Preliminary communication

Symmetrical cleavage of the metal—metal bond in decacarbonyldirhenium(0) by ultraviolet irradiation

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(Received December 13th, 1972)

SUMMARY

A study of the photoreaction of $Re_2(CO)_{10}$ with carbon tetrachloride has provided evidence supporting efficient symmetrical metal—metal bond scission upon photo-excitation of the rhenium carbonyl.

We report here evidence supporting efficient symmetrical metal—metal bond cleavage upon photoexcitation of $Re_2(CO)_{10}$. Generally, the dominant excited state decay mode of metal carbonyls is dissociation of CO[1], eqn. (1). However, the importance of

$$M(CO)_n \xrightarrow{h\nu} M(CO)_{n-1} + CO \tag{1}$$

$$(M = Ni^0, Fe^0, Cr^0, Mo^0, W^0)$$
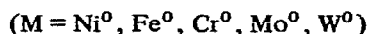
metal—metal bond cleavage upon electronic excitation of polynuclear carbonyls has not been evaluated. The use of $Re_2(CO)_{10}$ and its Mn analog has photoinitiators of methyl methacrylate polymerization led to studies which indicate that a primary photoprocess is unsymmetrical metal—metal bond cleavage to yield $M(CO)_6$ and $M(CO)_4$ fragments[2]. This conclusion is to be contrasted with qualitative observations in support of symmetrical M—M bond cleavage: photolysis of a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ yields some $ReMn(CO)_{10}$ [3], and photolysis of either $(CO)_5 Mn—Mn(CO)_3(1,10$-phenanthroline) or $(CO)_5 Mn—Re(CO)_3(1,10$-phenanthroline) yields $Mn_2(CO)_{10}$ and the corresponding $M_2(CO)_6(1,10$-phenanthroline)$_2$ [4]. We report here the first quantum efficiency and stoichiometric data which suggest that M—M bond cleavage is the major photoreaction in $Re_2(CO)_{10}$. Establishing the primary photoreaction in these systems founds a new class of excited state reactions of transition metal complexes.

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The photolysis of $Re_2(CO)_{10}$ in deoxygenated CCl_4 solutions results in the formation of $Re(CO)_5\text{-}Cl$ using either 313 nm or 366 nm light. Analysis by IR or UV spectroscopy gives 0.60 as the disappearance quantum yield for $Re_2(CO)_{10}$ upon 313 nm irradiation[*]. By IR absorbance measurements, the quantum yield for $Re(CO)_5Cl$ formation is 2.0 ± 0.1 times the disappearance yield for $Re_2(CO)_{10}$. A plot of moles $Re_2(CO)_{10}$ reacted and $Re(CO)_5Cl$ formed against 313 nm irradiation time appears in Fig. 1. Prolonged

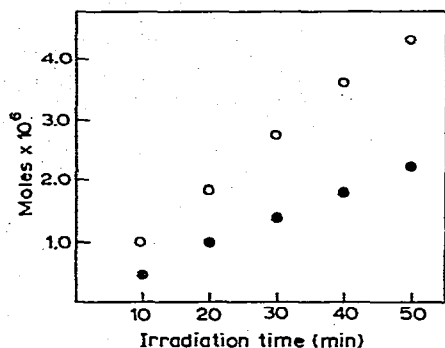Fig. 1. Number of moles of $Re_2(CO)_{10}$ reacted (•) and number of moles of $Re(CO)_5Cl$ produced (o) upon 313 nm (7.9×10^{-8} ein/min) irradiation of $Re_2(CO)_{10}$ in CCl_4 at room temperature.

irradiation at either 313 nm or 366 nm results in the formation of (I) which was established as a primary photoproduct from an authentic sample of $Re(CO)_5Cl$. The IR band maxima in the CO stretching region for both $Re(CO)_5Cl$ and (I) are in agreement with previously

(I)
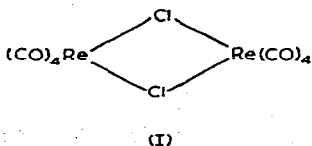
reported values[6]. Finally, upon photolysis of $Re_2(CO)_{10}$ in degassed benzene solutions containing either benzyl chloride or benzyl bromide bibenzyl is observed as a significant product.

The fact that $Re_2(CO)_{10}$ yields two molecules of $Re(CO)_5Cl$ upon electronic excitation is the first quantitative evidence in support of symmetrical metal—metal bond cleavage. Since the quantum yield is greater than 0.5 it can be concluded that this photo-process dominates all others. Two mechanisms could account for the observed initial products: (1) the electronically excited $Re_2(CO)_{10}$ may interact with an alkyl halide, RX,

[*](a) Samples were irradiated in a merry-go-round apparatus using appropriate filters to isolate the 313 nm Hg line from a 450 W medium pressure Hanovia lamp. The 313 nm light intensity was measured by ferrioxalate actinometry[5].

directly to yield $Re(CO)_5(X)$, $Re(CO)_5$, and R· followed by reaction of $Re(CO)_5$ with another molecule of RX to yield a second molecule of $Re(CO)_5 X$ and R·; or (2) the electronically excited $Re_2(CO)_{10}$ may decay via homolytic scission of the Re—Re bond to yield two $Re(CO)_5$ units each which react with RX to form $Re(CO)_5 X$ and R·. The observed formation of bibenzyl for RX = benzyl halide is consistent with either mechanism. The $Re(CO)_5$ species has the same number of d electrons as $Co(CN)_5{}^{3-}$. Thus, it is not surprising that, like $Co(CN)_5{}^{3-}$ [7], $Re(CO)_5$ reacts with alkyl halides.

     While the data presented here cannot rigorously exclude the possibility that the electronically excited state reacts directly with RX, the lifetime of excited $Re_2(CO)_{10}$ in fluid solution is probably too short to allow halogen atom abstraction[8]. Reaction of excited $Re_2(CO)_{10}$ and RX to give $Re(CO)_5(X)$ by a route not involving abstraction might be expected to also yield some $Re(CO)_5 R$ which is generally stable[9]. A homolytic scission mechanism of symmetrical Re—Re bond cleavage can be easily rationalized by consideration of the electronic structure of $Re_2(CO)_{10}$. The $Re_2(CO)_{10}$ can be viewed as a dimer derived from two d^7, $Re(CO)_5$ species of C_{4v} symmetry with the Re—Re single bond formed by overlap of the singly occupied d_{z^2} orbital of each $Re(CO)_5$ unit as diagrammed in Scheme I. The electronic absorption spectrum of $Re_2(CO)_{10}$ is dominated by an intense transition, λ_{max} 310 nm ($\epsilon \approx 17000$), associated with the $\sigma_b \rightarrow \sigma^*$ electronic excitation[10].
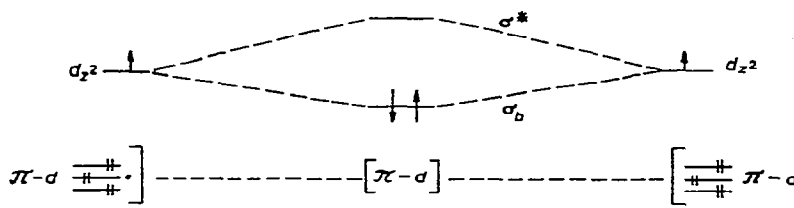
SCHEME I

Irradiation at either 313 nm or 366 nm promotes the $\sigma_b \rightarrow \sigma^*$ excitation which results in a significantly weakened Re—Re bonding interaction. Experiments designed to provide direct observation of the intermediates are in progress. Examples of molecules having single bonds which undergo homolytic cleavage upon population of low lying excited states are known and include halogens, peroxides, and alkanes[11].

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