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# Photochemical Metal–Halide Bond Cleavage Reactions. A Reexamination of the Photochemistry of $Re(CO)_5Br$

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Photochemical cleavage of metal–halide bonds in metal carbonyl halide complexes is rate; only several reactions are known in which this type of cleavage occurs. For example, irradiation of $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) in donor solvents was shown to produce $M(CO)_5^-$ [1]; the dimer $Cp_2Fe_2(CO)_4$ (Cp = $h^5$-$C_5H_5$) is formed when $CpFe(CO)_2X$ (X = Cl, Br) [2] or $CpFe(CO)(P(OPh)_3)Br$ [3] is irradiated with visible light in dimethyl sulfoxide or pyridine solvent; and irradiation of $Re(CO)_5X$ in a 2-methyltetrahydrofuran glass at 80 K has been claimed to cause Re–X bond cleavage [4]. Also, irradiation of $W(CO)_5Br^-$ in the presence of CO produces $W(CO)_6$ with low quantum efficiency [5]. As shown by these examples, there is no question that in some cases the *net* result of irradiating metal carbonyl halide complexes is metal–halide bond cleavage. What is not clear, however, is the claim that in many of these reactions metal–halide bond cleavage is the primary photoprocess. With the exception of the $W(CO)_5Br^-$ photoreaction [5], no mechanistic photochemical data exist to support this claim. Particularly questionable is the claim [4] that irradiation of $Re(CO)_5X$ in a low temperature matrix produces $Re(CO)_5^+$ or $Re(CO)_5$. Given the propensity of monomeric metal carbonyl complexes to undergo M–CO bond dissociation as a primary photoprocess [6], we seriously doubted whether Re–X dissociation (either homolytic or heterolytic) was occurring efficiently. Therefore, we reinvestigated the photochemistry of $Re(CO)_5Br$ at low temperature to determine if Re–Br photolysis does indeed occur.

## Experimental

All syntheses and manipulations were carried out on a Schlenk line using pre-purified nitrogen as an inert gas. Solutions for photolysis were degassed prior to irradiation by a stream of nitrogen. $Re_2(CO)_{10}$ was obtained from Strem Chemical Co. and 2-methyltetrahydrofuran (MeTHF) from Aldrich. Tetrahydrofuran (THF) and methylene chloride were purified and dried by standard procedures [7]. $Re(CO)_5Br$ was prepared using a standard procedure [8]. Triphenylphosphine (Aldrich) was recrystallized before use.

A 200 W high pressure Hg arc was used for the irradiations in conjunction with a pyrex filter ($\lambda > 320$ nm). The photoreactions were monitored with a Perkin-Elmer 621 infrared spectrophotometer. Wavelengths were calibrated using the known peaks of polystyrene. We estimate the frequencies reported in this letter to be accurate to within ±3 $cm^{-1}$. Low temperature infrared experiments were done with a Specac low temperature IR apparatus using a cell with NaCl windows. The sample was cooled using a Dry-Ice acetone mixture in the dewar section of the apparatus.

## Results and Discussion

It has been shown [4] that uv irradiation of $Re(CO)_5Br$ ($\nu(C{\equiv}O)$ = 2152(w), 2040(s), 2020(sh), 1981(m)) [9] in a MeTHF glass at 80 K results in the formation of a product with CO stretching bands at 2008 and 1927 $cm^{-1}$. This product was suggested to be either $Re(CO)_5^+$ or $Re(CO)_5$. The assignment of the new infrared bands to one of these species was based on the observation that no matrix-trapped CO band around 2130 $cm^{-1}$ was observed in the infrared spectrum of the glass after the irradiation [4]. It was argued that since no uncoordinated CO was present then the irradiation did not cleave any of the Re–CO bonds; consequently, photolysis of the Re–Br bond must have occurred. Whether the cleavage was homolytic or heterolytic was uncertain; the former would yield $Re(CO)_5$ and the latter would yield $Re(CO)_5^+$.

In order to check the possibility that irradiation of $Re(CO)_5Br$ resulted in the efficient photolysis of the Re–Br bond, we repeated the experiment described above. The following infrared spectral changes were observed in the CO stretching region when a 0.01 *M* solution of $Re(CO)_5Br$ in MeTHF at −78 °C was irradiated ($\lambda > 320$ nm): the $Re(CO)_5Br$ bands at 2152(w) and 2040(s) decreased in intensity; the $Re(CO)_5Br$ band at 1981 $cm^{-1}$ increased slightly in intensity and shifted to 1983 $cm^{-1}$; and three new bands appeared. The new bands were located at 2113(w), 2009(s) and 1928(m–s). The presence of new bands at 2009 and 1928 $cm^{-1}$ is in agreement with the results of the previous investigators [4]. What they failed to report, however, is the appearance of the weak band at 2113 $cm^{-1}$ and the slight energy shift and increase in intensity

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of the band at 1981 cm$^{-1}$*. The band at 1983 cm$^{-1}$ is not attributed to Re(CO)$_5$Br but to the product. This is easily demonstrated: prolonged irradiation of the Re(CO)$_5$Br solution causes the bands at 2152 and 2040 cm$^{-1}$ to completely disappear but the band at 1983 cm$^{-1}$ remains (as well as the bands at 2113, 2009, and 1928 cm$^{-1}$)**.

The photochemical experiment described above need not be done at low temperature; irradiation of the Re(CO)$_5$Br solution (using either MeTHF or THF as the solvent) at *room temperature* results in infrared spectral changes identical to those which occur at –78 °C.

The product of the photoreaction described above is neither Re(CO)$_5^+$ nor Re(CO)$_5$; rather, the product is Re(CO)$_4$(MeTHF)Br. The infrared spectrum of Re(CO)$_4$(THF)Br has been previously reported [9] and it is identical to the infrared spectrum of the product of the photoreaction. Calderazzo and Vitali have shown that when Re$_2$(CO)$_8$Br$_2$ is dissolved in THF solution, a rapid bridge-splitting reaction of the dimer occurs and Re(CO)$_4$(THF)Br is formed [9]. Re(CO)$_4$(THF)Br has $\nu$(C≡O) bands at 2113(w), 2009(s), 1984(m–s), and 1931(m). These frequencies are essentially identical to the frequencies reported above for the photoproduct.

Two other observations are consistent with the suggestion that the photoproduct is Re(CO)$_4$(MeTHF)Br. First, when a solution of PPh$_3$ in THF is added to a solution of the product, a dark reaction occurs: the bands at 2113, 2009, 1983, and 1921 cm$^{-1}$ decrease in intensity and new bands appear at 2105, 2002, and 1947 cm$^{-1}$. These latter frequencies agree with the $\nu$(C≡O) values reported for Re(CO)$_4$(PPh$_3$)Br [10]. The following reaction is suggested:

$$\mathrm{Re(CO)_4(THF)Br + PPh_3 \rightarrow Re(CO)_4(PPh_3)Br}$$

Displacement of a weakly coordinated THF ligand by a more strongly bonding ligand such as PPh$_3$ is common [11]. Second, we point out that the room temperature photochemical reactivity of Re(CO)$_5$Br has been studied many times [12]. None of the photochemical reactions is consistent with Re–Br bond cleavage. Rather, these reactions can always be interpreted in terms of a Re–CO bond dissociation photoprocess†.

Infrared spectral changes similar to those that occur at –78 °C in MeTHF also occur in methylene chloride solvent at –78 °C. Irradiation ($\lambda > 320$ nm) of a 0.01 *M* solution of Re(CO)$_5$Br in CH$_2$Cl$_2$ causes the Re(CO)$_5$Br bands at 2153 and 2046 cm$^{-1}$ to decrease in intensity and new bands to appear at 2114, 2012, and 1938 cm$^{-1}$. The Re(CO)$_5$Br band at 1987 cm$^{-1}$ does not decrease in intensity but it shifts in energy to 1989 cm$^{-1}$. The similarity of these spectral changes to those which occur in MeTHF suggests that Re–CO bond dissociation has also occurred at low temperature in CH$_2$Cl$_2$. The product is presumably Re(CO)$_4$(CH$_2$Cl$_2$)Br, a molecule in which the vacant coordination site is occupied by a weakly bonded solvent molecule. This product slowly disappears (in about 15 min) in a dark reaction at –78 °C to yield Re$_2$(CO)$_8$Br$_2$. This complex has infrared absorption bands at 2117, 2037, 1995 an 1957 cm$^{-1}$ (these values agree closely with the infrared frequencies of 2114(w), 2035(s), 2000(m–s), and 1960(m) cm$^{-1}$ reported for Re$_2$(CO)$_8$Br$_2$ in CHCl$_3$ [9]). Note that Re$_2$(CO)$_8$Br$_2$ is the product of the room temperature irradiation of Re(CO)$_5$Br in non-coordinating solvents [13].

In summary, the claim for Re–Br bond photolysis in Re(CO)$_5$Br at low temperature in a MeTHF glass is not justified; the low temperature photochemistry of Re(CO)$_5$Br in MeTHF or CH$_2$Cl$_2$ must be interpreted in terms of an initial Re–CO bond dissociation.

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*Note that while the band at 1983 cm$^{-1}$ was not reported in the irradiation of Re(CO)$_5$Br, this band was reported in the irradiation of Re(CO)$_5$Cl [4].

**Prolonged irradiation also causes bands at 2030, 1914, and 1981 cm$^{-1}$ to appear. These bands are assigned to Re(CO)$_3$(MeTHF)$_2$Br [9].

†Given that Re–CO bond dissociation is occurring, we can offer no suggestions as to why no matrix-trapped CO was observed in the original experiment at 80 K [4].

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