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LIGHT CATALYZED SUBSTITUTION AND DISPROPORTIONATION IN $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$

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Summary

The metal—metal bonded molybdenum dimer $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ undergoes an efficient light-catalyzed reaction with X^-(X is Cl, Br, or SCN) in acetone, acetonitrile, or tetrahydrofuran:

$$(\pi\text{-}C_5H_5)_2Mo_2(CO)_6 + X^- \xrightarrow{h\nu} (\pi\text{-}C_5H_5)Mo(CO)_3X + (\pi\text{-}C_5H_5)Mo(CO)_3^-$$

The reaction, which is a net disproportionation $[Mo^I_2 \rightarrow Mo^{II} + Mo^0]$, is followed by a second light-catalyzed step in which CO is displaced from $(\pi\text{-}C_5H_5)Mo(CO)_3X$ giving $(\pi\text{-}C_5H_5)Mo(CO)_2X_2^-$. The electronic spectrum of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ in acetone has two well separated bands at λ_{max} 382 nm (ϵ18,300) and λ_{max} 500 nm (ϵ1610). The wavelength dependence of the initial reaction (X = Cl) is remarkable, $\Phi_{546} = 0.36 \pm 0.06$ and $\Phi_{366} = 0.07 \pm 0.02$, since it indicates that the upper excited states are less reactive than the lower. The efficiencies of the photoreactions between $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and X^- or L (L is a tertiary phosphine or phosphite) are all strongly solvent dependent.

Introduction

From the synthetic work of Haines, Nyholm, and Stiddard, the metal—metal bonded dimer $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ reacts photochemically with tertiary phosphines or phosphites (L) in stepwise reactions [1]. The first step, in which CO is displaced

$$(\pi\text{-}C_5H_5)_2Mo_2(CO)_6 + L \xrightarrow{h\nu} (\pi\text{-}C_5H_5)_2Mo_2(CO)_5L + CO \qquad (1)$$

is followed either by a second photosubstitution for CO

$$(\pi\text{-}C_5H_5)_2Mo_2(CO)_5L + L \xrightarrow{h\nu} (\pi\text{-}C_5H_5)_2Mo_2(CO)_4L_2 + CO \qquad (2)$$

or by a photodisproportionation $[Mo^I_2 \rightarrow Mo^{II} + Mo^0]$.

$$(\pi\text{-}C_5H_5)_2Mo_2(CO)_5L + L \xrightarrow{h\nu} [(\pi\text{-}C_5H_5)Mo(CO)_2L_2^+][(\pi\text{-}C_5H_5)Mo(CO)_3^-] + CO \qquad (3)$$

We find that stepwise photochemical reactions occur between $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and X^- (X is Cl, Br, or SCN), but by a different photopathway in which an inital disproportionation is followed by displacement of CO from one of the disproportionation products ($(\pi\text{-}C_5H_5)Mo(CO)_3X$). The photoreactions of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ with both L and X^- show remarkable wavelength and solvent effects.

Experimental

Electronic spectra were recorded on Unicam S.P. 800B or Cary Model 14 spectrophotometers. Infrared spectra were recorded on a Perkin—Elmer 421 Spectrophotometer and PMR spectra were obtained using a Jeolco-C60HL spectrometer. A G.E. 275 watt sun lamp was used as the light source for all net photolysis studies. For quantum yield studies a standard merry-go-round [2] apparatus fitted with a Hanovia 450 watt medium pressure mercury lamp was employed. Wavelength selection was achieved by using appropriate Corning filters.

Photolytic reactions. Solutions to be irradiated (1×10^{-3} *M* in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and 5×10^{-3} *M* in X^-, X = Cl, Br, SCN) were placed in a 50 ml erlenmeyer flask fitted with a serum cap and a syringe needle (to allow for the escape of CO). The sun lamp was placed 1-2 cm from the reaction vessel.

Solutions of tetrahydrofuran and acetonitrile were cooled during photolysis by immersing the reaction vessel in a water bath. Electronic and infrared spectra were scanned at various photolysis times in each solvent. For PMR studies, a saturated solution of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and the appropiate halide salt was prepared and placed in an NMR tube. Solutions were irradiated in the NMR tube, and NMR spectra scanned at various times.

All studies employed nitrogen purged solvents.

Materials. Di-π-cyclopentadienyltricarbonylmolybdenum was purchased from Aldrich Chemical Company and recrystallized from dichloromethane prior to use. Ammonium reineckate $NH_4[Cr(NH_3)_2(SCN)_4] \cdot H_2O$ was obtained from Alfa Inorganics and converted into the anhydrous potassium salt. Tetra-n-butylammonium chloride was purchased from the Eastman Chemical Company, and was recrystallized from dichloromethane and dried at 70° C in a vacuum oven for 24 h prior to use. Tetra-n-butylammonium bromide was obtained from Eastman Chemical Company and was used without further purification. Potassium thiocyanate (Allied Chemical Company) was recrystallized from water and dried in a vacuum oven at 70° C for 12 h. Acetone was freshly distilled from magnesium sulfate. Acetonitrile was distilled twice from $KMnO_4$ and Na_2CO_3. Tetrahydrofuran was distilled from potassium metal and benzophenone.

Quantum yields. As the actinometer, $K[Cr(NH_3)_2(SCN)_4]$ was used essentially by the procedure reported by Wegner and Adamson [3]. Solutions for actinometry were prepared at the time of use by dissolving 0.9 g of $K[Cr(NH_3)_2(SCN)_4]$ in 20 ml of water and filtering. The filtrate was placed in a 25 ml volumetric flask and diluted to the mark. An aliquot of this solution was placed in a pyrex test tube and irradiated. The concentrations of SCN^- liberated in the photochemical reaction were determined by taking an aliquot of the solution, placing it in a volumetric flask and developing with a three-fold excess of an iron reagent [0.01 M $Fe(NO_3)_3 \cdot 9H_2O$ in 0.5 M $HClO_4$] and diluted to the mark with water. The UV-visible spectrum was scanned using water as a reference, and the difference in absorbance between irradiated and non-irradiated samples was determined at 450 nm (ϵ $4.3 \cdot 10^3$). To achieve a minimum blank the solutions were protected from ambient light. Quantum yields for the reaction with Br^- ($2 \cdot 10^{-3} M$ in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and $1 \cdot 10^{-2} M$ in Br^-) were obtained in acetonitrile and in acetone at both 546 and 366 nm. Four ml of the appropriate solution was placed in each of three test tubes which had been fitted with serum caps and deaerated. Two of the tubes were irradiated in the merry-go-round apparatus. An aliquot was withdrawn from each of the tubes and the UV-visible spectrum was scanned from 400 to 360 nm. The difference in absorbance between the irradiated and non-irradiated samples was determined at λ_{max} (382 nm), and the number of moles of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ which had reacted determined from the extinction coefficient (ϵ 18300), after correcting for the absorbances contributed by the photoproducts $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ and $(\pi\text{-}C_5H_5)Mo(CO)_3Br$.

Preparation of $(\pi\text{-}C_5H_5)_2Mo_2(CO)_4(P(OC_6H_5)_3)_2$. The molybdenum dimer (300 mg) was dissolved in 100 ml of acetone and 2 ml of triphenylphosphite was added. The solution was irradiated for 15 min at which time red crystals had appeared on the bottom of the reaction vessel. The crystals were collected by filtration and washed with benzene and then pentane. The yield of $(\pi\text{-}C_5H_5)_2Mo_2(CO)_4(P(OC_6H_5)_3)_2$ was 85%. Anal. Found: C, 56.53; H, 3.84. $C_{50}H_{40}O_{10}Mo_2P_2$ calcd.: C, 56.94; H, 3.03%.

Results

When deep red solutions of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ ($2 \cdot 10^{-3} M$) and excess X^- (X = Cl, Br, SCN; $10^{-2} M$) in acetone are photolyzed with a sunlamp (GE 275W) two distinct color changes occur, first to a less intense orange and then to purple. The reaction occurring during the first color change is a net photodisproportionation (Eqn. 4)*. The identity of the products was determined by spectral comparisons with known samples in the case of $(\pi\text{-}C_5H_5)Mo(CO)_3X$ and by infrared spectroscopy in the ν(CO) region for $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ **. The spectral properties of the various complexes are summarized in Table 1. The reactions were followed at various photolysis times by infrared, UV-visible, and PMR spectra. As shown in Fig. 1, the reactions proceeded smoothly with no evidence for the appearance of intermediates in the spectra. The sums of the integrated areas of the π-C_5H_5

$$(\pi\text{-}C_5H_5)_2Mo_2(CO)_6 + X^- \xrightarrow{h\nu} (\pi\text{-}C_5H_5)Mo(CO)_3X + (\pi\text{-}C_5H_5)Mo(CO)_3^- \quad (4)$$

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* In a preliminary communication, the reaction with X^- was incorrectly reported to involve displacement of CO [4].

** For $(\pi\text{-}C_5H_5)Mo(CO)_3^-$ strong ν(CO) bonds have been reported at 1892 and 1770 cm^{-1} in dichloromethane [5].

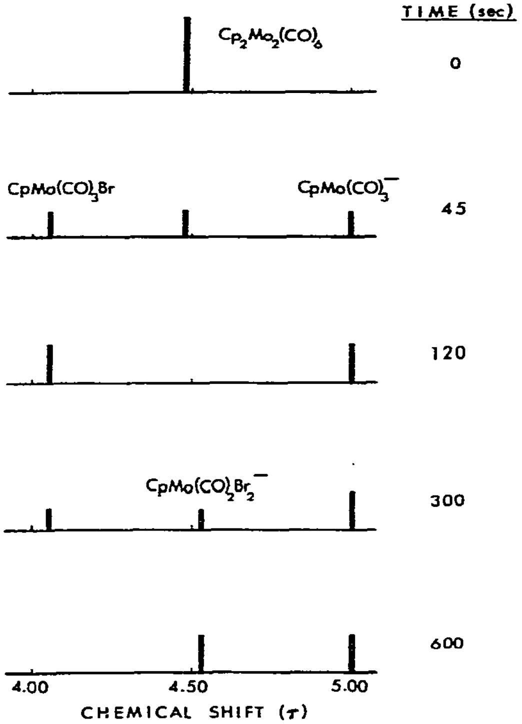


Fig. 1. Line drawing representing the cyclopentadienyl PMR spectra at various photolysis times for an acetone solution containing initially $(\pi\text{-}C_5H_5)_2Mo_2(CO)_6$ and Br^-. Line lengths are proportional to peak areas. Reference was acetone at τ 7.93 ppm.

resonances remained constant (± 10%) during the reactions, showing that reaction 4 is quantitative. The products, $(\pi\text{-}C_5H_5)Mo(CO)_3X$ and $(\pi\text{-}C_5H_5)Mo(CO)_3^-$, were determined quantitatively at the end of the reaction by measuring PMR peak areas. The spectral data given in Table 1 refer to solutions which had been photolyzed until reaction 4 was complete.

TABLE 1

SPECTRAL PROPERTIES IN ACETONE

Compound	λ_{max}(nm)^a	$\tau(\pi\text{-}C_5H_5)$	ν(CO)(cm^{-1})
$[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$	500 (1610) 382 (18300)	4.48	2011m, 1959s, 1913s
$(\pi\text{-}C_5H_5)Mo(CO)_3Cl$	472 (451)^b	4.14^c	2055s, 1968s(br)^d
$(\pi\text{-}C_5H_5)Mo(CO)_3Br$	478 (503)^b	4.06^c	2056s, 1968s(br)^d
$(\pi\text{-}C_5H_5)Mo(CO)_3SCN^e$	445	4.03^c	2056s, 1969s(br)^d
$(\pi\text{-}C_5H_5)Mo(CO)_3^-$		5.00	1895^f

^{a}± 2 nm; molar extinction coefficients (± 5%) are given in parentheses. ^{b}In dichloromethane. ^{c}± 0.05 versus acetone at τ 7.93. Solutions saturated in $N(n\text{-}C_4H_9)_4Cl$, $N(n\text{-}C_4H_9)_4Br$ or KSCN. ^{d}± 3 cm^{-1}; $[X^-] = 10^{-2}M$ as the tetra-n-butylammonium (for Cl^- or Br^-) or potassium (for NCS^-) salts. Abbreviations used are strong (s), broad (br), and medium (m). ^{e}Infrared spectral comparisons indicate that the photochemical product with thiocyanate is the S-bound isomer [11]. ^{f}A lower energy band which is masked in acetone appears in acetonitrile (1770 cm^{-1}) and tetrahydrofuran (1778 cm^{-1}).

Reaction 4 is followed by a photochemically less efficient step (under the conditions used for the photolyses) in which the release of CO is clearly detectable. It appears that in the second reaction CO is displaced from $(\pi\text{-}C_5H_5)Mo\text{-}$

$$(\pi\text{-}C_5H_5)Mo(CO)_3X + X^- \xrightarrow{h\nu} (\pi\text{-}C_5H_5)Mo(CO)_2X_2^- + CO \qquad (5)$$

$(CO)_3X$ by X^- (Eqn. 5). Attemps to isolate pure salts of the anions $(\pi\text{-}C_5H_5)Mo(CO)_2X_2^-$ (X = Cl, Br) were unsuccessful. The anions are air and moisture sensitive in the solid and react rapidly with hydroxylic and halocarbon solvents. We were unable to separate the anion salts from the tetraalkylammonium salts which were used as the source of halide ions in the photochemical experiments. Reaction 5 (X = Cl, Br, SCN) was also followed spectrally at various photolysis times. The reactions proceeded without the appearance of intermediates and quantitatively as shown by PMR (Fig. 1). The spectral properties of the completely photolyzed solutions are given in Table 2.

Although our inability to isolate pure salts of the anions introduces an element of uncertainty as to the products of reaction 5, the complexes $(\pi\text{-}C_5H_5)Mo(CO)_3X$ are known to react photochemically with neutral ligands giving the related complexes $(\pi\text{-}C_5H_5)Mo(CO)_2LX$ (L is PPh_3, $AsPh_3$, $SbPh_3$) [6], and furthermore, the spectral properties of the completely photolyzed solutions (Table 2) are consistent with the presence of the CO-substituted anions [6, footnote e in Table 1]

Both reactions (4 and 5) also occur quantitatively and stepwise in acetonitrile and tetrahydrofuran, but there is no apparent reaction in benzene on the same time scale used for the other solvents (10-25 min). The photoreactions between $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and $P(C_6H_5)_3$ or $P(OC_6H_5)_3$, are also considerably more efficient in polar organic solvents than in benzene. For example, reaction 6

$$(\pi\text{-}C_5H_5)_2Mo_2(CO)_6 + 2P(OC_6H_5)_3 \xrightarrow{h\nu} (\pi\text{-}C_5H_5)_2Mo_2(CO)_4[P(OC_6H_5)_3]_2 + 2CO \qquad (6)$$

is completed within 15 minutes in acetone under conditions where the reaction time is several hours in benzene.

In the electronic spectrum of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ in acetone there are two well separated transitions at λ_{max} 382 nm (ϵ18300) and λ_{max} 500 nm (ϵ 1610). Quantum yield measurements on reaction (7) in acetone gave the values $\Phi_{546} = 0.36 \pm 0.06$ and $\Phi_{366} = 0.07 \pm 0.02$ (at 25 ± 2°), which shows that photolysis into

$$(\pi\text{-}C_5H_5)_2Mo_2(CO)_6 + Br^- \xrightarrow{h\nu} (\pi\text{-}C_5H_5)Mo(CO)_3Br + (\pi\text{-}C_5H_5)Mo(CO)_3^- \qquad (7)$$

TABLE 2

SPECTRAL PROPERTIES OF THE $(\pi\text{-}C_5H_5)Mo(CO)_2X_2^-$ ANIONS IN ACETONE

Anion	λ_{max}(nm)[a,b]	$\tau(\pi\text{-}C_5H_5)$[c]	ν(CO)(cm^{-1})[b,d]
$(\pi\text{-}C_5H_5)Mo(CO)_2Cl_2^-$	514	4.48	1941s, 1827m
$(\pi\text{-}C_5H_5)Mo(CO)_2Br_2^-$	520	4.53	1940s, 1835s
$(\pi\text{-}C_5H_5)Mo(CO)_2I_2^-$	514	4.81	1936s, 1832s
$(\pi\text{-}C_5H_5)Mo(CO)_2(SCN)_2^-$	464	4.41	1956s, 1859s
$(\pi\text{-}C_5H_5)Mo(CO)_2(CN)_2^-$			1960s, 1870s [12]

[a] ± 2 nm. [b] $[X^-] = 10^{-2}M$ as $N(n\text{-}C_4H_9)_4^+$ or K^+ salts. [c] ± 0.05 versus acetone at τ 7.93. Solutions were saturated in $N(n\text{-}C_4H_9)_4^+$ or K^+ salts. [d] ± 3 cm^{-1} abbreviations used are strong(s) and medium(m).

the low energy band is considerably more efficient than photolysis into the high energy band. Φ_{546} is independent of [Br^-] over the range 0.5-10 × 10^{-3} M within experimental error. The value given for Φ at 366 nm is an upper limit for the reaction with Br^- since it was obtained by following the disappearence of [(π-C_5H_5)Mo($CO)_3$]$_2$ at 382 nm and a quantitative determination of the products arising solely from UV irradiation was not determined.

We have begun quantum yield measurements on the photoreactions between [(π-C_5H_5)Mo($CO)_3$]$_2$ and Cl^- or $P(OC_6H_5)_3$. From our initial results the same wavelength dependence holds, at least qualitatively, for the reactions with Cl^- and $P(OC_6H_5)_3$.

Discussion

The photochemistry of [(π-C_5H_5)Mo($CO)_3$]$_2$ [1,7] is summarized in Scheme 1*. The chemistry is remarkable for the existence of several carefully balanced photochemical pathways which arise from two basic net reactions: displacement of CO and disproportionation. Qualitatively, at least, reactions (A) and (B) in Scheme 1 are similar in wavelength dependence, solvent dependence, and quantum efficiency. The similarities are surprising for two net reactions seemingly as different as (A) and (B). However, both net reactions can be viewed as photosubstitutions, in (A) the displacement of CO by L and in (B) of (π-C_5H_5)Mo($CO)_3^-$ by X^-, and both may be similar in the primary photochemical act.

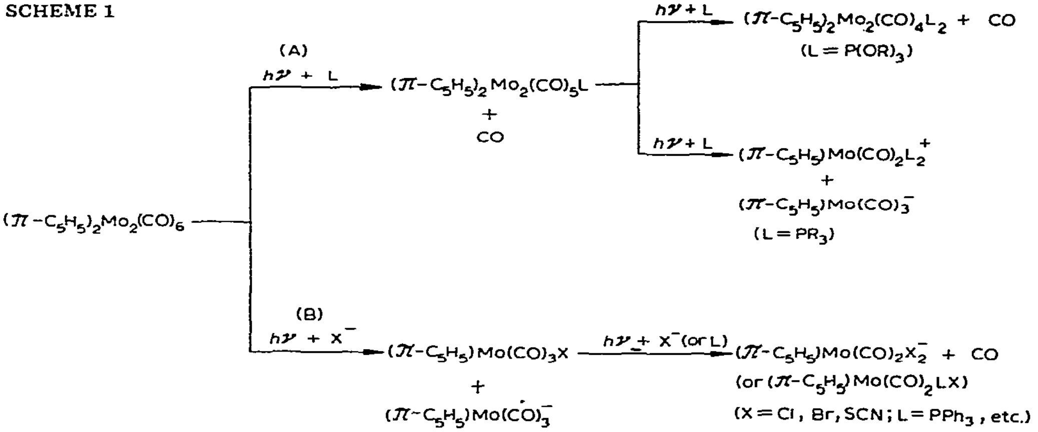
It should be noted that Scheme 1 is a summary of net reactions without implication for mechanistic details of the primary photochemical act or for the overall photochemical mechanism.

The thermal reactions (8) between [(π-C_5H_5)Mo($CO)_3$]$_2$ (2 × 10^{-3} M) and

$$(\pi\text{-}C_5H_5)_2Mo_2(CO)_6 + X^- \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_3X + (\pi\text{-}C_5H_5)Mo(CO)_3^- \qquad (8)$$

X^-(10^{-2} M) in acetone at 25° are slow; in the absence light no reaction was observed after one hour. However, the reverse reactions (9) are also slow or do not

SCHEME 1



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* In some cases the intermediate complexes (π-C_5H_5)$_2$Mo$_2$(CO)$_5$L have not been observed as products in synthetic studies, apparently because of the higher quantum efficiency of the second step.

$$(\pi\text{-}C_5H_5)Mo(CO)_3^- + (\pi\text{-}C_5H_5)Mo(CO)_3X \rightarrow (\pi\text{-}C_5H_5)_2Mo_2(CO)_6 + X^- \qquad (9)$$

occur [8] and the products of the light-catalyzed reaction (Reaction B) may be thermodynamically favored.

In the reactions with X^-, the quantum yields are considerably higher for the low energy transition in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ (λ_{max} 500 nm) than for the high energy transition (λ_{max} 382 nm). Although wavelength effects are not uncommon in photoreactions of transition metal complexes [9], the wavelength dependence observed here is interesting, because the upper excited states are less reactive than the lower.

In contrast to the reactions of the binary metal carbonyls [10], the photochemical reactions of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ with either X^- or L are strongly solvent dependent. They occur with relatively high efficiency in acetone, tetrahydrofuran, and acetonitrile, but with low efficiency in benzene. The solvent dependence has important synthetic consequences. For example, the net reaction

$$(\pi\text{-}C_5H_5)_2Mo_2(CO)_6 + 2P(OPh)_3 \rightarrow [(\pi\text{-}C_5H_5)Mo(CO)_2P(OPh)_3]_2 + 2CO \qquad (10)$$

(10) occurs in high yield (85%) in minutes in acetone, while in benzene the reaction times are longer (hours) and the yields considerably lower. We are currently investigating the detailed mechanisms of the light catalyzed reactions in an attempt to understand the wavelength and solvent dependencies, the origins of the electronic transitions, and the factors important in determining the favored photochemical pathways.

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