[16] IR (CH_2Cl_2): 2073 (m), 2012 (s), 1992 (m), 1959 (m), 1915 (m), 1889 (m) cm^{-1}. UV–vis Lit.[16] (CH_2Cl_2/CCl_4): 330 (ϵ 10 000), 350 (5200), 528 (7300).

eq-(Acetonitrile)dirhenium nonacarbonyl, *eq*-$Re_2(CO)_9(CH_3CN)$, was prepared by following a preparation by Koelle.[17]

IR (ν(CO), CH_2Cl_2): 2104 (w), 2048 (m), 1996 (s), 1988 (sh), 1961 (w), 1930 (m) cm^{-1}. Lit.[17] IR (hexane): 2099 (1), 2042 (5), 2012 (5.5), 1960 (?) (10, br), 1963 (4.6), 1942 (5.5) cm^{-1}. UV–vis (THF): 311 (ϵ 10 300), 325 (12 100), 366 nm (2500, sh). Satisfactory elemental analyses (C, H, N, Re) were obtained for all of the compounds.

***dieq*-Bis(acetonitrile)dirhenium Octacarbonyl, *dieq*-$Re_2(CO)_8(CH_3CN)_2$.** $Re_2(CO)_{10}$ (310 mg, 0.48 mmol) was dissolved in 10 mL of CH_2Cl_2 and 10 mL of CH_3CN. A 100-mg (0.99-mmol) quantity of $Me_3NO{\cdot}2H_2O$ was added and the solution stirred for 2 h. The solvent was removed under vacuum and the yellow solid recrystallized from Et_2O/petroleum ether. The product contains an impurity with IR bands at 2075 and 2001 cm^{-1}, which could not be effectively removed by sublimation, recrystallization, or chromatography; yield 109 mg (0.16 mmol), 34%.

IR (ν(CO), CH_3CN): 2070 (w), 2015 (m), 1962 (s), 1909 (m) cm^{-1}. Field desorption mass spectrum: parent ions at 676 (31), 678 (100), and 680 (86). Masses of daughter ions indicate that CH_3CN loss is favored over CO loss.

Infrared spectra were obtained with a Beckman IR-4240 spectrophotometer. CaF_2 solution cells of 0.206-mm path length were employed for solution samples.

Electronic spectra were recorded on a Cary 14 recording spectrophotometer with matching 1.0-cm quartz cells.

^{1}H NMR spectra were recorded at ambient temperature with a Varian EM-390 instrument.

Electron impact mass spectra were recorded at 70 eV with a Varian MAT CH-5 mass spectrometer. Field desorption mass spectra were obtained with a Varian MAT 731 spectrometer equipped with a field desorption source.

Hydrogen gas evolution and the H_2O content of liquid samples were measured by gas chromatography using a F & M Model 700 gas chromatograph with a thermal conductivity detector.

Computer-Assisted Simulation of Spectra. Contributions from more than one compound to IR and electronic spectra may be quantitatively determined with the aid of the program PLTSUB.[18,19] Several spectra of pure complexes may be added to match a spectrum containing several components, or the spectra of components may be subtracted from spectra of mixtures to yield spectra of compounds that are otherwise obscured. Quantitative measurements are possible by relating scaling factors to concentrations via Beer's law.

These quantitative IR techniques were employed to determine the H/Re ratio in a relatively unstable photolysis product obtained in THF solution. A solution of known initial $Re_2(CO)_{10}$ concentration was photolyzed at 313 nm, and contributions of $Re_2(CO)_{10}$, $HRe(CO)_5$, and $Re_4(CO)_{12}(OH)_4$ to the IR spectra were quantitatively subtracted with the assistance of the program PLTSUB. The resultant spectrum is that of the pure yellow product. The normality of Re atoms due to this compound is known by difference. The same sample is then concentrated and the ^{1}H NMR spectrum run in THF-d_8 with a known amount of *p*-chlorobenzaldehyde added as an internal standard. Comparison of the integrated intensity of the signal at τ 4 with the aldehyde proton intensity allows determination of the concentration of H atoms due to the yellow compound in the NMR sample. The concentration of H atoms in the NMR sample may then be compared with the concentration of Re atoms in the IR sample, after correction for concentrating the IR solution. With use of this approach, the H/Re ratio was found to be 0.89 ± 0.16 from analyses of four different samples, separately irradiated.

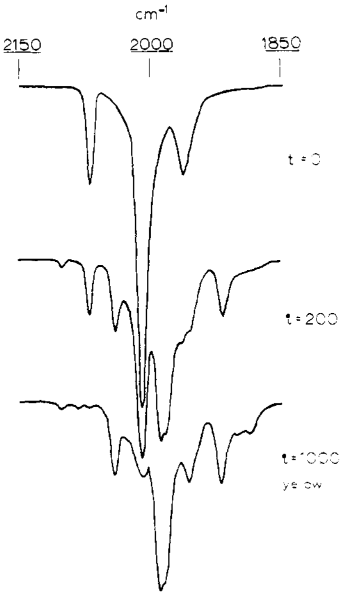

Figure 1. IR spectra of $Re_2(CO)_{10}$ in THF (1% H_2O) as a function of irradiation time with 313-nm radiation.

Results and Discussion

The photolysis of a solution containing $Re_2(CO)_{10}$ in wet THF under an argon atmosphere was monitored as a function of irradiation time with use of several analytical techniques. The reaction was found to be rather complex, and several intermediates were identified. The course of the reaction depends on the wavelength of irradiation, intensity level, and whether the reaction is carried out in a closed or flushed system.

313-nm Photolysis of $Re_2(CO)_{10}$. Photolysis of a 5×10^{-3} M solution of $Re_2(CO)_{10}$ in THF containing 1% H_2O by volume with 313-nm light results in the appearance of a single yellow product with an IR spectrum shown in Figure 1 (2100 (w), 2040 (m), 1988 (s), 1980 (sh), 1950 (m), and 1912 (m) cm^{-1} in THF). In the ^{1}H NMR spectrum, a broad singlet near τ 4 is seen. No H_2 evolution was detected when the gas above the sample was monitored with GLC. Continued photolysis at 313 nm causes slow decomposition of this compound to $HRe(CO)_5$ and $Re_4(CO)_{12}(OH)_4$.

The positions and intensities of the bands observed in the IR spectrum are characteristic of those reported for equatorially substituted $M_2(CO)_9L$ complexes (M = Mn, Re; L = nitriles,[17,20] pyridine,[20,21] $P(CH_3)_2Ph$,[22] $P(CH_3)Ph_2$[23]). The chemical shift of the singlet in the ^{1}H NMR spectrum is in the region expected for OH proton(s), $\tau \approx 4$. This signal also broadens and shifts to lower field at higher water concentrations, because of hydrogen bonding, as occurs with $Re_4(CO)_{12}(OH)_4$ (vide infra).

The yellow complex is formulated as the equatorial isomer of aquadirhenium nonacarbonyl, *eq*-$Re_2(CO)_9(OH_2)$, formed under the conditions of 313-nm photolysis. Support for assignment of the structure is the similarity of the IR spectrum to that of the monoequatorially substituted $Re_2(CO)_9(CH_3CN)$. Unfortunately, the yellow compound is unstable, and it was not possible to isolate it from the solvent. As a means of further establishing the assignment, a quantitative study was made using a combination of IR and NMR measurements, to determine the ratio of hydrogen to Re atoms (see Experimental Section) for four different samples this H/Re ratio was found to be 0.89 ± 0.16.

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Table I. Disappearance Quantum Yields (Φ_d) for the Photochemical Reaction of $Re_2(CO)_{10}$ (2×10^{-3} M) with H_2O at 313 nm in THF

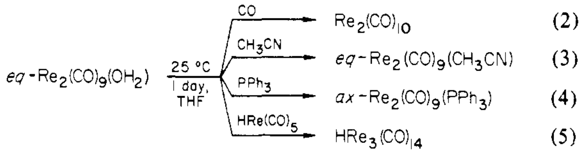
solvent	$10^3[H_2O]$, M	$10^8 I_a$, einstein/(L s)	Φ_d(313 nm)
THF	3–15	72	0.32 ± 0.01
THF	220	72	0.30 ± 0.04
THF[a]	6	72	0.18 ± 0.01
THF	6–10	6.6	0.58 ± 0.05
THF[b]	8	6.6	0.56 ± 0.03
acetonitrile	6, 45	72	0.20 ± 0.01
toluene	14	72	0.12 ± 0.02

[a] [CO] = 10^{-2} M. [b] 1.5×10^{-3} M $N(n\text{-}Bu)_4BPh_4$.

It is surprising that an H_2O-substituted compound is formed as photolysis product. Few examples of water coordinated to a zerovalent metal exist.[24,25] Formation of *eq*-$Re_2(CO)_9(OH_2)$ occurs in the presence of even trace quantities of water. For example, it is formed in high yield upon 313-nm photolysis of $Re_2(CO)_{10}$ in carefully dried THF containing 100 ppm or less of H_2O.

The electronic spectrum of the yellow product exhibits a maximum at 332 nm assigned to the σ–σ^* transition (10 600 M^{-1} cm^{-1}) and a less intense band at 407 nm (2000 M^{-1} cm^{-1}) assigned to the d_π–σ^* transition.

The coordinated water in *eq*-$Re_2(CO)_9(OH_2)$ is readily displaced by other more strongly nucleophilic ligands (eq 2–5). These reactions demonstrate that *eq*-$Re_2(CO)_9(OH_2)$ can be considered as a lightly stabilized form of the coordinatively unsaturated $Re_2(CO)_9$.



It is noteworthy that *eq*-$Re_2(CO)_9(OH_2)$ does not react with H_2 in THF at 25 °C during 2 days. The observation is of interest in that it would appear to rule out a facile oxidative addition to $Re_2(CO)_9$, which might be postulated as an intermediate in the photochemical reaction of $Re_2(CO)_{10}$ with H_2.[26]

Removal of THF causes *eq*-$Re_2(CO)_9(OH_2)$ to decompose rapidly to $HRe_3(CO)_{14}$ and $Re_4(CO)_{12}(OH)_4$. Attempts to prepare the compound in wet toluene or other noncoordinating solvent invariably lead to $HRe_3(CO)_{14}$ and $Re_4(CO)_{12}(OH)_4$ as products. We surmise that THF stabilizes the system by coordinating to $Re_2(CO)_9$ following H_2O dissociation, to temporarily trap the intermediate until replacement by another water molecule occurs.

A series of quantum yield measurements was undertaken to determine the mechanism for photosubstitution of $Re_2(CO)_{10}$ by H_2O. Photoinduced substitution of dinuclear metal carbonyls may result following either metal–metal bond homolysis or CO loss as the primary photochemical step. The disappearance quantum yield for $Re_2(CO)_{10}$, Φ_d, was measured for photolysis at 313 nm in water-containing solvents under a variety of conditions (Table I). The quantum yield measures the fraction of absorbing $Re_2(CO)_{10}$ molecules that proceeds to form product. Since *eq*-$Re_2(CO)_9(OH_2)$ is the only product formed in the early stages of the reaction, $\Phi_d = \Phi_a$, the quantum yield for appearance of *eq*-$Re_2(CO)_9(OH_2)$. Photolyses were carried out in a merry-go-round apparatus using a 200-W medium-pressure mercury arc lamp with a filter solution to isolate the 313-nm emission line. Totally absorbing $Re_2(CO)_{10}$ solutions were rigorously degassed and irradiated in quartz tubes. The quantum yields were calculated as in eq 6, where $t_{h\nu}$ is the time of irradiation and I_a the

$$\Phi_d = \frac{[Re_2(CO)_{10}]_0 - [Re_2(CO)_{10}]_t}{t_{h\nu} I_a} \tag{6}$$

incident light intensity in einstein/(L s) as measured by potassium ferrioxalate actinometry. The $Re_2(CO)_{10}$ concentration was monitored by the change in absorbance of the 2070-cm^{-1} band in the IR spectrum. Equation 6 is the expression for Φ_d in the absence of an inner filter effect. Conversion of $Re_2(CO)_{10}$ was limited to 6–9%; in these circumstances inner filter corrections are negligible, and complicating secondary photoreactions are minimized.

In THF, varying the H_2O concentration from approximately 10^{-3} to 0.2 M causes no significant change in Φ_d, measured as 0.32. In the presence of CO (~10^{-2} M) a considerable reduction of Φ_d to 0.18 is seen. By a decrease in the 313-nm light intensity by a factor of about 11, Φ_d nearly doubles to 0.58. These observations are consistent with the scheme shown in eq 7–10 as the predominant substitution mechanism.

$$Re_2(CO)_{10} \underset{k_{-1}}{\overset{h\nu(I_a f_0)}{\rightleftharpoons}} 2Re(CO)_5\cdot \tag{7}$$

$$Re(CO)_5\cdot \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Re(CO)_4\cdot + CO \tag{8}$$

$$Re(CO)_4\cdot + L \xrightarrow{k_3} Re(CO)_4L\cdot \tag{9}$$

$$Re(CO)_4L\cdot + Re(CO)_5\cdot \xrightarrow{k_4} Re_2(CO)_9L \tag{10}$$

Excitation of the $\sigma \rightarrow \sigma^*$ transition results in homolysis of the Re–Re bond to generate two 17-electron $Re(CO)_5\cdot$ free radicals, with fractional efficiency f_0. The 17-electron $Re(CO)_5\cdot$ free radicals may either recombine to re-form starting material or reversibly dissociate a coordinated CO. The dependence of Φ_d on CO concentration arises from the equilibrium of eq 8. Since the measured quantum yield values are substantial (all >0.1), the rate of substitution into $Re(CO)_5\cdot$ must be comparable to the rate of recombination of $Re(CO)_5\cdot$, indicating that k_2 is rather large. The nucleophile L in this system may be either H_2O or, more likely, a solvent molecule, since THF is present in much higher effective concentration. Since, however, the aqua complex is the thermodynamically favored product, coordinated THF is eventually displaced by H_2O to yield *eq*-$Re_2(CO)_9(OH_2)$. Equation 9 is not written as reversible since in this instance where L may be considered to be THF, equilibrium would lie far to the right.

It can be shown that in the limiting case [CO] → 0, Φ_d has the form of eq 11. This expression predicts that Φ_d will increase

$$\Phi_d = \frac{k_2^2}{2k_{-1}I_a}\left[\left(1 + \frac{4k_{-1}I_a}{k_2^2}\right)^{1/2} - 1\right] \tag{11}$$

for lower values of I_a, as observed. Furthermore, the observed values of Φ_d can be employed to estimate a value for k_2, the rate constant for dissociation of CO from $Re(CO)_5\cdot$. The value for k_{-1} for $Re(CO)_5\cdot$ radical recombination in hexane is 3.7×10^9 M^{-1} s^{-1}.[27] With the assumption of the same value for THF, and insertion of the values known for I_a and Φ_d into eq 11, values for k_2 on the order of 10 s^{-1} are obtained. Estimates of k_2 from our results are necessarily only approximate, because the solutions employed are highly absorbing, and the distribution of intermediates is therefore not uniform throughout. Nevertheless, the value obtained is consistent with many other observations that suggest that the 17-electron metal carbonyl radicals are especially labile toward CO loss. For example, a value of about 100 s^{-1} has been estimated for CO loss from $Re(CO)_5\cdot$ on the basis of flash photolysis results.[27] It must be noted, however, that the present results, while consistent with a rapid dissociative CO loss, could also be accounted for in terms of a facile associative displacement of CO by L.[28,29]

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The rate constants for recombination of $(\eta^5\text{-}C_5H_5)Mo(CO)_3\cdot$ radicals vary with solvent in the order cyclohexane > acetonitrile > THF.[30] Assuming the same order of solvent dependence for recombination of $Re(CO)_5\cdot$ radicals, one would predict from eq 11 that Φ_d will vary with solvent in the order THF > acetonitrile > toluene, assuming little solvent dependence on k_2. The observations (Table I) are in accord with these predictions. Thus, all of the observations taken together strongly support the model embodied in eq 2–5 for photosubstitution of $Re_2(CO)_{10}$ to form *eq*-$Re_2(CO)_9(OH_2)$.

It is significant that the monosubstituted compound is formed in this photosubstitution. By contrast, the disubstituted product is observed in photosubstitution of $Mn_2(CO)_{10}$ by phosphorus ligands.[29,31] The different behavior in the two cases is probably due mainly to the slower rate of CO loss from $Re(CO)_5\cdot$ as compared with that from $Mn(CO)_5\cdot$. Note that the disappearance quantum yield is much higher (near 0.9) for $Mn_2(CO)_{10}$, as compared with 0.3 for $Re_2(CO)_{10}$. Secondly, the conditions of the experiment differ, in that we have employed a higher photon flux in the present case. As expressed in eq 11, this favors recombination relative to substitution. Finally, the monosubstitution product *eq*-$Re_2(CO)_9(OH_2)$ is relatively stable toward further photolysis in the presence of the 313-nm irradiation. By contrast, the absorption spectra of the $Mn_2(CO)_9L$ products are quite close to that for $Mn_2(CO)_{10}$. As a result, a monosubstitution product in the latter case would be expected to undergo still additional photosubstitution.

The electronic spectrum of (1,10-phenanthroline)dirhenium octacarbonyl, $Re_2(CO)_8(phen)$, exhibits an absorption at about 500 nm, assigned as a σ–π^* transition.[16] Morse and Wrighton have shown that irradiation into this absorption band produces metal–metal bond cleavage with high quantum yield, to yield $Re(CO)_5\cdot$ and $Re(CO)_3(phen)\cdot$ radicals. Low-intensity irradiation with 500-nm light of $Re_2(CO)_8(phen)$ in THF with 1% H_2O yields mainly $Re_2(CO)_{10}$ and $Re_2(CO)_6(phen)_2$, as monitored by IR. Chromatography of the solids recovered following removal of solvent from the reaction mixture also leads to recovery of some $Re_4(CO)_{12}(OH)_4$, formed in overall 6% yield. One would expect any $Re_2(CO)_9(OH_2)$ formed to be photoreactive under the irradiation condition. These results are further evidence that the substitution leading to $Re_4(CO)_{12}(OH)_4$ as product occurs via labile radicals, and not by direct CO loss from the dinuclear carbonyl, because the long-wavelength irradiation employed does not produce CO loss directly.

Sunlamp Photolysis of $Re_2(CO)_{10}$. Sunlamp photolysis of $Re_2(CO)_{10}$ in wet THF quantitatively converts $Re_2(CO)_{10}$ and H_2O to $Re_4(CO)_{12}(OH)_4$ with evolution of H_2 (eq 1). The sunlamp source, in conjunction with the Pyrex flask as a filter, provides a distribution of light consisting primarily of wavelengths ≥366 nm. The use of longer wavelength radiation therefore remarkably alters the outcome of the photochemical reaction of $Re_2(CO)_{10}$ with H_2O, compared with the use of 313-nm light.

The carbonyl stretching region of the IR spectrum was monitored as a function of irradiation time with the sunlamp source for a 4×10^{-3} M $Re_2(CO)_{10}$ solution in THF containing 2% H_2O by volume (Figure 2). After 1850 min the reaction is completed; the only IR bands observed, centered at 2025 and 1919 cm^{-1}, are characteristic of $Re_4(CO)_{12}(OH)_4$. The identity of the final product was confirmed by mass spectrometry and ^1H NMR. H_2 evolution was detected at the end of the reaction by gas chromatography with a yield of roughly 85% of that expected on the basis of eq 1.

After 790 min of photolysis, a band ascribed to $HRe(CO)_5$ is also observed at 2009 cm^{-1}. The presence of this volatile hydride was also verified through separation from the mixture by trapping at a low temperature upon evacuation.

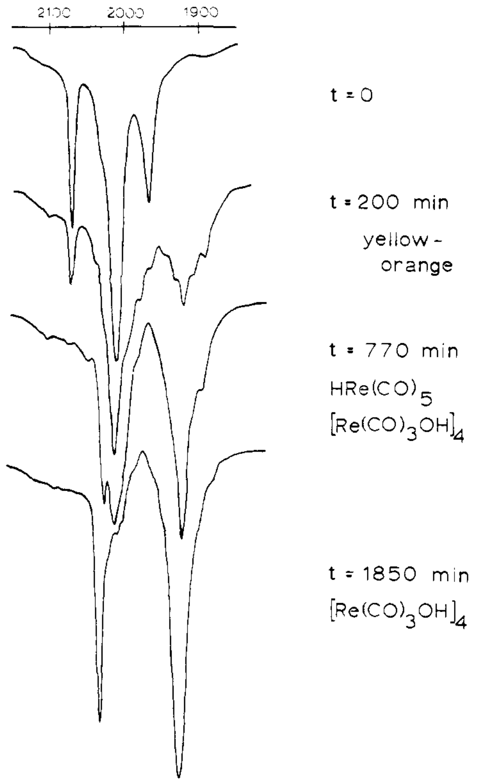

Figure 2. IR spectra of $Re_2(CO)_{10}$ in THF (2% H_2O) as a function of irradiation time with sunlamp irradiation.

During the early stages of the reaction (200 min), the recorded spectrum is quite complex and the solution takes on a yellow-orange color as opposed to the colorless appearance of the initial and final solutions. Aside from $Re_2(CO)_{10}$ (2070, 2009, and 1963 cm^{-1}), $HRe(CO)_5$ (2009 cm^{-1}), and the end product, $Re_4(CO)_{12}(OH)_4$ (2025 and 1918 cm^{-1}), most of these bands may be attributed to *eq*-$Re_2(CO)_9(OH_2)$. Weak bands at 1928 and 1889 cm^{-1} remain unaccounted for. Chromatography of the reaction solution at this stage of completion results in separation of $Re_2(CO)_{10}$, $Re_4(CO)_{12}(OH)_4$, $HRe_3(CO)_{14}$ (from decomposition of *eq*-$Re_2(CO)_9(OH_2)$, and a small yield (typically ≤2%) of an unstable red compound. The red color of this complex, typical of polynuclear metal carbonyl anions, arises from an absorption near 500 nm. The low R_f value (0.0 with 3/1 petroleum ether/THF; 0.5 with 3/1 acetone/benzene, both on silica) compared to that of the known neutral rhenium carbonyls is also characteristic of an ionic product. The red compound is fairly sensitive to O_2. Addition of salts containing large cations fails to appreciably stabilize it. Because the compound is unstable and formed in only small amounts, it was not isolated and completely characterized. The red color persisted toward the end of the photoreaction, disappearing only with prolonged photolysis. It is therefore formed by a side reaction and is not a consequential intermediate in the sequence of steps leading to the hydroxo complex.

^1H NMR spectra were also employed to follow the progress of sunlamp photolysis of 0.1 M $Re_2(CO)_{10}$ in THF-d_8 containing 3% H_2O by volume. (The solution was irradiated in an NMR tube attached to a bubbler by a needle and septum to prevent evolved gases from building up pressure.) The lower limit of detection of hydrido intermediates under these conditions is approximately 1–2% conversion to a hydride with a molecular weight in the range of 500–1500. An intense, featureless absorption occurs from τ 5 to 11 due to H_2O, proton-containing THF, and the sidebands associated with them. Identifications of the sources of new absorptions were made by comparisons with authentic samples. The first signal observed upon irradiation with the sunlamp is a singlet at τ 4.1, ascribed to *eq*-$Re_2(CO)_9(OH_2)$. However, as opposed to the results obtained with 313-nm light,

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the monoaqua complex is not the final product. Upon continued photolysis the growth of a second singlet at τ 3.0, ascribed to Re$_4$(CO)$_{12}$(OH)$_4$, directly follows the appearance of the τ 4.1 signal. After 170 min of irradiation, the intensity of the signal due to Re$_4$(CO)$_{12}$(OH)$_4$ is larger than that due to *eq*-Re$_2$(CO)$_9$(OH$_2$) and the first evidence of hydride formation is observed as a signal at τ 15.9, assigned to HRe(CO)$_5$. A weak peak at τ 18.3, ascribed to H$_2$Re$_2$(CO)$_8$, is also seen. Prolonged photolysis drives the reaction to completion.

These observations show that the reaction under sunlamp radiation is more complex than originally reported by Herberhold and Süss. The IR and ^{1}H NMR results indicate that the first-formed, and initially the only, intermediate is *eq*-Re$_2$(CO)$_9$(OH$_2$). The monoaqua complex is then converted under sunlamp photolysis primarily to HRe(CO)$_5$ and Re$_4$(CO)$_{12}$(OH)$_4$.

Upon alteration of the light intensity or the H$_2$O concentration, the formation of carbonyl hydrides other than HRe(CO)$_5$ may be observed. Decreasing the intensity of light produces little change in the IR spectrum from that in Figure 2. However, low concentrations of several polynuclear rhenium carbonyl hydrides may be detected in the sample monitored by ^{1}H NMR spectroscopy. These are formed from side reactions of the initially observed HRe(CO)$_5$, as the longer irradiation times necessary allow more of the evolved CO or H$_2$ to escape from the open system. When the light flux is decreased by about a factor of 10, signals at τ 15.7, 18.5, and 27.1 are seen at an intermediate state. These are due to HRe(CO)$_5$, H$_2$Re$_2$(CO)$_8$, and H$_3$Re$_3$(CO)$_{12}$, respectively. The latter hydride is the only complex reported as an intermediate by Herberhold and Süss. Also present is a singlet at τ 23.3, which remains unassigned but may possibly be due to the red ionic product.[32]

The intensity of the red color that develops during the course of the reaction in THF tends to increase with higher water concentrations in the solution. Conversely, with low H$_2$O concentrations (approximately 100 ppm or 6 × 10^{-3} M) and low light intensity, the only hydride observed was HRe$_3$(CO)$_{14}$ (τ 25.6).

All of the observations regarding rhenium carbonyl hydrides can be accounted for in terms of the known photochemistry of Re$_2$(CO)$_{10}$ in the presence of hydrogen[26] and the photochemical behaviors of the carbonyl hydrides themselves. Our concern is not so much with these reactions but with the processes that result in cleavage of the water molecule and formation of the initial metal carbonyl hydride and hydroxo compound. Accordingly, we have examined the photochemical reaction of the first-formed intermediate, *eq*-Re$_2$(CO)$_9$(OH$_2$).

Sunlamp Photolysis of *eq*-Re$_2$(CO)$_9$(OH$_2$). A 4 × 10^{-3} M solution of *eq*-Re$_2$(CO)$_9$(OH$_2$) was prepared by 313-nm photolysis of Re$_2$(CO)$_{10}$ in THF with 1% H$_2$O. After photolysis the solutions always contain unreacted Re$_2$(CO)$_{10}$ along with some HRe(CO)$_5$ and Re$_4$(CO)$_{12}$(OH)$_4$, as identified by IR spectra.

Irradiation of the *eq*-Re$_2$(CO)$_9$(OH$_2$) solution (which had been purged of CO) with the sunlamp for 30 min leads to changes in the IR spectrum as shown in Figure 3. HRe(CO)$_5$ (2010 cm^{-1}) and Re$_4$(CO)$_{12}$(OH)$_4$ (2027, 1920 cm^{-1}) are formed at the expense of *eq*-Re$_2$(CO)$_9$(OH$_2$) and Re$_2$(CO)$_{10}$ (2070, 2010 cm^{-1}). A small quantity of the red compound was also formed, as detected visually. The contributions of these compounds to the composite spectra were quantitatively determined by using the program PLTSUB. Under the high photon flux provided by the sunlamp, yields of HRe(CO)$_5$ and Re$_4$(CO)$_{12}$(OH)$_4$ as determined from the IR analysis are 4/1, respectively. That is, Re–H units and Re–OH units are formed in equal quantities. Essentially no H$_2$ is liberated at this stage of the reaction, as determined by gas chromatography.

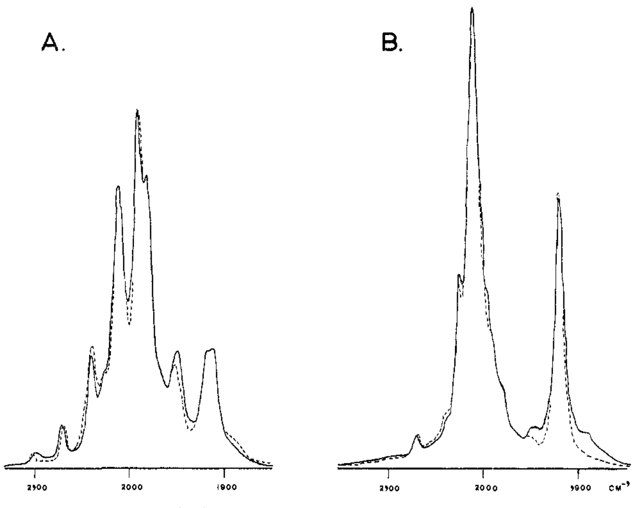
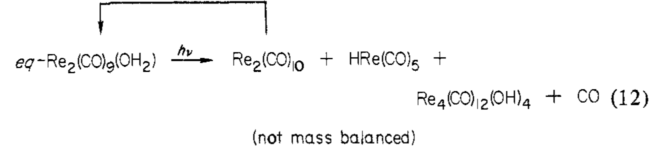


Figure 3. Actual (—) and computer-fitted (---) IR spectra of *eq*-Re$_2$(CO)$_9$(OH$_2$) in THF (1% H$_2$O) before and after 30-min irradiation with sunlamp radiation.

A similar reaction was carried out with the light intensity diminished by a factor of about 30. Under these conditions the concentration of Re$_2$(CO)$_{10}$ increases before it is consumed in the later stages of the reaction. The relative yields in the initial stage of the reaction from the low-intensity photolysis of *eq*-Re$_2$(CO)$_9$(OH$_2$) are Re$_2$(CO)$_{10}$, 62%, HRe(CO)$_5$, 8%, and Re$_4$(CO)$_{12}$(OH)$_4$, 30%, which correspond to mole ratios of about 4/1/1 based on rhenium.

The photolysis of *eq*-Re$_2$(CO)$_9$(OH$_2$) in wet THF therefore proceeds as in eq 12. Re$_2$(CO)$_{10}$, HRe(CO)$_5$, and Re$_4$(CO)$_{12}$(OH)$_4$ are produced, but Re$_2$(CO)$_{10}$ is itself photoreactive and regenerates *eq*-Re$_2$(CO)$_9$(OH$_2$) during the latter stages of the reaction when the absorbance by the monoaqua complex has diminished relative to that of Re$_2$(CO)$_{10}$.



(12)

(not mass balanced)

The quantum yield measurements on Re$_2$(CO)$_{10}$ substitution by H$_2$O at 313 nm indicate that metal–metal bond homolysis is the major primary photochemical process. The appearance of substantial amounts of Re$_2$(CO)$_{10}$ in the photolysis of *eq*-Re$_2$(CO)$_9$(OH$_2$) suggests that homolytic metal–metal bond cleavage is also occurring in this system. Cross coupling of the photogenerated radicals yields Re$_2$(CO)$_{10}$ and presumably also *dieq*-Re$_2$(CO)$_8$(OH$_2$)$_2$. The latter compound is not directly observed. The reactions suggested are summarized in eq 13–16. If the

$$eq\text{-Re}_2(\text{CO})_9(\text{OH}_2) \overset{h\nu}{\rightleftharpoons} \text{Re}(\text{CO})_5\cdot + \text{Re}(\text{CO})_4(\text{OH}_2)\cdot \quad (13)$$

$$2\text{Re}(\text{CO})_5\cdot \rightarrow \text{Re}_2(\text{CO})_{10} \quad (14)$$

$$2\text{Re}(\text{CO})_4(\text{OH}_2)\cdot \rightarrow dieq\text{-Re}_2(\text{CO})_8(\text{OH}_2)_2 \quad (15)$$

$$4dieq\text{-Re}_2(\text{CO})_8(\text{OH})_2 \rightarrow 4\text{HRe}(\text{CO})_5 + \text{Re}_4(\text{CO})_{12}(\text{OH})_4 \quad (16)$$

diaqua complex is indeed formed, it must react rapidly enough, either thermally or photochemically, to yield HRe(CO)$_5$ and Re$_4$(CO)$_{12}$(OH)$_4$ in 4/1 molar ratio, without accumulating sufficiently to be detected. The relative yield of Re$_2$(CO)$_{10}$ under low-intensity photolysis is higher than the maximum of 50% that may be expected from simple cross coupling of the photogenerated radicals. Substitution of Re(CO)$_4$(OH$_2$)· or *eq*-Re$_2$(CO)$_9$(OH$_2$) by CO (released following production of Re$_4$(CO)$_{12}$(OH)$_4$) increases the yield of Re$_2$(CO)$_{10}$. It is noteworthy also that with low-intensity irradiation the yield of the hydroxo product is much

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(32) The original report of the photochemical reaction of Re$_2$(CO)$_{10}$ with H$_2$O referred to Et$_2$O as solvent.[2] The course of this reaction under sunlamp irradiation as monitored by IR spectroscopy proceeds identically with that in THF. However, H$_3$Re$_3$(CO)$_{12}$, the hydride reported by Herberhold and Süss as an intermediate, was not precipitated or detected in solution by IR.

(33) In a following paper we present evidence for the involvement of Re(CO)$_3$L$_2$–Re(CO)$_4$ intermediates in the photochemical reactions of Re$_2$(CO)$_{10}$ with nitrogen bases. Similarly, an intermediate Re(CO)$_3$(OH$_2$)$_2$–Re(CO)$_4$ (II) could lead to III via oxidative addition of an O–H bond of coordinated OH$_2$, followed by replacement of the remaining coordinated water by CO.

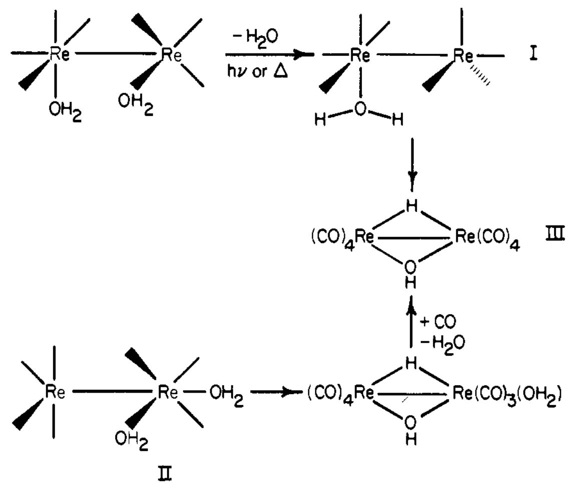


Figure 4. Suggested pathway for formation of a μ-hydrido, μ-hydroxo intermediate in the decomposition of $Re_2(CO)_8(OH_2)_2$.

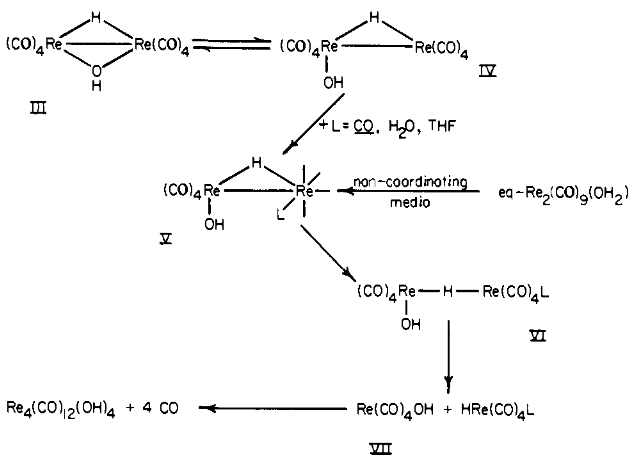


Figure 5. Suggested reaction scheme for formation of observed products from the proposed intermediate (μ-hydrido)(μ-hydroxo)dirhenium octacarbonyl (III).

higher than that of $HRe(CO)_5$. Under these conditions the hydride has apparently undergone further reaction.

The photochemical results indicate that *dieq*-$Re_2(CO)_8(OH_2)_2$ is a precursor to the formation of $HRe(CO)_5$ and $Re_4(CO)_{12}(OH)_4$. Thermal reaction pathways to the diaqua complex were explored to test this hypothesis. The reactions described below do not proceed through radical pathways; they were carried out at temperatures far below the 140 °C or so required to break the metal–metal bond in dinuclear rhenium carbonyl complexes.

The monosubstituted acetonitrile complex *eq*-$Re_2(CO)_9(CH_3CN)$ does not react with H_2O under reflux in THF at 66 °C for 20 h. In contrast, the CH_3CN ligands of *dieq*-$Re_2(CO)_8(CH_3CN)_2$ are easily and irreversibly displaced after only 3 h under the same conditions. The product is not, however, *dieq*-$Re_2(CO)_8(OH_2)$, but rather $Re_4(CO)_{12}(OH)_4$, formed in 37% yield, and *eq*-$Re_2(CO)_9(CH_3CN)$, formed in 10% yield. These are the only carbonyl-containing materials detected in the IR spectra, which leaves only about half the rhenium accounted for. The appearance of $Re_4(CO)_{12}(OH)_4$ indicates that it may be produced thermally from the expected intermediate, *dieq*-$Re_2(CO)_8(OH_2)_2$.

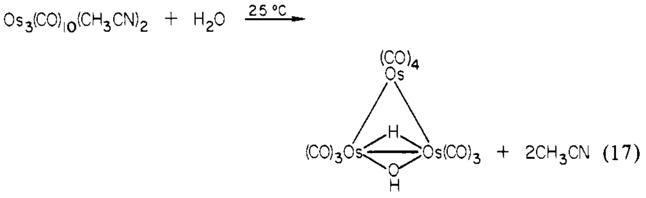
When it is treated with 2 equiv of $Me_3NO \cdot 2H_2O$ in wet THF (3% H_2O by volume), $Re_2(CO)_{10}$ readily undergoes substitution of one CO in 30 min at 25 °C. The resultant IR spectrum is that characteristic of *eq*-$Re_2(CO)_9L$. The solution probably contains a mixture of the aqua and trimethylamine complexes. Reaction with the second equivalent of Me_3NO requires heating to reflux at 66 °C for 20 h. A 32% yield of $Re_4(CO)_{12}(OH)_4$ was obtained. No rhenium carbonyl hydrides were observed in the IR spectrum. The fact that the diaqua complex was not observed in these experiments supports the contention that it is unstable at 66 °C. The results are consistent with the proposal that it is an intermediate in the sunlamp photolysis of *eq*-$Re_2(CO)_9(OH_2)$ or of $Re_2(CO)_{10}$ with H_2O.

Proposed Reaction Scheme. Our results suggest that in the photochemical reaction of $Re_2(CO)_{10}$ with H_2O *eq*-$Re_2(CO)_9(OH_2)$ and the unobserved *dieq*-$Re_2(CO)_8(OH_2)_2$ are formed via radical substitution and cross-coupling processes.

It is significant that $Os_3(CO)_{12}$ does not undergo a similarly facile photochemical substitution process. Irradiation of $Os_3(CO)_{12}$ in THF with 1% H_2O for a period of 1 week results in slight color change but no evidence of reaction in the IR spectra. The very low photochemical reactivity is related to the fact that homolytic cleavage of the metal–metal bond is highly reversible because the two radical fragments formed are constrained by bonding to the third Os to remain in close proximity. Thus, the quantum yields for photosubstitution and other photochemical reactions of $M_3(CO)_{12}$ (M = Fe, Ru, Os) are typically quite low,[34] <0.05, whereas those for reactions of dinuclear species are quite high, on the order of 0.3–0.9. These comparisons provide further evidence that metal–metal bond rupture rather than simply CO dissociation is the primary photochemical process in the reactions studied.

Because *eq*-$Re_2(CO)_9(OH_2)$ undergoes ready replacement of H_2O by nucleophiles at 25 °C (eq 2–5), dissociation of H_2O from *dieq*-$Re_2(CO)_8(OH_2)_2$ should also be facile. Loss of coordinated H_2O would leave the coordinatively unsaturated species $Re_2(CO)_8(OH_2)$ (I) (Figure 4). Formation of I may also occur photochemically through either a direct H_2O ejection from $Re_2(CO)_8(OH_2)_2$ or loss from $Re(CO)_4(OH_2)$ followed by recombination. Similarly, II, which would be formed by recombination of an $Re(CO)_3(OH_2)_2\cdot$ radical with a 15-electron $Re(CO)_4$ fragment, could undergo oxidative addition and replacement of a water molecule to yield III. ($Re_2(CO)_8(OH_2)$ could have either a CO-bridged or a nonbridged structure. The nonbridged version is depicted in Figure 4.)

The (μ-hydrido)(μ-hydroxo)triosmium complex $HOs_3(CO)_{10}(OH)$, analogous to III, is stable. It may be formed by reaction of $Os_3(CO)_{10}(CH_3CN)_2$ with water (eq 17).[35] The reaction probably proceeds through $Os_3(CO)_{10}(OH_2)_2$ and $Os_3(CO)_{10}(OH_2)$. However, III, unlike the thermally stable $HOs_3(CO)_{10}(OH)$, is not observed. Shown in Figure 5 is a reaction scheme that accounts for the fate of III.



Insertion of the bridging hydride ligand of V into the metal–metal bond to form a nearly linear M–H–M arrangement would weaken the Re–Re interaction (structure VI). Elimination of a hydride, $HRe(CO)_4L$, as a two-electron ligand (similar to the reverse of reaction 5) leaves $Re(CO)_4OH$ (VII), which leads through a series of aggregation and CO-loss steps to the stable final product. Again, in the photochemical reactions L = CO, and the hydride observed is $HRe(CO)_5$. In the thermal reactions expected to yield *dieq*-$Re_2(CO)_8(OH_2)_2$ under reflux conditions, most liberated CO is not available for coordination to IV and the eliminated hydride is $HRe(CO)_4L$ (L = H_2O, THF). This lightly stabilized hydride would be likely to decompose at 66 °C, which may explain why no hydride was observed under these reactions. Finally, in the case of *eq*-$Re_2(CO)_9(OH_2)$ in solvents more weakly coordinating than THF, $HRe(CO)_5$ quickly displaces the coordinated H_2O of the destabilized monoaqua complex to yield instead

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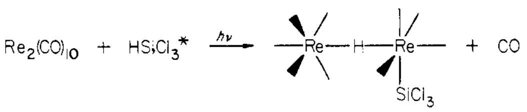
$HRe_3(CO)_{14}$ along with $Re_4(CO)_{12}(OH)_4$.

Though a similar progression of steps from IV to $HRe(CO)_4L$ and $Re_4(CO)_{12}(OH)_4$ has not been proposed in related systems, a few reactions are known that may model the individual reaction steps. A transformation similar to V → VI is found in the photochemical reaction of $Re_2(CO)_{10}$ with $HSiCl_{3-x}R_x$ (R = Me, Ph; $x = 0, 1$).[36] The structure of the product, $HRe_2(CO)_9SiCl_{3-x}R_x$, is as shown in eq 18; there is little direct bonding between the two



(18)

Re atoms. This structure is similar to several known polynuclear carbonyl hydrides, e.g., $HMnRe_2(CO)_{14}$ (∠Re-H-Re = 164°)[37] and $HCr_2(CO)_{10}^-$ (∠Cr-H-Cr = 180°).[38]

In a study of the substitution of $HM_2(CO)_{10}^-$ (M = Cr, Mo, W) by phosphorus ligands to yield $M(CO)_4L_2$, Darensbourg and co-workers suggested the initial steps outlined in eq 19.[39] Elimination of the 18-electron hydride from $L(CO)_4M\text{-}H\text{-}M(CO)_5^-$ is analogous to the transformation from VI to VII in the reaction proposed for the dirhenium–water system.

$$(CO)_5M\text{-}H\text{-}M(CO)_5^- \xrightarrow{-CO,\ +L} L(CO)_4M\text{-}H\text{-}M(CO)_5^- \rightarrow L(CO)_4M + HM(CO)_5^- \quad (19)$$

Elimination of a metal carbonyl hydride from $HOs_3(CO)_{10}(OH)$ by the mechanism proposed in Figure 5 is not likely; the bridging $Os(CO)_4$ group would keep the trinuclear framework intact. Other examples of relatively stable polynuclear (μ-hydrido)(μ-hydroxo)metal carbonyl compounds[40] substantiate this conclusion. Elimination of a metal carbonyl hydride is therefore a process particular to dinuclear compounds or, more generally, to ones containing terminally bound metal carbonyl fragments. In another paper we describe some reactions of disubstituted dirhenium carbonyl compounds involving nitrogen bases, in which reaction pathways of the sort described here are clearly evident.[41]

Registry No. $Re_2(CO)_{10}$, 14285-68-8; H_2O, 7732-18-5; THF, 109-99-9; *eq*-$Re_2(CO)_9(OH_2)$, 83214-31-7; $HRe(CO)_5$, 16457-30-0; $Re_4(CO)_{12}(OH)_4$, 56553-73-2; *eq*-$Re_2(CO)_9(CH_3CN)$, 67486-88-8; $Re(CO)_3(CH_3CN)_3^+BF_4^-$, 64012-16-4; $Re_2(CO)_8$(phen), 60166-20-3; *dieq*-$Re_2(CO)_8(CH_3CN)_2$, 83214-32-8; acetonitrile, 75-05-8; toluene, 108-88-3.

Supplementary Material Available: A derivation of the expression for the disappearance quantum yield, Φ_d, for $Re_2(CO)_{10}$ under photosubstitution conditions (3 pages). Ordering information is available on any current masthead page.

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Stereochemistry and Detailed Mechanism of the Conversion of ^{13}C-Labeled *cis*-Acetylbenzoyltetracarbonylrhenate(I) to *cis*-Acetylphenyltetracarbonylrhenate(I)

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Abstract: Decarbonylation of $N(CH_3)_4^+[cis\text{-}(CO)_4Re(COCH_3)(^{13}COC_6H_5)]^-$, **5B**, gives $N(CH_3)_4^+[fac\text{-}(CO)_3(^{13}CO)Re(COCH_3)(C_6H_5)]^-$, **6C**, stereospecifically at low conversion. Decarbonylation of $N(CH_3)_4^+[cis\text{-}(CO)_4Re(^{13}COCH_3)(COC_6H_5)]^-$, **5A**, gives mainly a 1:1 mixture of $N(CH_3)_4^+[(CO)_4Re(^{13}COCH_3)(C_6H_5)]^-$, **6A**, and $N(CH_3)_4^+[mer\text{-}(CO)_3(^{13}CO)Re(COCH_3)(C_6H_5)]^-$, **6-TA**, in which the ^{13}CO label is trans to the acetyl ligand. $N(CH_3)_4^+[fac\text{-}(CO)_3(^{13}CO)Re(COCH_3)(COC_6H_5)]^-$, **5C**, was prepared stereospecifically by reaction of $N(CH_3)_4^+[cis\text{-}(CO)_4Re(COC_6H_5)(CH_3)]^-$, **7**, with ^{13}CO. Decarbonylation of **5C** gives mainly $N(CH_3)_4^+[mer\text{-}(CO)_3(^{13}CO)Re(COCH_3)(C_6H_5)]$, **6-TP**, in which the ^{13}CO label is trans to the phenyl group. In addition to the stereospecific decarbonylation products obtained from **5A** and **5C**, some ^{13}CO scrambled products were also observed from **5A** (20% loss of stereochemistry) and from **5C** (52% loss of stereochemistry). At long reaction times, statistical scrambling of ^{13}CO in **6** was observed for materials obtained from decarbonylation of **5A–C**. These results are explained in terms of a mechanism involving the five-coordinate intermediate $[(CO)_3Re(COCH_3)(COC_6H_5)]^-$, **9**, which undergoes reversible methyl migration much more rapidly than it undergoes phenyl migration to give stable product **6**. Scrambling of ^{13}CO label in intermediate **9** occurs at a rate similar to the rate of phenyl migration of **9**, which gives **6**.

Introduction

The interconversions of acylmetal complexes and alkylmetal complexes are extremely common in organometallic chemistry[1] and are an essential step in many catalytic processes.[2] Several years ago in an effort to learn more about the detailed mechanism of this process, we synthesized *cis*-acetylbenzoyltetracarbonylmanganate(I) (**1**),[3] the first diacylmetal anion,[4] and attempted to determine the relative migratory aptitudes of phenyl and methyl

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