The Characteristics of $M(CO)_5$ and Related Metal Carbonyl Radicals; Abstraction and Dissociative and Oxidative Addition Processes[1]

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Abstract: Reaction of $HRe(CO)_5$ with L = $P(n\text{-}C_4H_9)_3$ or $P(C_6H_5)_3$ leads to $HRe(CO)_4L$ and $HRe(CO)_3L_2$. The reaction proceeds via a radial chain process, initiated by H atom abstraction from $HRe(CO)_5$. The reaction can be initiated by addition of $Re_2(CO)_{10}$, followed by irradiation at 310 nm, causing homolysis of the M–M bond. The reactions are inhibited by radical scavengers and by O_2. Reaction of $Re_2(CO)_{10}$ with H_2 under irradiation leads to $HRe_3(CO)_{14}$, $HRe(CO)_5$, $H_2Re_2(CO)_8$, and $H_3Re_3(CO)_{12}$, in amounts depending on conditions. Reaction of $Mn_2(CO)_{10}$ with H_2 under irradiation leads to $HMn(CO)_5$ as the major, identified product. These results, and the observation of a chain process for substitution, argue for facile substitution of CO in the 17-electron $M(CO)_5$ species, probably via a rapid dissociation of CO.

I. Introduction

In contrast to the present state of affairs in organic chemistry, the chemical properties of odd-electron transition metal organometallic species are not well known.[2] This is particularly true for transition metal carbonyl compounds; nearly all the well-characterized substances are spin-paired, diamagnetic compounds. $V(CO)_6$ affords a rare exception to the general rule;[3] in addition, some five-coordinate substituted carbonyl compounds of Re and Mn, e.g., $Re(CO)_3(PPh_3)_2$, appear to be fairly stable as radicals,[4-6] with 17 electrons in the valence orbitals of the metal.

By analogy with the chemistry of carbon compounds, one might expect that free radical carbonyl species could be generated by (a) homolysis of an M–C or M–M bond; (b) atom abstraction, as of H from $HRe(CO)_5$ or Cl from $ClMn(CO)_5$; (c) outer sphere electron transfer oxidation of an 18-electron metal carbonyl species, as in the oxidation of $Mn_2(CO)_{10}$ by tetracyanoethylene,[7] or in oxidation with NO^+;[8] (d) electrochemical oxidation or reduction of a stable 18-electron metal carbonyl compound, as in the oxidation of $Cr(CO)_6$[9a] or $C_5H_5Mn(CO)L_2$,[10] or in reduction of $M(CO)_6$ species.[9b] A fifth means of formation not common to carbon chemistry is synthesis via cocondensation of metal atoms and CO in an inert matrix at low temperatures.[11] Of the various means, the photochemical cleavage of metal–metal bonds has been the most widely studied.[12,13] On the basis of observed products in cross-coupling reactions,[14] the products of spin-trapping experiments[15] and on other grounds,[16,17] it has been quite well established that irradiation of metal–metal bonded metal carbonyls in the absorption band assigned to the σ–σ^* transition[18] causes homolysis with quantum yields in the range of 0.1 or higher.[16] Furthermore, it has been shown that the 17-electron species so generated recombine in an inert solvent medium with a rate constant near the diffusion-controlled limit.[17,19]

Our initial interest in the chemistry of transition metal carbonyl radicals derived from attempts to study the kinetics of substitution reactions of $HRe(CO)_5$ and $HMn(CO)_5$. These studies led to the interesting observation of a radical chain process for substitution at $HRe(CO)_5$,[20] and subsequently to observations regarding the characteristics of $Re(CO)_5$ radicals generated photochemically.[21] We report here in more detail on those experiments, and additional work undertaken to more fully characterize the 17-electron metal carbonyl species we have observed.

II. Experimental Section

Materials. Both $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were obtained from Pressure Chemical Co. and used without further purification. Triphenylphosphine, PPh_3, Aldrich Chemical Co. (99%), was recrystallized at least twice from methanol and stored in the inert atmosphere glove box. Tri-*n*-butylphosphine, PBu_3, Aldrich Chemical Co. (98%), was fractionally distilled under 40 mm of N_2, and stored in an amber bottle in the glove box. Triphenylarsine, $AsPh_3$, Aldrich Chemical Co. (97%), was used without further purification.

Since many reaction solutions were air sensitive, most sample preparations were carried out in a Vacuum Atmospheres glove box with an N_2 atmosphere purged as described previously.[22,23]

Tetrahydrofuran. Analytical reagent THF was obtained from Mallinckrodt Chemical Works. The solvent was purified by distillation under N_2 from $LiAlH_4$ and was stored over sodium wire in amber bottles to minimize peroxide formation. The THF was again distilled in the glove box prior to use. Even in dark bottles in the glove box, THF did not remain peroxide-free for more than a few days, as evidenced by a standard peroxide test employing NaI in glacial acetic acid.[24a]

Hexane. Using standard purification techniques,[24] spectral grade hexane was treated with concentrated sulfuric acid. The solvent was then washed repeatedly with deionized water, dried with anhydrous magnesium sulfate, and fractionally distilled. The main run was collected in clean, oven-baked amber bottles, deaerated by bubbling N_2 through the solution for about 0.5 h and stored over sodium wire in the glove box. Hexane was further purified by distillation in the glove box prior to use.

Hydridopentacarbonylmanganese(I), $HMn(CO)_5$. Starting with $Mn_2(CO)_{10}$, $HMn(CO)_5$ was prepared using a standard literature preparation.[25] The compound was stored at 5 °C, and distilled on a vacuum manifold before use. Traces of oxygen gradually decomposed some of the hydride to $Mn_2(CO)_{10}$, as evidenced by the appearance of a pale yellow color. To ensure high purity, the hydride was redistilled through P_4O_{10} at frequent intervals.

IR bands (hexane): 2117, 2043, 2014.5, 2007.5, 1981, 1966 cm^{-1}; lit.[26] (cyclohexane) 2116.7, 2042.0, 2014.5, 2006.7, 1981.8, 1965.4 cm^{-1}.

Hydridopentacarbonylrhenium(I), $HRe(CO)_5$. Using a procedure similar to that used for $HMn(CO)_5$,[25] except that $NaRe(CO)_5$ was washed with three 25-mL portions of cyclohexane[26] before being acidified, 2.9 g (50% yield) was synthesized. The hydride was stored in a manner similar to $HMn(CO)_5$. Introduction of air to hexane solutions of $HRe(CO)_5$ caused no detectable change in either the IR spectrum (after 60 days) or the NMR spectrum (after 0.5 h).

IR bands (hexane): 2131, 2122, 2042, 2016.5, 2007, 1984, 1966 cm^{-1}; lit.[26] (cyclohexane) 2131.1, 2123.1, 2053.2, 2042.5, 2014.5, 2005.3, 1982.3, 1966.9 cm^{-1}. NMR (hexane): singlet at τ 15.88; lit.[27] singlet at τ 15.66 (solvent not given). UV bands (hexane): 2725, 3000, 3125 Å; lit.[28] (cyclohexane) 1975, 2150, 2725, ~3020, ~3280 Å.

Table I. UV-Visible Filter Characteristics

λ_{max} (nm)	Type[a]	BWHH[b] (nm)	% T[c]
311	I	8.0	5
350	I	14.5	36
358	BP	78.0	61

[a] I = interference, BP = band-pass. [b] BWHH = bandwidth at half height. [c] % T = percent transmittance at λ_{max}.

***cis*-Hydridotetracarbonyltributylphosphinerhenium(I), $HRe(CO)_4PBu_3$, and *cis-mer*-Hydridotricarbonylbis(triphenylphosphine)rhenium(I), $HRe(CO)_3(PBu_3)_2$.** On adding dropwise 20 mL of benzene containing 0.2 g (1.0 mmol) of PBu_3 to 40 mL of benzene containing 0.2 g (0.6 mmol) of $HRe(CO)_5$ at ambient temperature, IR evidence indicated formation of both mono- and disubstituted species. An additional 0.2 g (1.0 mmol) of PBu_3 was added. After several hours, the benzene and excess PBu_3 were evaporated leaving a yellow viscous oil. No separation was attempted.

IR bands (hexane): 1910 (w), 1935 (vvw), 1954 (m), 1966 (s), 1985 (m-w), 2013.5 (vvw), 2074 (w) cm^{-1}. By comparison with the IR spectra of similar compounds, the peaks at 1954, 1966, and 2074 cm^{-1} were assigned to $HRe(CO)_4PBu_3$ and the absorption at 1910 cm^{-1} to $HRe(CO)_3(PBu_3)_2$. The NMR spectrum of the sample in hexane shows a doublet at τ 15.85 ascribed to $HRe(CO)_4PBu_3$ (J(P-H) = 24.3 Hz) and a triplet at τ 16.58 ascribed to $HRe(CO)_3(PBu_3)_2$ (J(P-H) = 20.0 Hz), in agreement with closely related work.[29]

Sample Preparation and Handling. Solutions of solid compounds were prepared by weighing samples into actinic volumetric flasks. Stock solutions of $HMn(CO)_5$ or $HRe(CO)_5$ were prepared by distilling on a vacuum manifold the neat liquids into small Pyrex flasks containing degassed purified solvent. After transfer to the inert atmosphere glove box, stock solutions were prepared and stored behind black plastic in the box.

The reaction vessel for photochemical reactions was usually a 25-mL cylindrical quartz flask. (On occasion an IR cell was filled within the box and used as the irradiation vessel. The IR spectrum of the sample in this case could be directly examined.) Exclusion of O_2 from the reaction vessel was very critical. The filled cells were maintained under a positive pressure of purified N_2 during photolysis. In the H_2 activation experiments, H_2 gas was bubbled through the solution for about 15 min prior to irradiation. During irradiation a slow flow of H_2 through the solutions was maintained. In all photochemical reactions syringe needles and barrels were carefully purged with N_2 before sample withdrawals.

Instrumentation. All infrared spectral measures were made on a Beckman IR-7 spectrophotometer, frequency-calibrated using water vapor.

Ultraviolet and visible radiation was provided by a Xenon 1000-W high pressure arc lamp (PEK 1000B). Filtering was accomplished by either narrow bandwidth interference (Corion Instrument Corporation) or wider bandwidth band-pass filters (Oriel Corporation). Their parameters, listed in Table I, were measured using a Cary Model 14 spectrophotometer.

Results and Discussion

Substitution of $HRe(CO)_5$ by PPh_3 and other Lewis bases has previously been detailed,[29-32] but no kinetics studies have been reported. We found that it was exceedingly difficult to obtain reproducible kinetics results. Under the most rigorous attainable conditions of solvent and reagent purity, with exclusion of light, the thermal reaction in hexane, under N_2, of 10^{-3} M $HRe(CO)_5$ with $\sim 10^{-2}$ M tributylphosphine, PBu_3, exhibited no reaction after 60 days at 25 °C. Thus $HRe(CO)_5$ is extraordinarily inert toward substitution via CO dissociation or hydride migration pathways. Exposure to light, failure to exhaustively purify the reagents, surface effects, and various other circumstances caused the reaction to go to completion at widely varying rates to yield $HRe(CO)_4L$ and $HRe(CO)_3L_2$. With PPh_3, $HRe(CO)_4L$ was formed at similarly erratic rates. The disubstituted species, $HRe(CO)_3(PPh_3)_2$, reported to be insoluble in hydrocarbons,[29] was not observed.

Similar results were obtained in THF as solvent, except that the reactions were generally faster. Stock solutions of $HRe(CO)_5$ and PBu_3 were prepared in the glove box using freshly purified THF. On combining aliquots of these stock solutions, a slow reaction occurred, yielding $HRe(CO)_4PBu_3$ and $HRe(CO)_3(PBu_3)_2$ as products. As the age of these stock solutions increased, the rate of substitution (in solutions freshly prepared from these aging stock solutions) similarly increased. From UV spectra and peroxide tests of neat THF, it was possible to show that the older stock solutions contained peroxides. Exposure to air or hydroquinone in low concentrations retarded these substitution reactions in THF. Similarly, reaction 1 was significantly retarded by hydroquinone and almost completely inhibited by air. Transition metal hydrides are known to react with haloalkanes via reactions similar to eq 1.[33,34]

$$HRe(CO)_5 + CCl_4 \xrightarrow{hexane} ClRe(CO)_5 + CHCl_3 \quad (1)$$

Recently, Booth and Shaw[25] proposed a mechanism for the reaction between $HMn(CO)_4PPh_3$ and haloalkanes at 20 °C:

$$R + HMn(CO)_4PPh_3 \rightarrow RH + Mn(CO)_4PPh_3 \quad (2)$$

$$CF_3I + Mn(CO)_4PPh_3 \rightarrow CF_3 + IMn(CO)_4PPh_3 \quad (3)$$

$$CF_3 + HMn(CO)_4PPh_3 \rightleftarrows CF_3H + Mn(CO)_4PPh_3 \quad (4)$$

where R is any radical initiator. A similar mechanism also obtains for the reaction between alkyltin hydrides and alkyl halides.[36-38] Since these hydrogen abstraction reactions are retarded by radical scavengers, it seems reasonable to suggest homolytic Re-H bond cleavage in the substitution reactions, which are also retarded by radical scavengers.

These considerations suggest a radical pathway involving adventitious radicals as initiators. The following mechanism accounts for the observations:

$$R + HRe(CO)_5 \rightarrow RH + Re(CO)_5 \quad (5)$$

$$Re(CO)_5 \rightleftarrows Re(CO)_4 + CO \quad (6)$$

$$Re(CO)_4 + L \rightleftarrows Re(CO)_4L \quad (7)$$

$$Re(CO)_4L \rightleftarrows Re(CO)_3L + CO \quad (8)$$

$$Re(CO)_3L + L \rightleftarrows Re(CO)_3L_2 \quad (9)$$

$$Re(CO)_4L + HRe(CO)_5 \rightarrow Re(CO)_5 + HRe(CO)_4L \quad (10)$$

$$Re(CO)_3L_2 + HRe(CO)_5 \rightarrow Re(CO)_5 + HRe(CO)_3L_2 \quad (11)$$

$$Re(CO)_3L_2 + HRe(CO)_4L \rightarrow Re(CO)_4L + HRe(CO)_3L_2 \quad (12)$$

$$Re(CO)_{5-n}L_n + Re(CO)_{5-m}L_m \rightarrow Re_2(CO)_{10-m-n}L_{n+m} \quad (13)$$

R is any radical initiator. Equations 10 through 12 are chain propagating steps, while step 13 terminates the process. Chain termination steps involving formation of $RRe(CO)_5$, $Re_2(CO)_9L$, and $Re_2(CO)_8L_2$ (but probably not $Re_2(CO(_6L_4R_7)$[5] are all possible.

Equations 6 through 9 suggest that the facile substitution of CO in the $Re(CO)_5$ radical occurs via CO dissociation. Unambiguous evidence that the process is dissociative (as opposed to an associative process in which CO is displaced by incoming L) is difficult to obtain. However, careful studies of the photochemical substitution of $Mn_2(CO)_{10}$ under a variety of conditions support the CO dissociative pathway.[39] Furthermore, reaction of $Re_2(CO)_{10}$ with H_2 under photolysis (vide infra) is best accounted for in terms of a rapid CO loss.

If the proposed mechanism for substitution is correct, addition of $Re(CO)_5$ radicals should greatly affect the rate of substitution. Such addition can be achieved through homolytic cleavage of the Re–Re bond in $Re_2(CO)_{10}$ via photolysis:[14,16,18]

$$Re_2(CO)_{10} \underset{k_{-1}}{\overset{h\nu}{\rightleftarrows}} 2Re(CO)_5 \qquad (14)$$

The following results support this hypothesis: a solution containing 10^{-3} M $HRe(CO)_5$ with 10^{-2} M PBu_3 in hexane was irradiated at 311 nm. There resulted a slow substitution to form initially $HRe(CO)_4Bu_3$. After 2 h the reaction was only about 10% complete. Continued irradiation yielded $HRe(CO)_3(PBu_3)_2$ in addition to $HRe(CO)_4PBu_3$. After 12 h of irradiation the reaction was only about 66% complete. Substitution in this system is presumably due to CO photodissociation from $HRe(CO)_5$ and later from $HRe(CO)_4PBu_3$.

A similar hexane solution containing 10^{-3} M $HRe(CO)_5$, $\sim10^{-2}$ M PBu_3, and 10^{-4} M $Re_2(CO)_{10}$ showed no evidence of reaction in the dark over a period of several hours. The reaction solution was then irradiated at 311 nm. Typically, the parent hydride disappeared very slowly during the first 6–10 min, during which time only $HRe(CO)_4PBu_3$ was formed as product. After this initial induction period, the reaction proceeded very rapidly under irradiation; reaction was essentially complete after about 6–8 min. Both $HRe(CO)_4L$ and $HRe(CO)_3L_2$ are formed concurrently, in roughly 3:1 ratio. During the time required for complete reaction only small decreases in the IR absorptions due to $Re_2(CO)_{10}$ are seen.

The results from a particular experiment are shown in Figure 1. The slow decrease in the low-frequency A_1 absorption of $HRe(CO)_5$ in the absence of added $Re_2(CO)_{10}$ represents reaction 15;

$$HRe(CO)_5 + PBu_3 \xrightarrow[\text{hexane}]{311\text{ nm}} HRe(CO)_4PBu_3 \qquad (15)$$

the more rapid loss in absorption due to $HRe(CO)_5$, and concurrent increases in absorptions due to $HRe(CO)_4PBu_3$ and $HRe(CO)_3(PBu_3)_2$, as shown, represents the process:

$$HRe(CO)_5 + PBu_3 + Re_2(CO)_{10} \xrightarrow[\text{hexane}]{311\text{ nm}} HRe(CO)_4PBu_3 + HRe(CO)_3(PBu_3)_2 \qquad (16)$$

The experiment shown is atypical only in that the induction period is longer than average.

It is obvious from the figure that in the interval between 7 and 20 min substitution occurs rapidly. This is consistent with the proposed chain process, in which steps 6 through 11 proceed very rapidly. Apparently formation of $Re(CO)_3L_2$ is slower than step 10. This accounts for the observation that the reaction does not proceed immediately to $HRe(CO)_3L_2$. The relatively slow formation of $HRe(CO)_3L_2$ following consumption of $HRe(CO)_5$ suggests that step 12 may also be slow. In this connection, it is noteworthy that $Re(CO)_3L_2$ is relatively stable; it has been isolated for L = PPh_3,[2] PMe_2Ph,[5] and $PMePh_2$.[5b]

If the light beam is blocked while the chain reaction is in progress, reaction immediately ceases. Renewed irradiation usually necessitates a new induction period before the process continues. Since the chain process is quenched rapidly on removal of irradiation, the termination steps, eq 13, or other radical removal processes must be rapid. In view of this rapid quenching, the proposed mechanism requires $Re(CO)_5$ to be labile toward substitution, since it apparently has a rather short lifetime in solution. Hughey and Meyer[19] have studied the processes in eq 17,

$$Mn_2(CO)_{10} \underset{k_{-1}}{\overset{h\nu}{\rightleftarrows}} 2Mn(CO)_5 \qquad (17)$$

and determined k_{-1} in cyclohexane at 20 °C to be 3.9×10^9 (±10%) $M^{-1}\ s^{-1}$. Presumably, the analogous recombination of $Re(CO)_5$ radicals is similarly rapid, consistent with rapid quenching on cessation of irradiation. The substitution lability of $Mn(CO)_5$ produced by irradiation of $Mn_2(CO)_{10}$ has been recently demonstrated;[14] it is reasonable to suppose that $Re(CO)_5$ is also substitution labile. This view is supported by experiments on the photosubstitution of $Re_2(CO)_{10}$. A 5×10^{-4} M solution of $Re_2(CO)_{10}$ with excess PBu_3 in hexane does not undergo substitution at room temperature over a period of several hours. Irradiation at 311 nm for a period of 150 min, however, results in about 15% loss of $Re_2(CO)_{10}$ and formation of several products.

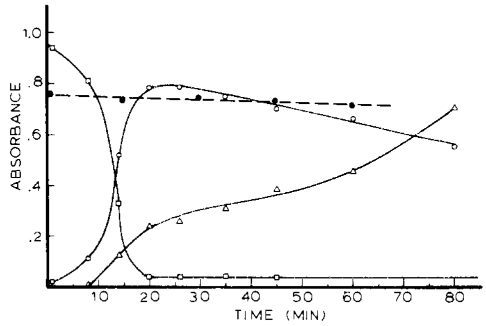

Figure 1. IR absorbances as a function of time, showing the effect of 1.4×10^{-4} M $Re_2(CO)_{10}$ on the reaction of 1×10^{-3} M $HRe(CO)_5$ with 2×10^{-2} M PBu_3 in hexane, under 311-nm irradiation. The closed circles indicate loss of $HRe(CO)_5$ (2006 cm^{-1}) in the absence of $Re_2(CO)_{10}$, while the squares show the loss of $HRe(CO)_5$(2006 cm^{-1}) in the presence of $Re_2(CO)_{10}$. Product formation for the latter reaction is also shown: open circles represent the absorbance due to $HRe(CO)_4PBu_3$ (1954 cm^{-1}) and the triangles $HRe(CO)_3(PBu_3)_2$ (1910 cm^{-1}).

Because of the complexity of the IR spectra, it was not possible to unequivocally assign all the product absorptions to specific products. However, by analogy with the spectra of other substitution products of $Re_2(CO)_{10}$[4,5,10] it appears that the major products include $Re_2(CO)_9PBu_3$, $Re_2(CO)_8(PBu_3)_2$, and $Re(CO)_3(PBu_3)_2$.

In all experiments carried out using the 311-nm filter the flux of photons is constant. The results thus indicate that the quantum yield for substitution of $HRe(CO)_5$ with photocatalysis by $Re_2(CO)_{10}$ is enormously higher than for photosubstitution of $Re_2(CO)_{10}$, consistent with the proposed chain mechanism.

Effect of PPh_3. After 1 min of irradiation of 10^{-3} M $HRe(CO)_5$, 10^{-2} M PPh_3, and 10^{-5} M $Re_2(CO)_{10}$ in hexane at 311 nm, the reaction to yield $HRe(CO)_4PPh_3$ as the sole product is 25–75% complete. Within 10 min of irradiation (and often much less) the reaction is complete. One minute of irradiation of a similar hexane solution containing no $Re_2(CO)_{10}$ produces <2% reaction, yet 20 min of irradiation at 311 nm produces complete reaction; again only $HRe(CO)_4PPh_3$ is formed. The interpretation of these results is complicated by intense absorption of 311-nm radiation by PPh_3. The ligand may in this case be acting to sensitize $Re_2(CO)_{10}$ dissociation. Alternatively, since reaction occurs on photolysis without $Re_2(CO)_{10}$ present, irradiation of PPh_3 may generate PPh_2 and Ph radicals[41] which could then abstract hydrogen from $HRe(CO)_5$ and initiate the chain process.

O_2 Inhibition. The induction period observed in reaction 16 is attributed to traces of radical chain inhibitors, notably O_2, present in low concentrations even in carefully purified systems. Support for this hypothesis is obtained by adding known amounts of air, using a gas-tight syringe, to reaction solutions before irradiation. The induction period is longer when air is added. On the basis of measurements of the rate of $Re_2(CO)_{10}$ dissociation under photolysis, the extensions of the induction period upon addition of air are consistent with formation of a 1:1 $Re(CO)_5$–O_2 adduct.

Inhibition of the reaction by dissolved O_2 is consistent with the proposed mechanism. Formation of O_2 complexes of carbonyl radicals has been demonstrated in ESR experiments with $Co(CO)_4$ and $Mn(CO)_5$.[42] In $Re(CO)_5O_2$ the unpaired spin could be localized on O_2, so that the metal possesses a coordinatively saturated (i.e., 18-electron) configuration. The metal is thus probably not substitutionally labile, nor capable of hydrogen abstraction from $HRe(CO)_5$.

Further evidence for the involvement of $Re(CO)_5$ in the induction period is obtained by lowering the concentration of $Re(CO)_5$, by using lower concentrations of $Re_2(CO)_{10}$. Using $\sim 10^{-5}$ M $Re_2(CO)_{10}$, induction periods of 30–45 min are observed.

Photochemical Reaction of $M_2(CO)_{10}$ with H_2. The fate of $Re(CO)_5$ radicals produced by hydrogen atom abstraction from $HRe(CO)_5$ or by homolysis of $Re_2(CO)_{10}$ is of importance in the reaction scheme outlined in eq 5–13. By one means or another $Re(CO)_5$ undergoes rapid substitution by L to form $Re(CO)_4L$, which may in turn undergo still further substitution. The equilibrium

$$H_2 + N_2Co(PPh_3)_3 \rightleftharpoons N_2 + H_2Co(PPh_3)_3 \qquad (18)$$

which involves two 17-electron systems, has been reported.[43] While there is no evidence regarding the possible intermediacy of a 15-electron species, this seems a likely possibility. It is possible that the substitution lability of $M(CO)_5$ radicals is due to a rapid first-order dissociation of CO to yield $M(CO)_4$, as in eq 6. With this as a working hypothesis, we investigated the photochemical reaction of $Re_2(CO)_{10}$ with H_2.

It has been shown that photochemical generation of a coordinatively unsaturated, 16-electron transition metal carbonyl species can result in activation of molecular hydrogen.[44,45] It is reasonable to suppose that oxidative addition to the metal occurs. Reaction of a 17-electron transition metal species with H_2 is exemplified by the much studied $Co(CN)_5^{3-}$ system.[46,47] The intimate mechanism of the step in which H_2 undergoes reaction is not clear. Oxidative addition to $Co(CN)_5^{3-}$ would result in a seven-coordinate species with 19 electrons about cobalt. Prior dissociation of CN^- would result in a species with 15 electrons, which might then undergo the reaction with H_2, but the lack of dependence on CN^- concentration in the reaction of $Co(CN)_5^{3-}$ with H_2[48] argues against this. Oxidative addition to the 16-electron, Co(I) species, $Co(CN)_4^{3-}$, formed from disproportionation, has been suggested.[49] However, the most compelling evidence relating to this system[48] suggests that there is either reaction of $Co_2(CN)_{10}^{6-}$ with H_2, or a termolecular process involving successive steps,

$$Co(CN)_5^{3-} + H_2 \rightleftharpoons Co(CN)_5H_2^{3-} \qquad (19)$$

$$Co(CN)_5H_2^{3-} + Co(CN_5)^{3-} \rightarrow 2Co(CN)_5H^{3-} \qquad (20)$$

in analogy to the H_2–I_2 gas phase reaction.[50]

When $Re_2(CO)_{10}$ is irradiated at 311 nm, using a narrow band-pass, low transmittance interference filter, in the presence of H_2 (1 atm) in hexane solution, slow formation of $HRe_3(CO)_{14}$ results. This compound is easily identified by its IR spectrum in the carbonyl region.[51] No other product is formed in substantial amount. When the narrow band-pass 311-nm filter is replaced by a wider band-pass, high transmittance filter with λ_{max} 358 nm, irradiation of $Re_2(CO)_{10}$ in the presence of H_2 yields $H_2Re_2(CO)_8$ and $HRe(CO)_5$ identified by their IR spectra.[26,52] Initially, small amounts of $HRe_3(CO)_{14}$ are also observed. Less than 80 min of irradiation served to completely remove $Re_2(CO)_{10}$, as indicated by the absorbance at 2069 cm^{-1}. Continued irradiation over several hours caused decomposition of $HRe(CO)_5$ and to a lesser extent of $H_2Re_2(CO)_8$, with formation of a light brown CO-containing solid of unknown composition. Representative spectroscopic changes are shown in Figure 2 for a reaction involving use of a cutoff filter consisting only of 4.5-mm Pyrex glass. After 10 min of irradiation of $Re_2(CO)_{10}$ in the presence of H_2, absorbances attributed to $HRe_3(CO)_{14}$ and $H_2Re_2(CO)_8$ are observed. Peaks corresponding to $HRe(CO)_5$ are hidden under remaining $Re_2(CO)_{10}$ peaks. After 40 min of irradiation with Pyrex filtering, absorbances due to $H_2Re_2(CO)_8$ and $HRe(CO)_5$ are dominant, while those due to $HRe_3(CO)_{14}$ are substantially reduced. The appearance of $H_3Re_e(CO)_{12}$[53] is observed by the growth of a shoulder at 2030 cm^{-1}. Other peaks attributed to $H_3Re_3(CO)_{12}$, at 2093 and 2008 cm^{-1}, overlap with absorbances due to $H_2Re_2(CO)_8$ and $HRe(CO)_5$, respectively.

These results suggest that the processes occurring under photolysis are as follows:

$$Re_2(CO)_{10} \underset{k_{-1}}{\overset{h\nu}{\rightleftharpoons}} 2Re(CO)_5 \qquad (21)$$

$$Re(CO)_5 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Re(CO)_4 + CO \qquad (22)$$

$$Re(CO)_4 + H_2 \rightarrow H_2Re(CO)_4 \qquad (23)$$

$$H_2Re(CO)_4 + Re(CO)_5 \rightarrow HRe(CO)_5 + HRe(CO)_4 \qquad (24)$$

$$HRe(CO)_4 + Re(CO)_5 \rightleftharpoons HRe_2(CO)_9 \qquad (25)$$

$$HRe(CO)_5 + Re(CO)_4 \rightarrow HRe_2(CO)_9 \qquad (26)$$

$$HRe_2(CO)_9 + Re(CO)_5 \rightarrow HRe_3(CO)_{14} \qquad (27)$$

$$HRe(CO)_4 + HRe(CO)_4 \rightarrow H_2Re_2(CO)_8 \qquad (28)$$

$$H_2Re_2(CO)_8 + HRe(CO)_4 \rightarrow H_3Re_3(CO)_{12} \qquad (29)$$

An important element in this scheme is oxidative addition to $Re(CO)_4$, a 15-electron intermediate species. The product of oxidative addition, $H_2Re(CO)_4$, should be subject to facile hydrogen abstraction by $Re(CO)_5$ as indicated in eq 24. Postulating $HRe(CO)_4$ as an intermediate provides a reasonable explanation for the appearance of $H_2Re_2(CO)_8$ when the photon flux is high. Under these conditions, the steady state concentration of $HRe(CO)_4$ could increase to the point where simple dimerization dominates as a reaction pathway. However, the rates of other, competing pathways for reaction of $HRe(CO)_4$, e.g., eq 25, should also be increased. The higher yield of $H_2Re_2(CO)_8$ may be due to secondary photolysis of initial reaction products. Reaction of $H_2Re_2(CO)_8$ with still another $HRe(CO)_4$ leads to $H_3Re_3(CO)_{12}$, observed as a minor product. $H_3Re_3(CO)_{12}$ is, however, also known to be produced by thermal decomposition of $HRe_3(CO)_{14}$:[51]

$$3HRe_3(CO)_{14} \xrightarrow[C_6H_{12}]{\Delta} H_3Re_3(CO)_{12} + 3Re_2(CO)_{10} \qquad (30)$$

One alternative to the proposed scheme is photodissociation of CO from $Re_2(CO)_{10}$, leading to oxidative addition and subsequent reductive elimination of $HRe(CO)_5$:

$$Re_2(CO)_{10} + h\nu \rightarrow Re_2(CO)_9 + CO \qquad (31)$$

$$Re_2(CO)_9 + H_2 \rightarrow H_2Re_2(CO)_9 \qquad (32)$$

$$H_2Re_2(CO)_9 \rightarrow HRe(CO)_5 + HRe(CO)_4 \qquad (33)$$

The remaining steps, eq 25 through 29, are the same. This pathway is similar to that suggested for activation of H_2 by

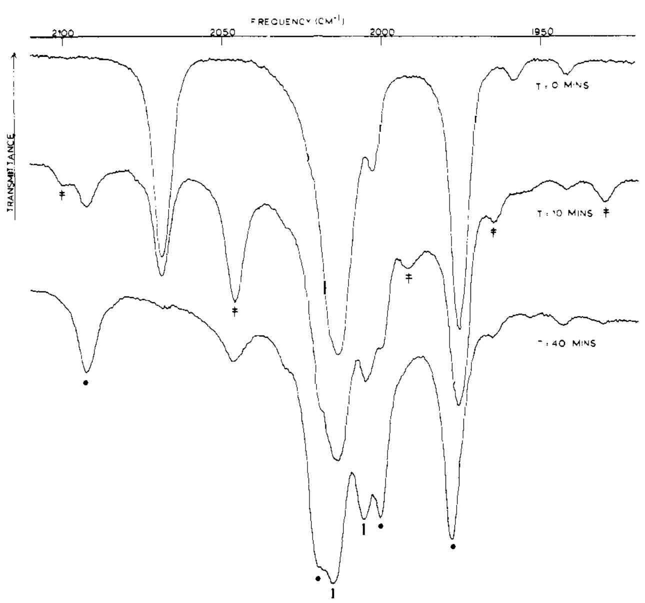

Figure 2. Infrared spectral changes as a function of time of irradiation using a cutoff filter consisting only of 4.5-mm Pyrex glass, for the reaction of 10^{-3} M $Re_2(CO)_{10}$ with H_2 gas (1 atm) in hexane at ambient temperature. Absorbances labeled ‡ are assigned to $HRe_3(CO)_{14}$; * to $H_2Re_2(CO)_8$, and † to $HRe(CO)_5$.

$Co_2(CO)_8$ in the oxo process, in which $HCo(CO)_4$ is formed;[54,55] $Mn_2(CO)_{10}$ was proposed[56] to activate H_2 in a similar manner. Indeed, a synthesis for $HMn(CO)_5$[57] involves the interaction of H_2 with $Mn_2(CO)_{10}$ according to eq 34.

$$Mn_2(CO)_{10} + H_2 \xrightarrow[CO]{200\ °C,\ 250\ atm} 2HMn(CO)_5 \quad (34)$$

In a similar thermal reaction between $Re_2(CO)_{10}$ and H_2, the products observed[58] are $H_3Re_3(CO)_{12}$ and $H_4Re_4(CO)_{12}$. The possible formation of $HRe(CO)_5$ or other species was not discussed. At the elevated temperatures employed, 150–170 °C, $HRe(CO)_5$ is not very stable and may, therefore, only be an intermediate in the formation of the polynuclear species.

These thermal reactions may occur via metal-metal bond homolysis, or alternatively via CO dissociation. In any case, photodissociation of CO from $Re_2(CO)_{10}$ does not seem to account for the photochemical reaction with H_2. It is unlikely that significant dissociation of CO occurs as a result of irradiation at 358 nm. In a similar case, $Mn_2(CO)_8(PPh_3)_2$ is a primary photoproduct of irradiation of $Mn_2(CO)_{10} + PPh_3$,[14] consistent with a pathway involving Mn–Mn bond rupture.

It is perhaps worth noting that reaction of $Re(CO)_5$ with H_2 along the lines suggested by Halpern and Pribanic[48] for reaction of $Co(CN)_5{}^{3-}$,

$$Re(CO)_5 + H_2 \rightleftarrows Re(CO)_5H_2 \quad (35)$$

$$Re(CO)_5H_2 + Re(CO)_5 \rightarrow 2Re(CO)_5H \quad (36)$$

would not yield the observed array of products; $HRe(CO)_5$ does not undergo photodissociation of CO under 350-nm radiation at a rate sufficient to account for the abundance of $HRe_3(CO)_{14}$ or $H_2Re_2(CO)_8$ seen upon irradiation at this wavelength.

In an attempt to further test the proposed mechanism for activation of molecular H_2, a hexane solution containing $\sim 10^{-3}$ M $Re_2(CO)_{10}$ and $\sim 10^{-3}$ M $HRe(CO)_5$ was irradiated with 311-nm radiation for 2.5 h; $HRe_3(CO)_{14}$ was observed. Additional irradiation through a 350-nm filter produced more $HRe_3(CO)_{14}$. After removal of the filters (quartz flask employed) $H_2Re_2(CO)_8$ and a carbonyl-containing solid formed on further irradiation, accompanied by loss of $HRe_3(CO)_{14}$. After remaining in the dark for 20 h, the solution contained some $H_3Re_3(CO)_{12}$ and considerably less $HRe_3(CO)_{14}$. Since $HRe_3(CO)_{14}$ is reported to be thermally unstable, decomposing according to eq 30,[51] the formation of $H_3Re_3(CO)_{12}$ is most likely due to this decomposition. These observations are consistent with the proposed mechanism, in particular eq 26 and 27. Hydridopentacarbonylrhenium oxidatively adds to $Re(CO)_4$ producing $(CO)_5Re{-}Re(CO)_4H$ which can then either homolytically cleave, producing $HRe(CO)_4$ and $Re(CO)_5$, or interact with another molecule of $Re(CO)_5$ producing $HRe_3(CO)_{14}$.

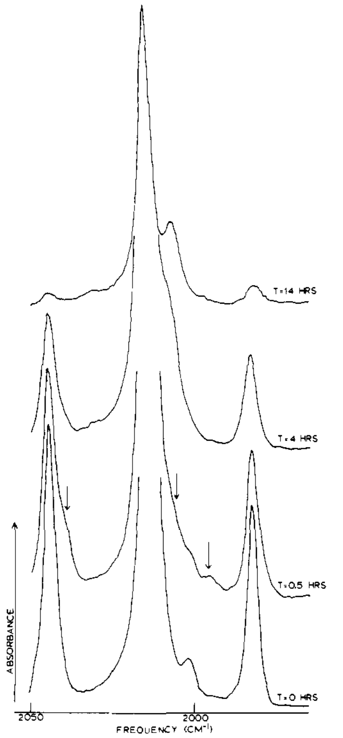

Figure 3. Infrared spectral changes as a function of time of 358-nm irradiation of a hexane solution containing 5.87 × 10^{-4} M $Mn_2(CO)_{10}$ saturated with H_2 (1 atm) at ambient temperature. Arrows indicate the first new absorbances observed (1996, ~2006, and 2040 cm^{-1}) after 0.5 h of protolysis. Irradiation for 14 h converted most of the $Mn_2(CO)_{10}$ to $HMn(CO)_5$, as indicated by the absorbances at 1983, 2007, and 2014.5 cm^{-1}.

Another possible example of oxidative addition of $HRe(CO)_5$ to a coordinatively unsaturated species is found in the reaction

$$HRe(CO)_5 + H_2Os_3(CO)_{12} \rightarrow (OC)_5ReOs(CO)_4H \quad (37)$$

which is proposed to involve insertion of $Os(CO)_4$ into the Re–H bond.[59]

To determine whether $Mn_2(CO)_{10}$ is capable of photochemical reaction with H_2, a hexane solution containing 5.87 × 10^{-4} M $Mn_2(CO)_{10}$, saturated with H_2 at 25 °C, was irradiated with 358-nm light. After 0.5 h, IR absorbances at 1996, 2006, and 2040 cm^{-1} were observed, as shown in Figure 3. Continued irradiation produced an increase in the 2006-cm^{-1} absorbance, ascribed to $HMn(CO)_5$, while the other two peaks disappeared. After 14 h of irradiation, essentially all the $Mn_2(CO)_{10}$ was converted to $HMn(CO)_5$ (IR absorbances at 1983 (w), 2007 (m), 2014.5 (vvs)) and a small amount of yellow precipitate. The IR spectrum of this unidentified solid in $CHCl_3$ showed only two peaks, at 1900 and 2010 cm^{-1}. The species $H_2Mn_2(CO)_8$ and $HMn_3(CO)_{14}$ are as yet unreported. It is possible that they are formed in the course of the photochemical reaction of $Mn_2(CO)_{10}$ with H_2, and then subsequently decompose. Photochemical reaction at low temperature might provide an avenue to these systems.

It is noteworthy that the photochemical reaction of $Mn_2(CO)_{10}$ with H_2 is much slower than for $Re_2(CO)_{10}$, even though the rates of M–M bond rupture are comparable. Studies of the quantum yield for photosubstitution of $Mn_2(CO)_{10}$[14,39] suggest that dissociative loss of CO from $Mn(CO)_5$ is facile. We ascribe the slower reaction with H_2 to a less favorable oxidative addition equilibrium, eq 38. This is to be expected, since the Mn–H bond is undoubtedly weaker than the Re–H bond.[61]

$$Mn(CO)_4 + H_2 \rightleftarrows Mn(CO)_4H_2 \qquad (38)$$

Graham and co-workers have reported several interesting compounds related to $HRe_3(CO)_{14}$ resulting from photolysis of $Re_2(CO)_{10}$ in the presence of R_3SiH compounds.[64] It seems reasonable to suggest that these compounds are probably also formed via reactions analogous to those detailed above. More recently, photolysis of $Re_2(CO)_{10}$ in aqueous ether has been found to result in formation of $H_3Re_3(CO)_{12}$ and $Re_4(CO)_{12}(OH)_4$.[65] This reaction may proceed via formation of $Re(CO)_5$, then $Re(CO)_4$, followed by oxidative addition of water.

In summary, the results reported in this paper demonstrate the existence of a radical chain pathway for substitution in a metal carbonyl compound. Similar radical chain processes should be observable in other hydridocarbonyl compounds, in carbonyl halides and other systems in which radical abstraction of a metal-bonded atom or group is possible.

Studies have also been carried out on the substitution of $HMn(CO)_5$ by PBu_3 and other ligands. These are reported on in detail elsewhere,[66] but we note here that there is evidence in these reactions also for a radical chain pathway. However, the reactions with $HMn(CO)_5$ are more rapid than for $HRe(CO)_5$; even under conditions which minimize the contribution from a radical chain path, reaction is readily observed. Substitution occurs, we believe, via a hydride migration pathway.

We have also shown in the present work that the 17-electron species formed by either radical abstraction or metal–metal bond homolysis are very labile toward substitution, and that they are apparently capable also of oxidative addition reactions. An oxidative addition process may in fact be operative in the photochemical reactions of $M_2(CO)_{10}$ and $MM'(CO)_{10}$ compounds with alkyl halides, CCl_4 or I_2.[14]

Photolyses of metal–metal bonded carbonyl compounds in the presence of H_2 have obvious synthetic possibilities. For example, the synthesis of $H_2Re_2(CO)_8$ by this method[67] is simpler than the reported synthesis via $Ph_2SiH_2Re_2(CO)_8$.[52] Since 17-electron radical intermediates generated photochemically appear to be very labile and their dissociation products reactive, it might be expected that these species should serve as catalysts for a variety of interesting reactions.

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References and Notes

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