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Photochemistry of Nitrogen Ligand Substituted Dinuclear Rhenium Carbonyl Compounds[1]

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The reactions of *eq*-$Re_2(CO)_9$ L (L = CH_3CN, pyridine, CH_3NH_2, or $C_2H_5NH_2$) and of 1,2-*eq*,*eq*-$Re_2(CO)_8L_2$ (L = CH_3CN, pyridine (py)) have been examined under sunlamp irradiation. 1,2-*eq*,*eq*-$Re_2(CO)_8(CH_3CN)_2$ is observed as the primary photoproduct under continuous photolysis of $Re_2(CO)_9(CH_3CN)$. $Re_4(CO)_{12}(OH)_4$ is formed from a side photochemical reaction of the CH_3CN compounds with residual H_2O in the THF or heptane solvent. The initial rhenium-containing products of the photochemical reaction of *eq*-$Re_2(CO)_9$(pyridine) or of 1,2-*eq*,*eq*-$Re_2(CO)_8$(pyridine)$_2$ under continuous photolysis in THF are $Re_2(CO)_{10}$, $Re(CO)_3(py)_3^+$, $HRe_4(CO)_{16}^-$, and 1,1-(μ-H)$Re_2(CO)_7(py)(NC_5H_4)$ (formed in similar yields with either starting compound). Flash irradiation of *eq*-$Re_2(CO)_9(py)$ in THF allows detection of the intermediate 1,2-*eq*,*eq*-$Re_2(CO)_8(py)_2$·(μ-H)$Re_2(Co)_8(NC_5H_4)$ can be prepared in a thermal reaction from 1,2-*eq*,*eq*-$Re_2(CO)_8(py)_2$. It reacts slowly with pyridine to yield 1,1-(μ-H)$Re_2(CO)_7(py)(NC_5H_4)$. Photolysis of *eq*-$Re_2(CO)_9(RNH_2)$ (R = CH_3, C_2H_5) in heptane yields $Re_2(CO)_{10}$ and a precipitate of 1,1-$Re_2(CO)_8(RNH_2)_2$. Mechanisms are proposed for the photochemical reactions of the nitrogen-base compounds. The primary photoprocess in all cases is homolytic cleavage of the Re-Re bond. Loss of CO or L from the $Re(CO)_4L\cdot$ radicals allows formation of $Re(CO)_5\cdot$ and $Re(CO)_3L_2\cdot$ species. The rate of dissociation of L from photogenerated $Re(CO)_4L\cdot$ appears to be comparable to that of CO. Analogies to the photochemical reaction of $Re_2(CO)_{10}$ with H_2O are noted.

Introduction

A study of the photochemical reactions of nitrogen base substituted dinuclear carbonyl compounds *eq*-$Re_2(CO)_9L$ and *eq*,*eq*-$Re_2(CO)_8L_2$, where L represents a nitrogen base such as pyridine (py), was initiated in the likelihood that their behavior might parallel that of *eq*-$Re_2(CO)_9(OH_2)$ and *eq*,*eq*-$Re_2(CO)_8(OH_2)_2$, proposed as intermediates in the photochemical reaction of $Re_2(CO)_{10}$ with H_2O.[2] Nitrogen bases, like H_2O, bond to the metal center principally through a σ-donor interaction. Because nitrogen ligands are generally stronger donors than H_2O or other oxygen-derived bases, nitrogen base substituted compounds are commonly more robust. Photochemical reactions of *eq*-$Re_2(CO)_9L$ and 1,2-*eq*,*eq*-$Re_2(CO)_8L_2$[3] may therefore be expected to yield stable, characterizable products which are analogs of intermediates postulated in the photochemical reaction of $Re_2(CO)_{10}$ with H_2O.

The photochemical behavior of dinuclear metal carbonyl compounds substituted by nitrogen bases has been little studied. Although some similarities to the behavior of phosphorus-substituted analogues are expected,[4-6] nitrogen and oxygen base substituted compounds frequently give rise to different products. As shown in the results described below, we have found that to be the case in the present study.

Experimental Section

Much of the experimental detail has been described elsewhere.[2]

Reagents. Methylamine, CH_3NH_2 (40% in H_2O), and ethylamine, $C_2H_5NH_2$ (anhydrous), were purchased from Eastman Chemicals and used without further purification. Pyridine, C_5H_5N(py), and acetonitrile, CH_3CN, both Mallinckrodt AR, were dried over 3A molecular sieves. Pyridine-d_5 (Merck and Co., >99%D) was used directly.

Preparation of Compounds. *eq*-Dirhenium nonacarbonyl acetonitrile, *eq*-$Re_2(CO)_9(CH_3CN)$, was prepared following a preparation by Koelle.[7]

The preparation of *eq*,*eq*-dirhenium octacarbonyl bis(acetonitrile), *eq*,*eq*-$Re_2(CO)_8(CH_3CN)_2$ is described in a previous paper.[2]

***eq*-Dirhenium nonacarbonyl pyridine, *eq*-$Re_2(CO)_9(py)$,** was prepared by using the method of Koelle:[7] IR ν_{CO} (CH_2Cl_2): 2101 (w), 2040 (m), 1986 (s), 1957 (w-m), 1921 (m) cm^{-1} (lit.[7] (hexane) 2099 (1.4), 2039 (3.6), 2011 (3.3), 1985, 1982 (10), 1972 (sh), 1960 (3.9), 1946 (1.6), 1933 (5.9) cm^{-1}); UV-vis (THF) 291 (ϵ 10 000), 312 (10 500), 337 (13 600).

1,2-*eq*,*eq*-Dirhenium octacarbonyl bis(pyridine), *eq*,*eq*-$Re_2(CO)_8(py)_2$, and 1,2-*eq*,*eq*-dirhenium octacarbonyl bis(perdeuteriopyridine), *eq*,*eq*-$Re_2(CO)_8(py\text{-}d_5)_2$, were prepared following a synthesis by Koelle:[7] IR ν_{CO} (CH_2Cl_2) 2061 (w), 2005 (m), 1955 (s), 1922 (vw), 1907 (m) cm^{-1}; UV-vis (THF) 288 (ϵ 11 000), 355 (13 800), 430 nm (4900, sh); field desorption mass spectrum (FDMS), parent ions at *m*/*e* (relative intensity) 752 (31), 754 (100), 756 (94) for the bis(pyridine) complex. No daughter ions observed.

Satisfactory elemental analyses (C, H, N) were obtained for all of the compounds mentioned above.

***eq*-Dirhenium nonacarbonyl methylamine, *eq*-$Re_2(CO)_9(CH_3NH_2)$,** was prepared by adding $Re_2(CO)_{10}$ (352 mg, 0.54 mmol) to 15 mL of THF and 6 mL of 40% CH_3NH_2 in H_2O. A 60-mg sample of $(CH_3)_3NO\cdot 2H_2O$ (0.54 mmol) was then added, the flask stoppered, and the mixture warmed to 50 °C while being stirred for 12 h. The solvent was removed under vacuum, and the solids were chromatographed on silica with hexane/CH_2Cl_2: yield 150 mg (0.23 mmol), 42%; IR ν_{CO} (CH_2Cl_2) 2100 (w), 2038 (m), 1983 (s), 1951 (w-m), 1913 cm^{-1}; UV-vis (THF) 310 (ϵ 9700), 334 (11 400), 380 nm (2300, sh), (cyclohexane) 308, 383 nm; ^1H NMR (acetone-d_6) τ 3.67, (br, 0.61, (NH_2), 2.70 (t, *J* = 6 Hz, 1.00, CH_3); FDMS, parent ions at *m*/*e* (relative intensity) 653 (41), 655 (100), 657 (87). $Re_2(CO)_9^+$ daughter ions present. Anal. Calcd for $Re_2(CO)_9(CH_3NH_2)$ (655.6): C, 18.32; H, 0.77; N, 2.14; O, 21.97; Re, 56.81. Found: C, 18.53; H, 0.75, N, 2.15.

***eq*-Dirhenium nonacarbonyl ethylamine, *eq*-$Re_2(CO)_9(C_2H_5NH_2)$,** was prepared by dissolving $Re_2(CO)_{10}$ (1.041 g, 1.60 mmol) in 30 mL of THF. A 3-mL sample of ($C_2H_5NH_2$ was then

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[1] This research was supported by the National Science Foundation through Research Grants CHE76-17570 and CHE79-13-8010730.

[2] Gard, D. R.; Brown, T. L. *J. Am. Chem. Soc.*, in press.

[3] The numerical prefixes in compound names denote the metal centers. The stereochemistry of ligand placement, where known, is denoted by the terms ax (for axial) and eq (for equatorial).

[4] Wrighton, M. S.; Ginley, D. S. *J. Am. Chem. Soc.* **1975**, *97*, 2065.

[5] Kidd, D. R.; Brown, T. L. *J. Am. Chem. Soc.* **1975**, *97*, 2065.

[6] Geoffroy, G. L.; Wrighton, M. S. "Organometallic Photochemistry"; Academic Press: New York, 1979.

[7] Koelle, V. *J. Organomet. Chem.* **1978**, *155*, 33.

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added, followed by 185 mg of $(CH_3)_3NO\cdot 2H_2O$ (1.66 mmol). The solution was stirred at 25 °C for 4 h. The solvent was then removed under vacuum, and the gummy solids continued to be pumped on without heating until dried (about 3 days). The precipitate was extracted with a small volume of CH_2Cl_2; the soluble yellow portion is *eq*-$Re_2(CO)_9(C_2H_5NH_2)$. The less soluble yellow complex has not been characterized, but it has an IR spectrum coincident with that of the desired product except for a band at 1891 cm^{-1} instead of 1912 cm^{-1}. Attempts to purify *eq*-$Re_2(CO)_9(C_2H_5NH_2)$ by chromatography, sublimation, or drying by warming to 50 °C under vacuum resulted in decomposition to $HRe_3(CO)_{14}$. As a result, *eq*-$Re_2(CO)_9(C_2H_5NH_2)$ generally contains a small amount of this impurity and some $Re_2(CO)_{10}$: yield 600 mg (0.90 mmol), 56%; IR ν_{CO} (CH_2Cl_2) 2100 (w), 2039 (m), 1983 (s), 1952 (m), 1912 (m) cm^{-1}; ^1H NMR (acetone-d_6) τ 6.45 (br, 0.33, NH_2), 7.18 br m, 0.58, CH_2), 8.95 (t, $J = 7$ Hz, 1.00, CH_3); FDMS, parent ions at m/e (relative intensity) 667 (33), 669 (100), 671 (92). $Re_2(CO)_9^+$ daughter ions present.

Photolyses. Continuous photolysis was performed with Pyrex-filtered sunlamp radiation which consists primarily of 366-nm wavelength.[8]

A brief (60-ms), intense flash of white light is furnished by discharging a Sylvania M3 flashbulb with a 3-V source.

Results

Photochemical Reactions of *eq*-$Re_2(CO)_9(CH_3CN)$. Sunlamp photolysis of *eq*-$Re_2(CO)_9(CH_3CN)$ in THF leads to the production of $Re_2(CO)_{10}$, 1,2-*eq*,*eq*-$Re_2(CO)_8(CH_3CN)_2$, and $Re_4(CO)_{12}(OH)_4$, as observed with IR spectroscopy (eq 1). An additional compound, I, with an

$$eq\text{-}Re_2(CO)_9(CH_3CN) \xrightarrow[\text{THF or heptane}]{h\nu} Re_2(CO)_{10} + eq,eq\text{-}Re_2(CO)_8(CH_3CN)_2 + Re_4(CO)_{12}(OH)_4 + \underset{\text{I}}{\text{red (ionic) complex}} \quad (1)$$

intense red color was also isolated by chromatographic separation. The red compound was not completely characterized as it is formed in low yields (<2%) and is unstable. It is believed to be ionic; intense IR absorptions ascribed to this species are observed near 2000 and 1890 cm^{-1}.

The only stable product resulting from prolonged irradiation of *eq*-$Re_2(CO)_9(CH_3CN)$ in THF is $Re_2(CO)_{12}(OH)_4$. The hydroxo compound is formed by a photochemical side reaction of the initially formed compounds with residual amounts of H_2O in the THF solvent.

Sunlamp photolysis of *eq*-$Re_2(CO)_9(CH_3CN)$ in heptane yields the same products as in THF: 1,2-*eq*,*eq*-$Re_2(CO)_8(CH_3CN)_2$, compound I, and some of the $Re_4(CO)_{12}(OH)_4$ are precipitated from solution. Compound I is formed only after continued irradiation. Complete conversion of all rhenium compounds to $Re_4(CO)_{12}(OH)_4$ does not take place because there is inadequate trace water in heptane for quantitative reaction.

Photochemical Reactions of *eq*-$Re_2(CO)_9(py)$ and 1,2-*eq*,*eq*-$Re_2(CO)_8(py)$. Sunlamp photolysis of *eq*-$Re_2(CO)_9(py)$ (py = pyridine) in THF produces $Re_2(CO)_{10}$ in 49% spectroscopic yield (IR) after 70 min. Chromatography of the reaction mixture on silica with THF/petroleum ether eluent allows separation of two additional products. One is an unstable red compound, II, collected with about 10% yield, and the second a colorless material, III, formed in approximately 20% yield.

Absorptions in the IR spectrum of II occur at 2071 (w), 2047 (m), 2035 (sh), 2002 (s), 1952 (m), and 1932 (m) cm^{-1} in THF. A precipitate is formed by addition of $Bu_4N^+I^-$ in EtOH to a concentrated acetone solution. The precipitate exhibits IR bands expected for $Re(CO)_3(py)_3{}^+I^-$ (2038 (s), 1928 (vs, br) cm^{-1} in acetone). The red supernatant has IR absorptions at 2050 (m), 2005 (s), and 1959 (m, br) cm^{-1} in acetone. The anion of II is surmized to be $HRe_4(CO)_{16}^-$. Bau and co-workers treated $Re_4(CO)_{16}^{2-}$ with acid to yield a red compound thought to be either $HRe_4(CO)_{16}^-$ or $H_2Re_4(CO)_{16}$ (2049 (m), 2004 (s), 1956 (m, br) cm^{-1} in CH_2Cl_2).[9] The ^1H NMR of II supports the assignment as $Re(CO)_3(py)_3{}^+HRe_4(CO)_{16}^-$. Signals for coordinated pyridine are observed at τ 1–2.5 in acetone-d_6 as well as a singlet at τ 24.29. The intensity ratio of the pyridine proton signals to the hydride singlet is 15:1. Ions attributed to $Re(CO)_3(py)_3{}^+$ are seen in the field desorption mass spectrum of II.

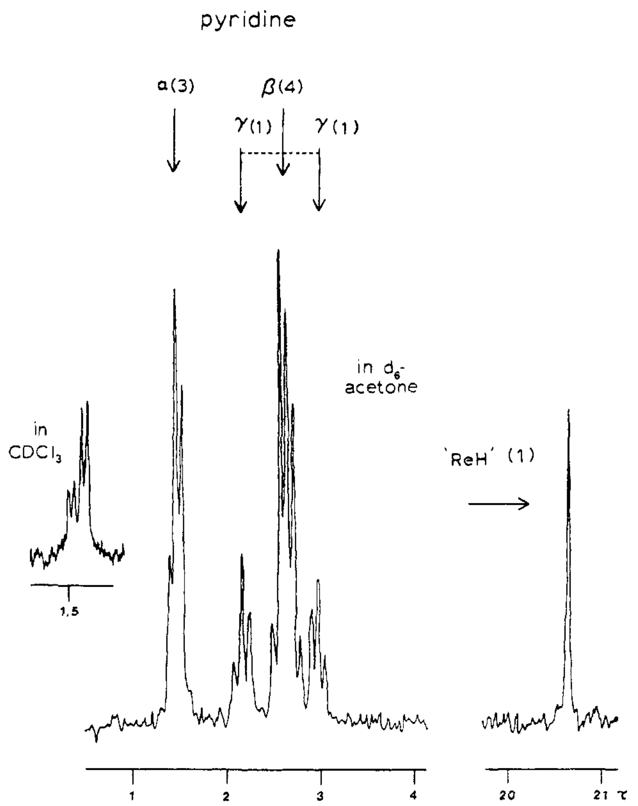

Figure 1. ^1H NMR spectrum of 1,1-(μ-H)$Re_2(CO)_7(py)(NC_5H_4)$ (III) in acetone-d_6 (inset: in $CDCl_3$ near τ 1.5).

Product III exhibits IR bands at 2086 (w), 2021 (s), 1983 (s, br), 1939 (m-s), and 1910 (s) cm^{-1} in acetone. In benzene, the 1983-cm^{-1} absorption is separated into two bands at 1992 and 1975 cm^{-1}. Elemental analysis (C, H, N) is consistent with formulation as $Re_2(CO)_7(py)_2$. A parent ion is observed in the field desorption mass spectrum at m/e (relative intensity) 725 (37), 727 (100), and 729 (87), corresponding to the formula $Re_2(CO)_7(py)_2{}^+$. Daughter ions correspond to successive losses of CO.

The ^1H NMR of III in acetone-d_6 is shown in Figure 1. The presence of two nonequivalent nitrogen environments per molecule is established, as two triplets are seen due to two chemically inequivalent pyridine γ-protons at τ 2.02 and 2.84. The pyridine β-hydrogen signals are clustered near τ 2.5 and the α-hydrogen signals appear at τ 1.29. Also seen is a singlet at τ 21.30 due to a hydridic hydrogen. The intensity ratio for the α:β:γ:ReH signals is 3:4:2:1, indicating that the hydride originated as a pyridine α-hydrogen. This point was confirmed by photolysis of *eq*-$Re_2(CO)_9(py\text{-}d_5)$ in THF. In $CDCl_3$ solution, the signals

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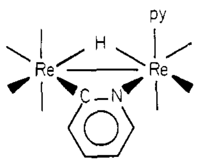
(8) General Electric Lighting Business Group, "RS Sunlamp Report", Nela Park, Cleveland, OH.

(9) Bau, R.; Fontal, B.; Kaesz, H. D.; Churchill, M. R. *J. Am. Chem. Soc.* **1967**, *89*, 6374.

due to the α-hydrogen for each pyridine moiety are shifted slightly to reveal that the apparent asymmetric triplet observed in acetone-d_6 is actually two doublets (τ 1.45, 1.59; $J_{\alpha\beta}$ = 6 Hz) with a ratio of intensities 1:2.

The formulation $Re_2(CO)_7(py)_2$ can be accounted for by the presence of one normally coordinated N-bound pyridine and one pyridine ligand which is ortho metalated. Compound III is therefore hereafter referred to as (μ-H)$Re_2(CO)_7(py)(NC_5H_4)$. Both nitrogen atoms are coordinated to the same Re atom. The IR spectrum of $HRe_2(CO)_7(py)(NC_5H_4)$ is similar to that of (μ-H)$Re(CO)_7(Me_3NO)(NC_5H_4)$ for which an X-ray structural determination places both the Me_3NO ligand and the pyridine nitrogen on the same metal atom of the complex.[10] A triosmium complex structurally similar to III has been prepared from $Os_3(CO)_{10}(CH_3CN)_2$ and pyridine at 80 °C.[11] The IR spectrum in the 1650–1000-cm^{-1} region displays weak aromatic ring vibrations and from 800 to 650 cm^{-1} C–H deformation modes of medium intensity. Some of these are at nearly the same frequencies as for eq-$Re_2(CO)_9(py)$ and 1,2-eq,eq-$Re_2(CO)_8(py)_2$. Others are shifted considerably as a result of metalation of the second pyridine.



III, 1,1-(μ-H)$Re_2(CO)_7(py)(NC_5H_4)$

The sunlamp photolysis of eq-$Re_2(CO)_9(py)$ in THF, therefore, proceeds initially as in eq 2. An important point is the absence of any observable 1,2-eq,eq-$Re_2(CO)_8(py)_2$. The nearly 50% yield of $Re_2(CO)_{10}$ is accounted for by cross-coupling of the radicals formed following homolysis of the metal–metal bond of eq-$Re_2(CO)_9(py)$. However, 1,2-$Re_2(CO)_8(py)_2$, which would also be expected, is not seen under continual photolysis conditions. On the other hand, when eq-$Re_2(CO)_9(py)$ solution is irradiated with a single, intense flash, the products observed are $Re_2(CO)_{10}$, 1,2-eq,eq-$Re_2(CO)_8(py)_2$, and III (eq 3). The 1,2-eq,eq-$Re_2(CO)_8(py)_2$ produced is itself quite light-sensitive; it reacts to yield $Re(CO)_3(py)_3{}^+HRe_4(CO)_{16}{}^-$ and (μ-H)$Re_2(CO)_7(py)(NC_5H_4)$ under continuous photolysis.

$$eq\text{-}Re_2(CO)_9(py) \xrightarrow[THF]{h\nu} Re_2(CO)_{10}\ (49\%) + Re(CO)_3(py)_3{}^+HRe(CO)_{16}{}^-\ (10\%) + (\mu\text{-H})Re_2(CO)_7(py)(NC_5H_4)\ (20\%) \quad (2)$$

$$eq\text{-}Re_2(CO)_9(py) \xrightarrow[THF]{flash} Re_2(CO)_{10} + eq,eq\text{-}Re_2(CO)_8(py)_2 + (\mu\text{-H})Re_2(CO)_7(py)(NC_5H_4) \quad (3)$$

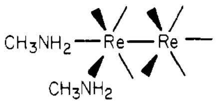
The contention that the bis(pyridine) compound is the precursor to the above products is supported by the observation that photolysis of 1,2-eq,eq-$Re_2(CO)_8(py)_2$ in THF forms the same products, in similar yields (eq 4). Remarkably, the yield of $Re_2(CO)_{10}$, as estimated from IR intensities, is 42%. Whereas $Re_2(CO)_{10}$, $Re(CO)_3(py)_3{}^+$-$HRe_4(CO)_{16}{}^-$, and (μ-H)$Re_2(CO)_7(py)(NC_5H_4)$ are formed initially in the photolysis of eq-$Re_2(CO)_9py$ or 1,2-eq,eq-$Re_2(CO)_8(py)_2$ in THF, a species giving rise to IR bands at 2001 and 1878 cm^{-1} is generated under prolonged photolysis with complete consumption of the initially formed products. The final product, not completely characterized, is thought to be ionic. In heptane, a compound with a similar IR spectrum is very rapidly formed as the sole product upon photolysis of eq-$Re_2(CO)_9(py)$ or 1,2-eq,eq-$Re_2(CO)_8(py)_2$.

$$1,2\text{-}eq,eq\text{-}Re_2(CO)_8(py)_2 \xrightarrow[THF]{h\nu} Re_2(CO)_{10}\ (42\%) + eq\text{-}Re_2(CO)_9py\ (\text{small amount}) + Re(CO)_3(py)_3{}^+HRe_4(CO)_{16}{}^-\ (20\%) + \underset{\text{III}}{(\mu\text{-H})Re_2(CO)_7(py)(NC_5H_4)}\ (20\%) \quad (4)$$

Photochemical Behavior of eq-$Re_2(CO)_9(RNH_2)$ (R = CH_3, C_2H_5). Sunlamp photolysis of eq-$Re_2(CO)_9(CH_3NH_2)$ in heptane yields $Re_2(CO)_{10}$ and a light-colored precipitate. Elemental analysis of the precipitate is consistent with the formula $Re_2(CO)_8(CH_3NH_2)_2$. Anal. Calcd: C, 18.24; H, 1.53; N, 4.25. Found: C, 18.33; H, 1.72; N, 3.89. FDMS confirms assignment of the precipitated material as $Re_2(CO)_8(CH_3NH_2)_2$ with a parent ion at m/e (relative intensity) 656 (29), 658 (100), and 660 (90). Daughter ions indicate a preferential loss of CH_3NH_2. The ^{1}H NMR of $Re_2(CO)_8(CH_3NH_2)_2$ in acetone-d_6 exhibits a broad feature at τ 6.25 and a triplet at τ 7.05 attributed to the amino and the methyl protons, respectively. The IR spectrum indicates that the amine ligands have not undergone metalation; ν_{NH} near 3330 cm^{-1} is a doublet, and bands characteristic of a methylene group (single δ(CH) absorption, strong CH_2 rocking made at 720–750 cm^{-1}) are absent.

Carbonyl stretching modes of $Re_2(CO)_8(CH_3NH_2)_2$ are observed at 2070 (m), 1990 (s), 1955 (s, br), 1883 (m), and 1867 (m) cm^{-1} in THF. This pattern is, however, not characteristic of 1,2-eq,eq-$Re_2(CO)_8(CH_3CN)_2$, 1,2-eq,eq-$Re_2(CO)_8(py)_2$, or 1,2-$M_2(CO)_8P_2$ (M = Mn, Re; P = phosphorus atom donor ligand). $Re_2(CO)_8(CH_3NH_2)_2$ is therefore judged to be 1,1 disubstituted; i.e., both amine ligands are bound to the same metal atom. The photolysis of eq-$Re_2(CO)_9(CH_3NH_2)$ in heptane thus proceeds as in eq 5.

$$2\ eq\text{-}Re_2(CO)_9(CH_3NH_2) \xrightarrow[heptane]{h\nu} Re_2(CO)_{10} +$$



(5)

Sunlamp photolysis of eq-$Re_2(CO)_9(C_2H_5NH_2)$ in heptane proceeds as for the corresponding CH_3NH_2 complex. The precipitated $Re_2(CO)_8(C_2H_5NH_2)_2$ has an IR spectrum identical with that of $Re_2(CO)_8(CH_3NH_2)_2$ in the ν_{CO} region. $Re_2(CO)_{10}$ and an unstable red material, probably ionic (ν_{CO} 2005, 1880 cm^{-1}), are produced following sunlamp irradiation of eq-$Re_2(CO)_9(CH_3NH_2)$ in THF solvent. The red compound is not thought to be a primary photoproduct. Prolonged photolysis generates higher yields of the red material.

Thermal Reactivity of eq-$Re_2(CO)_9L$ and eq,eq-$Re_2(CO)_8L_2$ (L = Nitrogen Ligand). eq-$Re_2(CO)_9(CH_3CN)$ does not react after 20 h in refluxing THF either by itself or in the presence of H_2O. In contrast, the bis(acetonitrile) complex is quite reactive with H_2O, yielding $Re_4(CO)_{12}(OH)_4$ (eq 6). Refluxing eq-$Re_2(CO)_9(py)$ in benzene (80 °C) for 20 h leads to no reaction. In contrast, after only 30 min in refluxing benzene, 1,2-eq,eq-$Re_2(CO)_8(py)_2$ converts in substantial yield to (μ-H)$Re_2(CO)_8(NC_5H_4)$, IV (eq 7). This product was absent in the

$$2eq,eq\text{-}Re_2(CO)_8(CH_3CN)_2 + 4H_2O \xrightarrow[THF]{66°C} Re_4(CO)_{12}(OH)_4 + 4CO + 4CH_3CN + 2H_2 \quad (6)$$

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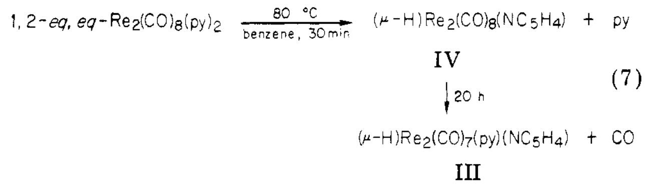
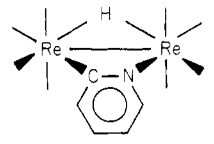
[10] Nubel, P. O.; Brown, T. L., unpublished observations.

[11] Tachikawa, M.; Shapley, J. R. *J. Organomet. Chem.* **1977**, *124*, C19.



$$1,2\text{-}eq,eq\text{-}Re_2(CO)_8(py)_2 \xrightarrow[\text{benzene, 30 min}]{80\ °C} (\mu\text{-}H)Re_2(CO)_8(NC_5H_4) + py \quad \text{IV}$$
$$\xrightarrow{20\ h} (\mu\text{-}H)Re_2(CO)_7(py)(NC_5H_4) + CO \quad \text{III} \qquad (7)$$

photochemical reactions (eq 2–4). After 20 h at 80 °C, the displaced pyridine replaces a CO to quantitatively yield III.



IV, $(\mu\text{-}H)Re_2(CO)_8(NC_5H_4)$

IV was characterized as follows: IR ν_{CO} (acetone) 2114 (w), 2087 (w-m), 2018 (s), 1991 (m, sh), 1955 (m) cm^{-1}; ^1H NMR (acetone-d_6) τ 1.76 (α-H, (d, $J_{\alpha\beta}$ = 6 Hz, relative intensity of 1), 2.70 (β,β'-H, complex multiplet, relative intensity of 2), 3.14 (γ-H, triplet of doublets, $J_{\beta\gamma}$ = 7 Hz, $J_{\alpha\gamma}$ = 2 Hz, relative intensity of 1), 24.52 (μ-H, s, relative intensity of 1). FDMS, m/e (relative intensity) parent ions at 673 (32), 675 (100), 677 (80) (no substantial daughter ions observed). Anal. Calcd for $HRe_2(CO)_8(NC_5H_4)$ (675.6): C, 23.11; H, 0.76; N, 2.07. Found: C, 23.28; H, 0.78; N, 2.08.

Compound IV may also be prepared by displacement of both acetonitrile ligands from 1,2-*eq*,*eq*-$Re_2(CO)_8(CH_3CN)_2$ (eq 8).

$$eq,eq\text{-}Re_2(CO)_8(CH_3CN)_2 + py \xrightarrow[\text{benzene}]{80\ °C} (\mu\text{-}H)Re_2(CO)_8(NC_5H_4) \quad (8)$$

Discussion

Our results indicate that photochemical reactions of $Re_2(CO)_9N$ compounds proceed via metal–metal bond homolysis, with subsequent formation of $Re_2(CO)_{10}$ and $Re_2(CO)_8N_2$ as the radicals recombine. 1,2-*eq*,*eq*-$Re_2(CO)_8(CH_3CN)_2$ is the major initial product in photolysis of $Re_2(CO)_9CH_3CN$. The corresponding substituted pyridine compound, 1,2-*eq*,*eq*-$Re_2(CO)_8(py)_2$, is observed upon flash irradiation of Re(CO)$_9$(py). The intermediacy of 1,2-*eq*,*eq*-$Re_2(CO)_8(py)_2$ in the continuous photolysis of *eq*-$Re_2(CO)_9$py is supported by the observation that similar yields of the same products are obtained when 1,2-*eq*,*eq*-$Re_2(CO)_8(py)_2$ is irradiated.

The electronic spectra of $Re_2(CO)_{10-x}(py)_x$ (x = 0–2), are shown in Figure 2. Note that the absorption maximum at 310 nm, attributed to the σ–σ^* transition in $Re_2(CO)_{10}$, is shifted to longer wavelengths upon substitution by pyridine. Given the predominant contribution of 366-nm wavelength light in the irradiation source, it is not surprising that the steady-state concentration of the intermediate 1,2-$Re_2(CO)_8(py)_2$ should be low during photolysis. A similar absence of 1,2-*eq*,*eq*-$Re_2(CO)_8(RNH_2)_2$ during irradiation of the corresponding *eq*-$Re_2(CO)_9(RHN_2)$ or of $Re_2(CO)_8(OH_2)_2$ during irradiation of *eq*-$Re_2(CO)_9(OH_2)$[2] can be explained by using the same argument.

The photochemical reactions of *eq*-$Re_2(CO)_9L$ compounds can be accounted for in terms of reaction in Scheme I. Though not directly observed under all conditions, 1,2-*eq*,*eq*-$Re_2(CO)_8L_2$ is probably formed initially, as discussed above. For L = CH_3CN, reaction proceeds only as far as 1,2-*eq*,*eq*-$Re_2(CO)_8(CH_3CN)_2$ before reaction with residual water leads to conversion to $Re_4(CO)_{12}(OH)_4$. In this case the reaction pathway is determined by the lability of the nitrogen ligand.

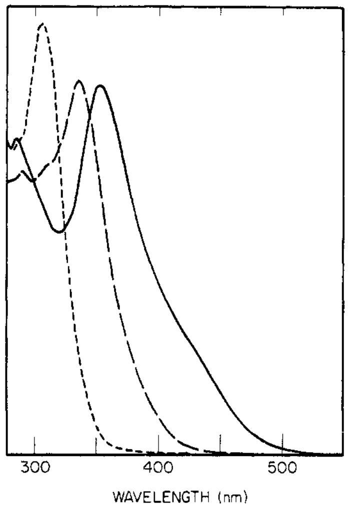
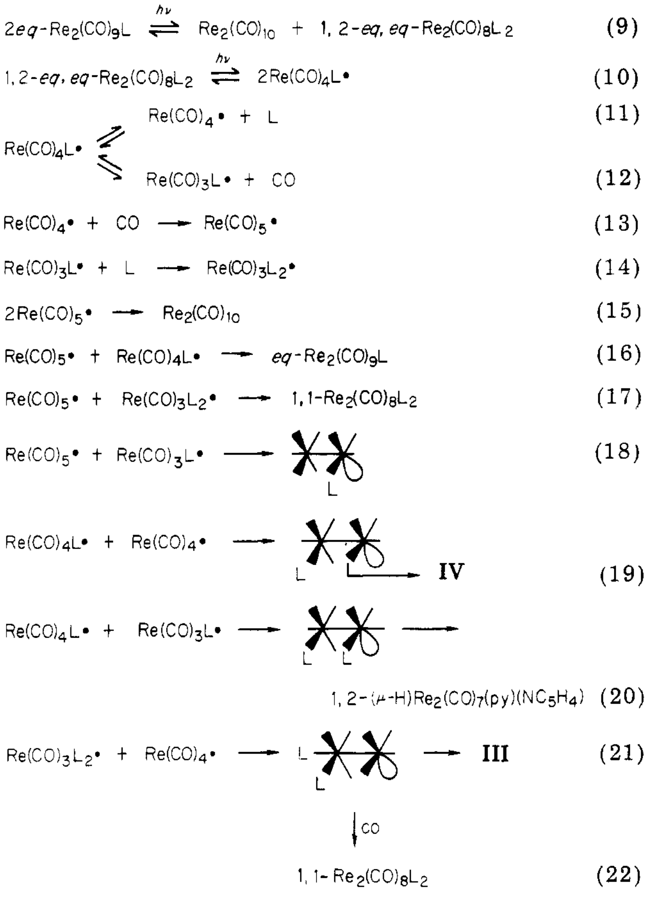


Figure 2. Electronic absorption spectra of equal concentrations of $Re_2(CO)_{10}$ (- - -), *eq*-$Re_2(CO)_9(py)$ (— — —), and 1,2-*eq*,*eq*-$Re_2(CO)_8(py)_2$ (—) in THF.

Scheme I



Homolytic cleavage of $Re_2(CO)_8L_2$ leads to the Re(CO)$_4$L· radical. The appearance of products other than those resulting from simple cross-coupling requires that ligand-exchange reactions occur. Either the nitrogen ligand or CO may be lost, as shown in eq 11 and 12. We do not know in detail about the relative rates of these reactions, but the product distributions would suggest that they must occur at comparable rates. Similarly, we do not know in detail the relative rates of recombination of the 15-electron intermediates, Re(CO)$_4$ or Re(CO)$_3$L, with nucleophiles such as L or CO. Recombination with CO and subsequent recombination to form $Re_2(CO)_{10}$ must be quite facile, because $Re_2(CO)_{10}$ is formed in high yield upon photolysis of 1,2-*eq*,*eq*-$Re_2(CO)_8(py)_2$. One reason for the high yield of this product has already been alluded to; it possesses a lower cross section for absorption of photons from the irradiation source than the other substituted dinuclear species and thus serves as a kind of sink for $Re(CO)_5\cdot$ radicals once they are formed.

In accounting for the results of a flash photolysis study of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$,[12] recombination of a 17-electron radical with a 15-electron species formed by loss of a ligand from a 17-electron radical was invoked. The products observed in the present study are consistent with a dominant role for the analogous reactions, (21) and (22).

Recent studies of substituted manganese carbonyl radicals $Mn(CO)_3L_2\cdot$, where L is a phosphorus ligand, indicate that the labilities of radicals toward ligand loss vary in the order $M(CO)_n\cdot > M(CO)_{n-1}L\cdot > M(CO)_{n-2}L_2\cdot$.[13] If this same type of behavior applies to rhenium carbonyl radicals with nitrogen ligands, then it is reasonable to expect that reaction 21 will be more important than recombination processes involving substituted 15-electron metal centers, as in eq 18 or 19. An important role for reaction 17 is ruled out by the absence of the 1,1-disubstituted product when L is pyridine. While reactions 18 and 19 could occur, the coordinatively unsaturated species so formed do not react when L = py to form compound IV, formed under thermal reaction conditions. Certain other pathways are ruled out by the observation, based on X-ray crystallographic results, that the same rhenium center carries both nitrogen coordination sites in the oxidative addition product, as in III. The distinction between the pyridine and alkylamine cases in this scheme arises in the relative rates of oxidative addition of C–H bonds to the second metal center. We propose that this process is sufficiently rapid in the case of pyridine to compete effectively with addition of a nucleophile from the medium, eq 21, whereas addition of CO dominates when L is either CH_3NH_2 or $C_2H_5NH_2$, eq 22. The dinuclear product molecules are removed from the system upon formation by their low solubility in heptane.

Disproportionation processes, probably involving electron transfer from highly substituted metal carbonyl species to less substituted molecules,[14] are competitive with the reactions shown in Scheme I. We have not accounted for reactions of this type in any detail. Indeed, the chemical processes involved in arriving at the complex ionic products formed will be difficult to sort out. However, one generality that emerges from these studies of substituted rhenium compounds is that the relative amounts of ionic compounds formed in the photochemical reactions of $Re_2(CO)_{10}$ with bases L increase in the order $CH_3CN < H_2O <$ THF $<$ py $< CH_3NH_2$. This is the order of increasing donor strength of these ligands as measured, for example, by the donicity parameter,[15] or *E* and *C* values.[16,17]

The results obtained for photolysis of $Re_2(CO)_9L$ compounds lend support to the reaction scheme proposed to account for the reaction of $Re_2(CO)_{10}$ with water.[2] In particular, the formation of $Re_2(CO)_8L_2$ compounds as intermediates is analogous to the proposed formation of an unstable $Re_2(CO)_8(OH_2)_2$. Compounds III and IV are analogous to $(\mu\text{-H})Re_2(CO)_7(OH)(OH_2)$ and $(\mu\text{-H})Re_2(CO)_8(OH)$, respectively, postulated as intermediates in the reaction pathways leading to the final product $Re_4(CO)_{12}(OH)_4$.

Registry No. *eq*-$Re_2(CO)_9(py)$, 67486-87-7; *eq*-$Re_2(CO)_8(py)_2$, 67605-95-2; *eq*-$Re_2(CO)_8(py\text{-}d_5)_2$, 82390-33-8; *eq*-$Re_2(CO)_9(CH_3NH_2)$, 82390-34-9; *eq*-$Re_2(CO)_9(C_2H_5NH_2)$, 82390-35-0; Re, 7440-15-5.

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[17] The tendency toward disportionation behavior appears to be greater for manganese, as evidenced by the results obtained in photochemical reactions of $Mn_2(CO)_{10}$ with pyridines.[14] Further, whereas it is possible to form *eq*-$Mn_2(CO)_9(py)$ by thermal reaction of $Mn_2(CO)_{10}$ with py, using $(CH_3)_3NO$ to promote CO loss, use of 2 equiv of the amine oxide leads to formation of ionic products.