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Photochemistry of Transition Metal Hydride Complexes. 3. Photoinduced Elimination of Molecular Hydrogen from $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$

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Ultraviolet irradiation of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ results in elimination of molecular hydrogen and generation of $[Mo(\eta^5\text{-}C_5H_5)_2]$ with a 366-nm quantum yield of 0.1 ± 0.02. The reactive molybdenocene intermediate is readily trapped by CO and C_2H_2 to yield known adducts and by PEt_3 and PPh_3 to give the new tertiary phosphine complexes $[Mo(\eta^5\text{-}C_5H_5)_2PEt_3]$ and $[Mo(\eta^5\text{-}C_5H_5)_2PPh_3]$. In the absence of substrate an uncharacterized, presumably oligomeric $[Mo(\eta^5\text{-}C_5H_5)_2]_x$ complex results. Mechanistic experiments suggest that the photochemical reaction proceeds through concerted elimination of molecular hydrogen but that additional H_2 is formed through a subsequent secondary reaction between $[Mo(\eta^5\text{-}C_5H_5)_2]$ and $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$. The nature of the active excited state which leads to H_2 elimination is discussed in view of the electronic absorption spectrum of the complex and published molecular orbital calculations.

Introduction

We have previously demonstrated that photoinduced elimination of molecular hydrogen from thermally stable di- and trihydride complexes is a common reaction pathway.[1-3] For example, $[IrClH_2(PPh_3)_3]$ and $[RuH_2(CO)(PPh_3)_3]$ do not lose hydrogen under thermal conditions but undergo efficient elimination of H_2 upon photolysis, eq 1 and 2.[1,2] We

$$[IrClH_2(PPh_3)_3] \xrightarrow{h\nu} H_2 + [IrCl(PPh_3)_3] \quad (1)$$

$$[RuH_2(CO)(PPh_3)_3] \xrightarrow{h\nu} H_2 + [Ru(CO)(PPh_3)_3] \quad (2)$$

have now set out to demonstrate the generality of this photoreaction and especially its usefulness for the generation of reactive, coordinatively unsaturated intermediates. We have accordingly undertaken a study of the photochemistry of polyhydride complexes of the early transition metals and herein report the results of our investigation of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ and $[W(\eta^5\text{-}C_5H_5)_2H_2]$.

The latter complex has been previously studied by Green and co-workers who showed that UV irradiation of solutions of $[W(\eta^5\text{-}C_5H_5)_2H_2]$ led to the formation of the insertion products $[W(\eta^5\text{-}C_5H_5)_2H(R)]$ and $[W(\eta^5\text{-}C_5H_5)_2(R)_2]$, in which R is derived from the solvent or from added substrate.[4-7] Irradiation of $[W(\eta^5\text{-}C_5H_5)_2H_2]$ in benzene, for example, gave $[W(\eta^5\text{-}C_5H_5)_2H(C_6H_5)]$,[4] and in methanol $[W(\eta^5\text{-}C_5H_5)_2H(OMe)]$ and $[W(\eta^5\text{-}C_5H_5)_2Me(OMe)]$[6] were formed. The mechanisms of these reactions have not been worked out although it was recently noted[7] that three possibilities should be considered for the initial photochemical step. Photolysis could lead to direct concerted elimination of H_2 and generation of tungstenocene, eq 3, or irradiation could induce hydrogen migration to one of the C_5H_5 rings to give a coordinated diene, eq 4. Alternately, photolysis could induce one of the C_5H_5 rings to slip to give an intermediate with an $\eta^3\text{-}C_5H_5$ ligand, eq 5. Each of these three possible intermediates is a 16-valence-electron complex that should be reactive enough to undergo the initial insertion reaction. No experiments designed to elucidate the actual photochemical mechanism have been reported, and the quantum efficiencies of the $[W(\eta^5\text{-}C_5H_5)_2H_2]$ reactions have not been given.

$$[M(\eta^5\text{-}C_5H_5)_2H_2] \xrightarrow{h\nu} H_2 + [M(\eta^5\text{-}C_5H_5)_2] \quad (3)$$

$$[M(\eta^5\text{-}C_5H_5)_2H_2] \xrightarrow{h\nu} [M(\eta^5\text{-}C_5H_5)H(C_5H_6)] \quad (4)$$

$$[M(\eta^5\text{-}C_5H_5)_2H_2] \xrightarrow{h\nu} [M(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)H_2] \quad (5)$$

The photochemical properties of the corresponding carbonyl complexes have been studied by Brintzinger et al.[8] who showed that irradiation leads to loss of carbon monoxide and transient generation of molybdenocene and tungstenocene, eq 6.

$$[M(\eta^5\text{-}C_5H_5)_2(CO)] \xrightarrow{h\nu} [M(\eta^5\text{-}C_5H_5)_2] + CO \quad (6)$$

Although the reactive metallocenes could not be isolated, they were readily trapped by irradiation in the presence of added substrate to yield adduct complexes. Photolysis of $[Mo(\eta^5\text{-}C_5H_5)_2(CO)]$ in the absence of substrate led only to a poorly characterized material which was suggested to contain "polymeric" $[Mo(\eta^5\text{-}C_5H_5)_2]_x$.[8-10] This material is similarly obtained upon reduction of $[Mo(\eta^5\text{-}C_5H_5)_2Cl_2]$ with Na(Hg).[9,10]

Experimental Section

The complexes $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$, $[Mo(\eta^5\text{-}C_5H_5)_2D_2]$, $[W(\eta^5\text{-}C_5H_5)_2H_2]$, and $[W(\eta^5\text{-}C_5H_5)_2D_2]$ were prepared by published procedures.[11] Triphenylphosphine was obtained from Aldrich Chemical Co. and was recrystallized from benzene/ethanol before use. Triethylphosphine was obtained from Orgmet, Inc. Other chemicals were reagent grade and were used without further purification. All solvents employed were dried by standard methods and were rigorously degassed prior to use. Manipulations and reactions with air-sensitive compounds were carried out under purified N_2 or argon atmospheres unless otherwise indicated. Acetylene and carbon monoxide gases were obtained from Matheson Gas Products. The carbon monoxide was deoxygenated and dried by passing it through BASF BTS Katalysator and Linde 5-Å molecular sieve columns.

General Irradiation Procedures. Irradiations were conducted at 366 nm using a 450-W Hanovia medium-pressure Hg lamp equipped with Corning Glass 0-52 and 7-37 filters ($I \approx 10^{-6}$ einstein/min), with a 100-W Blak-Ray B100A lamp equipped with a 366-nm narrow band-pass filter, or in a 350-nm Rayonet photoreactor. The complex to be studied was placed in an evacuable quartz UV cell or a Schlenk tube, and after degassing, the appropriate solvent was distilled onto the sample. Solutions for infrared studies were transferred in an inert-atmosphere glovebox to 0.5-mm NaCl solution infrared cells. Solutions were irradiated with the appropriate lamp and electronic and infrared spectra periodically recorded. Samples for ^1H and ^{31}P NMR spectra were similarly prepared and the NMR tubes sealed under vacuum. Lamp intensities were measured by ferrioxalate actinometry.[12] The quantum yields of H_2 loss from $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ and $[W(\eta^5\text{-}C_5H_5)_2H_2]$ were determined by 366-nm irradiation ($I = 1.42 \times 10^{-6}$ einstein/min) of multiple samples of thoroughly degassed hexane solutions placed in sealed UV cells. The reactions were monitored by measuring the decrease in intensity of the complexes' characteristic 270-nm absorption bands. Since the products do not absorb appreciably at 270 nm and the conversions were limited to <10%, corrections for inner filter effects were not made.

Photolysis of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$. Prolonged photolysis of degassed isooctane, benzene, and hexane solutions of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ with UV light gave a color change from yellow to brown and slow deposition of an amorphous red-brown precipitate. Analysis of the gases above the irradiated solutions by mass spectroscopy and gas chromatography on a Linde 5-Å molecular sieve column in series with a 60–80 mesh Fluorosilicone column demonstrated the production of H_2. Toepler

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Table I. Electronic Absorption Spectral Data[a]

complex	λ_{max}, nm	ϵ
$[Mo(\eta^5\text{-}C_5H_5)_2H_2]$	270	4800
	315	1300
$[W(\eta^5\text{-}C_5H_5)_2H_2]$	270	5000
	325	880
$[Mo(\eta^5\text{-}C_5H_5)_2CO]$	270	3400
	322	960
	620	20

[a] Measured in hexane solution.

pump analysis of an exhaustively photolyzed pentane solution of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ gave a value of 1.62 mol of H_2 released/mol of complex irradiated.

Preparation of $[Mo(\eta^5\text{-}C_5H_5)_2PEt_3]$ and $[Mo(\eta^5\text{-}C_5H_5)_2PPh_3]$. Irradiation of a degassed isooctane solution (75 mL) containing $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ (100 mg, 4.4×10^{-4} mol) and excess PPh_3 (1.15 g, 4.4×10^{-3} mol) gave a color change from yellow to red-orange. Removal of solvent and sublimation at 80–90 °C (10^{-3} mmHg) yielded red-orange $[Mo(\eta^5\text{-}C_5H_5)_2PPh_3]$. The product is often contaminated with cosublimed PPh_3 and $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$.

Photolysis of a degassed isooctane solution (75 mL) containing $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ (100 mg, 4.4×10^{-4} mol) and excess PEt_3 (0.52 g, 4.4×10^{-3} mol) gave a color change from yellow to red-orange. Removal of solvent followed by prolonged evacuation to remove excess PEt_3 yielded red-orange $[Mo(\eta^5\text{-}C_5H_5)_2PEt_3]$ which was purified by sublimation at 70–80 °C (10^{-3} mmHg). The product is more easily collected by evaporation of solvent and excess PEt_3, slow sublimation of unreacted $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ at 50 °C (10^{-3} mmHg), and finally sublimation of $[Mo(\eta^5\text{-}C_5H_5)_2PEt_3]$ at 70–80 °C (10^{-3} mmHg). This method gave nearly quantitative conversion based on reacted dihydride, although small amounts of $[Mo(\eta^5\text{-}C_5H_5)_2]_x$ were sometimes present. Elemental analyses of these PR_3 adducts were not attempted because of their extreme air sensitivity.

Mechanistic Experiments. Sample solutions of $[M(\eta^5\text{-}C_5H_5)_2H_2]$ and $[M(\eta^5\text{-}C_5H_5)_2D_2]$ (M = Mo or W) were prepared by distillation of the appropriate degassed solvent into Schlenk tubes containing the complex. The sample solutions were subjected to short-term photolysis (<5 min) in a 350-nm Rayonet photoreactor. The solutions were immediately frozen after photolysis and the mass spectra of the gases above the frozen solutions recorded.

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 621 grating infrared spectrophotometer using KBr disks prepared from IR spectroquality powder (MC&B) or 0.5-mm path length NaCl solution infrared cells. Electronic absorption spectra were recorded with a Cary 17 spectrophotometer using degassable 1-cm or 1-mm path length quartz spectrophotometer cells. Mass spectra were recorded with an AEI MS902 mass spectrometer and ^1H and ^{31}P NMR spectra with a JEOL PS-100 FT Fourier transform NMR spectrometer. ^{31}P samples were recorded in 1:1 C_6H_6/C_6D_6 solutions and referenced to external H_3PO_4 (85%). All downfield resonances are reported as positive. ^1H NMR spectra were recorded in C_6D_6 solution and referenced to $(CH_3)_4Si$.

Results

Electronic Absorption Spectra. The electronic absorption spectra of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$, $[W(\eta^5\text{-}C_5H_5)_2H_2]$, and $[Mo(\eta^5\text{-}C_5H_5)_2CO]$ are shown in Figure 1 and the data summarized in Table I. The three compounds show surprisingly similar spectra with a sharp, intense band near 270 nm (ϵ (3–5) $\times 10^3$) that is weakly shouldered at 315–330 nm. The carbonyl complex shows an extended absorption into the visible region with an apparent band maximum at 620 nm. The spectrum of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ sharpens considerably on cooling of the compound to 77 K, Figure 2, and the shoulder at 310 nm is clearly resolved.

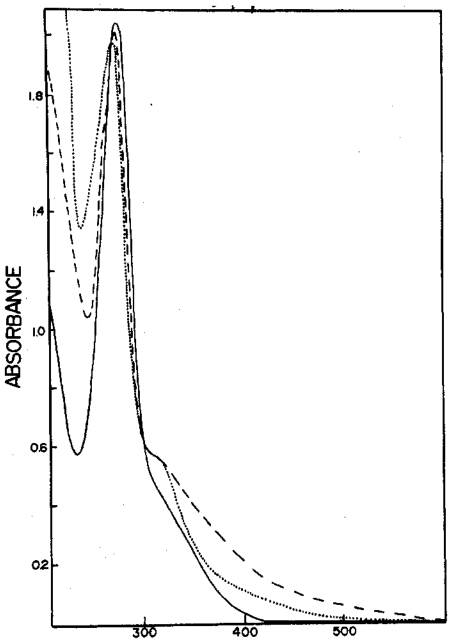


Figure 1. Electronic absorption spectra of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ (---), $[W(\eta^5\text{-}C_5H_5)_2H_2]$ (—), and $[Mo(\eta^5\text{-}C_5H_5)_2CO]$ (···) in degassed hexane solution.

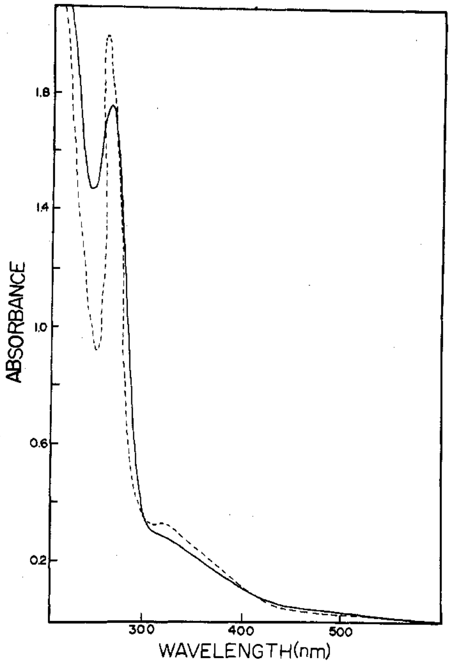


Figure 2. Electronic absorption spectrum of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ in ethanol solution at 300 (—) and 77 K (---).

Photolysis of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$. $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ is an exceedingly stable compound in the absence of air. It can be readily purified by vacuum sublimation at 100 °C, and it shows no tendency to lose H_2 under a variety of thermal conditions. The complex is quite photosensitive, however. Irradiation of degassed isooctane, benzene, and hexane solutions of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ with 366-nm light results in a rapid color change from yellow to brown. Analysis of the gases above an irradiated hexane solution showed the presence of molecular hydrogen, and exhaustive photolysis gave a value of 1.62 mol of H_2 released/mol of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ irradiated. As the irradiation proceeds, a smooth decrease in intensity of the 1847-cm^{-1} ν_{M-H} of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ occurs, and no new bands appear in the ν_{M-H} region. Smooth electronic spectral changes were not obtained, however, and after several hours of photolysis a very air-sensitive red-brown precipitate was deposited. This material showed a complex pattern of ^1H NMR resonances between τ 4.5 and 6.0 indicative of multiple nonequivalent cyclopentadienyl protons but no infrared or ^1H NMR evidence for a hydride ligand. A similar red-brown

Table II. Spectral Data for $[Mo(\eta^5\text{-}C_5H_5)_2PR_3]$ Complexes

complex	^1H NMR,[a] ppm	$^{31}P\{^1H\}$ NMR,[b] ppm	mass spectral data
$[Mo(\eta^5\text{-}C_5H_5)_2PEt_3]$	3.83 d ($J_{P-H} = 5$ Hz)	34.9 s	349 (7), 348 (36), 347 (17), 346 (100), 345 (52), 344 (76), 343 (71), 342 (40), 341 (12), 340 (57), 339 (3)[c]
$[Mo(\eta^5\text{-}C_5H_5)_2PPh_3]$	3.82 d ($J_{P-H} = 4$ Hz)	18.9 s	490[d]

[a] Value given is for the η^5-C_5H_5 protons; d = doublet. [b] s = singlet. [c] Isotopic distribution of parent ion from electron impact mass spectrum. Values in parentheses are the relative intensities. [d] Center of poorly resolved isotope pattern from a chemical ionization mass spectrum.

precipitate obtained by Brintzinger et al.[8] upon photolysis of $[Mo(\eta^5\text{-}C_5H_5)_2CO]$ was suggested to contain "polymeric" $[Mo(\eta^5\text{-}C_5H_5)_2]_x$. The lack of evidence for a hydride ligand and the complex ^1H NMR spectrum suggest a similar formulation for our product. The formation of H_2 and the $[Mo(\eta^5\text{-}C_5H_5)_2]_x$ product is consistent with the overall reaction shown in eq 7.

$$[Mo(\eta^5\text{-}C_5H_5)_2H_2] \xrightarrow[366\text{ nm}]{h\nu} H_2 + [Mo(\eta^5\text{-}C_5H_5)_2] \rightarrow [Mo(\eta^5\text{-}C_5H_5)_2]_x \quad (7)$$

Irradiation induces elimination of molecular hydrogen and generation of molybdenocene which in the absence of substrate apparently oligomerizes to $[Mo(\eta^5\text{-}C_5H_5)_2]_x$. No insertion products analogous to those reported[4,5] for $[W(\eta^5\text{-}C_5H_5)_2H_2]$ were formed. The 366-nm quantum yield for disappearance of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ is 0.1 ± 0.02. The quantum yield was measured in a sealed UV cell because of the air sensitivity of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$, and the reverse reaction with H_2 was not prevented. The quantum yield must thus be considered as a lower limit value for photoelimination of H_2.

Although the molybdenocene intermediate cannot be isolated as such, it can be readily trapped by added substrate. Irradiation of thoroughly deoxygenated benzene or hexane solutions of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ with 366-nm light in the presence of a carbon monoxide purge gave a color change from yellow to green. Removal of solvent followed by vacuum sublimation at 25–35 °C (10^{-3} mmHg) gave volatile dark green air-sensitive crystals which were characterized as $[Mo(\eta^5\text{-}C_5H_5)_2(CO)]$ by their infrared ($\nu_{C\equiv O}$ 1910 cm^{-1}), ^1H NMR (τ 5.75) and mass spectra ($[Mo(\eta^5\text{-}C_5H_5)_2(CO)]^+$ at $m/e = 258$).[9,10] The photogenerated molybdenocene is thus scavanged by CO to form $[Mo(\eta^5\text{-}C_5H_5)_2(CO)]$, eq 8. The conversion of the dihydride to the carbonyl complex appears to be nearly quantitative, although small quantities of $[Mo(\eta^5\text{-}C_5H_5)_2]_x$ are sometimes obtained.

$$[Mo(\eta^5\text{-}C_5H_5)_2H_2] + CO \xrightarrow[366\text{ nm}]{h\nu} [Mo(\eta^5\text{-}C_5H_5)_2(CO)] + H_2 \quad (8)$$

Irradiation of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ in the presence of an acetylene purge gave a color change from yellow to orange-brown. Removal of solvent followed by vacuum sublimation at 25–35 °C (10^{-3} mmHg) yielded extremely air-sensitive orange crystals of $[Mo(\eta^5\text{-}C_5H_5)_2(C_2H_2)]$, identified by the two singlets in its ^1H NMR spectrum at τ 2.3 and 5.7.[8]

$$[Mo(\eta^5\text{-}C_5H_5)_2H_2] + C_2H_2 \xrightarrow[366\text{ nm}]{h\nu} [Mo(\eta^5\text{-}C_5H_5)C_2H_2] + H_2 \quad (9)$$

The molybdenocene intermediate can also be trapped by photolysis in the presence of tertiary phosphines, eq 10. The photoreactions are mose conveniently monitored by $^{31}P\{^1H\}$ NMR spectroscopy. Photolysis of a C_6D_6 solution of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ and PPh_3 gave a smooth decrease in the relative intensity of the −6.0 ppm resonance of free PPh_3 and the appearance of a new singlet at 18.9 ppm. Similarly, photolysis of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ in the presence of PEt_3 led to the appearance of a new singlet at 34.8 ppm and a decrease in relative intensity of the −20.5 ppm resonance of uncoordinated PEt_3. Crystalline complexes were isolated from the photoreactions by removal of solvent and vacuum sublimation. The products were characterized as $[Mo(\eta^5\text{-}C_5H_5)_2PEt_3]$ and $[Mo(\eta^5\text{-}C_5H_5)_2PPh_3]$ by the mass spectral and NMR data summarized in Table II. The PPh_3 adduct is difficult to obtain free of uncoordinated PPh_3, but the PEt_3 adduct can be obtained pure. Reaction of the $[Mo(\eta^5\text{-}C_5H_5)_2PR_3]$ complexes with CO or diphenylacetylene (DPA) gave ready conversion to the known $[Mo(\eta^5\text{-}C_5H_5)_2CO]$ and $[Mo(\eta^5\text{-}C_5H_5)_2DPA]$[13] derivatives.

$$[Mo(\eta^5\text{-}C_5H_5)_2H_2] + PR_3 \xrightarrow{h\nu} [Mo(\eta^5\text{-}C_5H_5)_2PR_3] + H_2 \quad (10)$$

Photolysis of $[W(\eta^5\text{-}C_5H_5)_2H_2]$. Irradiation of degassed hexane solutions of $[W(\eta^5\text{-}C_5H_5)_2H_2]$ with 366-nm light gave slow deposition of a precipitate similar to that previously described[10] as $[W(\eta^5\text{-}C_5H_5)_2]_x$. Mass spectral analysis of the gases above the irradiated solutions showed considerable amounts of molecular hydrogen. The reaction shown in eq 11 presumably obtains. Irradiation in aromatic solvents leads to the previously described insertion products.[4,5] Photolysis of $[W(\eta^5\text{-}C_5H_5)_2H_2]$ in the presence of CO and C_2H_2 under identical conditions to which $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ gave adduct complexes did not yield the tungstenocene adducts but instead gave $[W(\eta^5\text{-}C_5H_5)_2]_x$. The lower limit 366-nm quantum yield for elimination of H_2 from $[W(\eta^5\text{-}C_5H_5)_2H_2]$ is 0.01 ± 0.002.

$$[W(\eta^5\text{-}C_5H_5)_2H_2] \xrightarrow[366\text{ nm}]{h\nu} H_2 + [W(\eta^5\text{-}C_5H_5)_2] \rightarrow [W(\eta^5\text{-}C_5H_5)_2]_x \quad (11)$$

Discussion

The results reported herein clearly demonstrate that elimination of molecular hydrogen from $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ can be induced by irradiation with ultraviolet light. In degassed solutions the reaction proceeds with moderate efficiency giving a lower limit 366-nm quantum yield of 0.1. In the absence of added substrate, an apparently oligomeric material results, presumably from insertion of the metal into C–H bonds of the cyclopentadienyl rings (see below). In the presence of substrate, however, the reactive molybdenocene intermediate can be readily trapped to give known CO and C_2H_2 adducts and the new PEt_3 and PPh_3 complexes.

Electronic Structure. The nature of the photoactive excited state which gives rise to elimination of molecular hydrogen is of considerable importance. Spectral studies of the di- and trihydride complexes which we previously examined[1-3] provided little information concerning the active excited states because of poor spectral resolution and lack of supportive calculations. However, the electronic absorption spectra of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ and $[W(\eta^5\text{-}C_5H_5)_2H_2]$ appear amenable to interpretation. They are shown in Figure 1 along with that of $[Mo(\eta^5\text{-}C_5H_5)_2CO]$ for comparison. To interpret these spectra

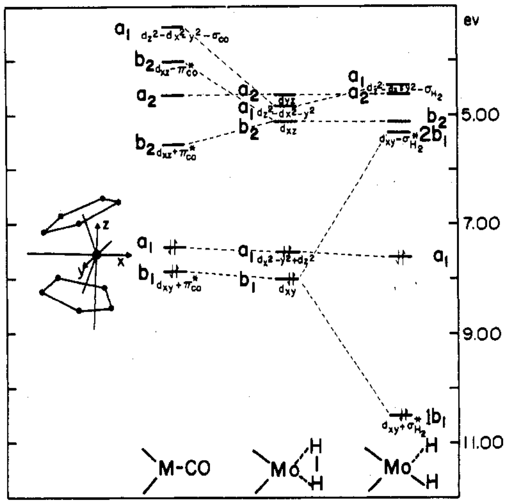


Figure 3. Molecular orbital diagrams for $[Mo(\eta^5\text{-}C_5H_5)_2(CO)]$ and $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$, adapted from ref 15.

we make use of the molecular orbital calculations of Peterson et al.[14] and Brintzinger et al.[15] for these complexes. These two independent calculations used different theoretical approaches, but they gave remarkably good agreement in both the order and the relative energies of the molecular orbitals. Further, the calculated orbital orderings are fully consistent with recent photoelectron spectral studies on these complexes.[16]

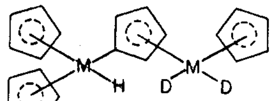
The important features of the orbital diagrams for $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ and $[Mo(\eta^5\text{-}C_5H_5)_2CO]$ are redrawn in Figure 3 from the diagram given by Brintzinger et al.[15] The highest occupied orbital in each of the complexes is a largely nonbonding combination of d_{z^2} and $d_{x^2-y^2}$ of a_1 symmetry. The calculations of Brintzinger et al.[15] gave the lowest unoccupied orbital in $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ as $2b_1$ (d_{xy}–H_2*) which is strongly antibonding between the metal and the two hydrogens, although a series of other orbitals are calculated to be in close proximity to $2b_1$.[14,15] It is reasonable to assume that population of this strongly antibonding orbital would lead to elimination of molecular hydrogen. The quantum yield of 0.1 as a *lower limit* for elimination of H_2 suggests that this orbital must be significantly populated upon excitation, and hence a reasonable assignment for the lowest energy shoulder in the spectra of both $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ and $[W(\eta^5\text{-}C_5H_5)_2H_2]$ is $^1A_1 \rightarrow {}^1B_1$ ($1b_1{}^2a_1{}^2 \rightarrow 1b_1{}^2a_12b_1$). The breadth of this band, especially in the molybdenum complex, is consistent with an excited state which is largely dissociative in nature.

Assignment of the intense 270-nm band in the spectra of the dihydride complexes and $[Mo(\eta^5\text{-}C_5H_5)_2CO]$ is less clear. This band could be assigned as a transition between the largely nonbonding a_1 and a_2 orbitals since the calculations of Brintzinger et al.[15] give a similar energy separation between these orbitals for both the CO and the H_2 complexes. The relative sharpness of this band and its constancy in position are consistent with such an assignment. However, in the C_{2v} point group appropriate for these complexes the $^1A_1 \rightarrow {}^1A_2$ ($1b_1{}^2a_1 \rightarrow 1b_1{}^2a_1a_2$) transition is forbidden, yet the 270-nm band has an extinction coefficient near 5000. A more likely assignment is metal to cyclopentadienyl charge transfer. The energy of such an MLCT transition should be similar for the CO and H_2 complexes since the highest occupied a_1 orbitals of the two complexes are calculated to be nearly isoenergetic.[15] The lack of any intensity decrease in this band upon cooling to 77 K argues against a forbidden transition and supports an MLCT assignment.

Mechanism of H_2 Elimination. The mechanism of the photoelimination reaction is of some importance. Hydrogen could be eliminated from the complex directly as H_2 or stepwise as H·, H^+, or H^-. However, heterolytic cleavage of a Mo–H bond to generate H^+ or H^- would appear unlikely in the nonpolar aliphatic and aromatic solvents employed in this study. Mass spectral analysis of the gases above irradiated toluene-d_8 solutions of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ showed predominantly H_2 with less than 10% HD produced. Since toluene is an efficient scavenger for free hydrogen atoms, the lack of an appreciable amount of HD indicates that hydrogen atoms are not produced to a significant extent in the photolysis. Thus, elimination of hydrogen from the complex directly as H_2 is implied.

Elimination of H_2 can occur via three different routes: direct concerted elimination of H_2, forced concerted loss of H_2 from a photogenerated $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)H_2]$ intermediate (eq 5), and intramolecular hydrogen abstraction from a η^5-C_5H_5 ligand. Irradiation of $[Mo(\eta^5\text{-}C_5H_5)_2D_2]$ in C_6H_6 or C_6D_6 solution gave a mixture of D_2 and HD in an approximate ratio of 1.6/1, in each case. The substantial production of D_2 must arise via *concerted elimination* of D_2 since abstraction of hydrogen from a C_5H_5 ring would yield HD. The labeling experiments do not allow us to distinguish between direct concerted loss of H_2 from the photoexcited complex and forced concerted loss of H_2 caused by interaction of solvent or substrate with a $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)H_2]$ intermediate. However, we can see no priori reason why a 16-valence-electron $[Mo(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_5H_5)H_2]$ intermediate would spontaneously lose H_2, and it is extremely unlikely that a solvent such as hexane would interact with this species in such a way as to force H_2 loss. Furthermore, the above discussion of the electronic structure of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ is consistent with direct concerted elimination of H_2, as is our previous demonstration of concerted photochemical loss of H_2 from $[IrClH_2(PPh_3)_3]$.[1] We thus prefer the latter mechanistic path.[17]

The HD produced upon photolysis of $[Mo(\eta^5\text{-}C_5H_5)_2D_2]$ in C_6H_6 or C_6D_6 solution likely arises through a subsequent thermal reaction of photogenerated $[Mo(\eta^5\text{-}C_5H_5)_2]$ with unreacted $[Mo(\eta^5\text{-}C_5H_5)_2D_2]$. This could proceed by hydrogen abstraction to give a dimeric intermediate with an η^1,η^5-C_5H_4 ligand, such as that shown in **1**, which could then eliminate HD. Such a process would lead to the oligomeric $[Mo(\eta^5\text{-}C_5H_5)_2]_x$ product isolated from photolysis of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ in degassed solution. Dimeric intermediates similar to **1** have recently been described by Green and co-workers[18] and are analogous to well-known niobocene and titanocene structures.[19-21] The 1.62 mol of H_2 released/mol of $[Mo(\eta^5\text{-}C_5H_5)_2H_2]$ irradiated is consistent with this suggestion. The excess H_2 can only be produced through metalation followed by further elimination of H_2.



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Registry No. $Mo(\eta^5\text{-}C_5H_5)_2H_2$, 1291-40-3; $W(\eta^5\text{-}C_5H_5)_2H_2$, 1271-33-6; $Mo(\eta^5\text{-}C_5H_5)_2CO$, 12701-85-8; $Mo(\eta^5\text{-}C_5H_5)_2PEt_3$, 63672-65-1; $Mo(\eta^5\text{-}C_5H_5)_2PPh_3$, 63672-64-0; $[Mo(\eta^5\text{-}C_5H_5)_2]_x$, 9061-89-6; $[W(\eta^5\text{-}C_5H_5)_2]_x$, 39330-65-9.

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Mechanism of the Reaction of *cis*-Bis(*N*,*N*-diethyldithiocarbamato)dinitrosylmolybdenum with Azide or Cyanate and Related Reactions

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The reaction of *cis*-bis(*N*,*N*-diethyldithiocarbamato)dinitrosylmolybdenum with either azide, cyanate, cyanide, or diethyldithiocarbamate in hot dimethyl sulfoxide yields dinitrogen oxide. The reactions are initiated by coordination of the anion leading to activation of a nitrosyl group. ^{15}N labeling and kinetic studies show that an intermolecular mechanism is involved. This is suggested to involve coupling of two molecules of reactive complex through a nitrosyl ligand on each to give a bridged hyponitrito type species. In the presence of excess azide the rate law is of the form $-\mathrm{d}/\mathrm{d}t[\mathrm{Mo(Et_2dtc)_2(NO)_2}] = (k_1[\mathrm{N_3}] + k_2)[\mathrm{Mo(Et_2dtc)_2(NO)_2}]$. At 63.7 °C k_1 is 1.86×10^{-3} L mol^{-1} s^{-1} and k_2 is 0.78×10^{-5} s^{-1} and for the second-order path $\Delta H^\ddagger$ is 91 ± 4 kJ mol^{-1} and $\Delta S^\ddagger$ is -29 ± 12 J deg^{-1} mol^{-1}.

Introduction

In a previous paper[1] we reported the unusual reaction between *cis*-bis(*N*,*N*-diethyldithiocarbamato)dinitrosylmolybdenum ($\mathrm{Mo(Et_2dtc)_2(NO)_2}$) and either azide or cyanate which gives dinitrogen oxide and complexes of the type $[\mathrm{MoL(Et_2dtc)_2(CH_3)_2SONO}]$ (L = $\mathrm{N_3}$, NCO). The gas originates entirely from the nitrosyl ligands. Several reactions which appear to be related to the above have recently been described in which various metal nitrosyl complexes yield dinitrogen oxide upon treatment with ligands such as CO and NO. These include compounds of Fe, Co, Rh, and Ir.[2-6] In this paper the mechanism of the reaction for molybdenum nitrosyls has been elucidated by means of ^{15}N labeled complexes and kinetic measurements.

Experimental Section

Materials. The various $\mathrm{Mo(R_2dtc)_2(NO)_2}$ and $\mathrm{W(R_2dtc)_2(NO)_2}$ complexes were prepared by the literature method.[8] All preparations had the correct C, H, N, and S analyses. The reagents $\mathrm{Mo(CO)_6}$, $\mathrm{W(CO)_6}$, $\mathrm{Br_2}$, $\mathrm{NaS_2CN(C_2H_5)_2{\cdot}H_2O}$, $\mathrm{NaS_2CN(CH_3)_2}$, $\mathrm{NaN_3}$, $\mathrm{KN_3}$, various amines (see later), and NO were laboratory grade chemicals used without further purification. Sodium and potassium cyanates were recrystallised from water to which glacial acetic acid was added until neutral to phenolphthalein. Their purities, estimated gravimetrically using semicarbazide, were found to be 99.3 and 98.7%, respectively. Solvents were AR grade and unless otherwise stated were used as supplied. For ^{15}N labeling and kinetic experiments the dimethyl sulfoxide was freshly distilled from calcium hydride under vacuum. The ligands pyrrolidyl-, di(*n*-butyl)-, and dibenzyldithiocarbamate were generated in situ by slow addition of the appropriate diamine (1.9×10^{-2} mol) to carbon disulfide (1.45 g; 1.9×10^{-2} mol) in methanol (40 cm^3). Sodium hydroxide (0.76 g; 1.9×10^{-2} mol) was added and the solution stirred until it had dissolved. Sodium diisopropyldithiocarbamate was prepared similarly using 1:1 ethanol–water as solvent.

Table I. Isotopic Composition (Atom % ^{15}N)

NO	$\mathrm{Mo(Et_2dtc)_2(^{15}NO)_2}$	$\mathrm{Mo(Et_2dtc)_2(^{15}NO)NO}$	$\mathrm{Mo(Et_2dtc)_2(NO)_2}$
95	90.25	9.50	0.25
48	23.04	49.92	27.04

Preparation of ^{15}N Labeled Complexes. The literature synthesis[8] of *cis*-$\mathrm{Mo(R_2dtc)_2(NO)_2}$ using labeled NO and adapted to vacuum line techniques was employed. ^{15}NO (95 atom %) was obtained from the reaction of $\mathrm{K^{15}NO_3}$ (Bio-Rad, Richmond, Calif.; 0.09 g; 8.8×10^{-4} mol) and mercury (2 g; 1×10^{-2} mol) in concentrated sulfuric acid (2.5 cm^3; 4.5×10^{-2} mol).[9] ^{15}NO (48 atom %) was obtained similarly using a 1:1.07 mixture of $\mathrm{KNO_3}$ to 95 atom % $\mathrm{K^{15}NO_3}$. A mass spectrum using a freshly prepared sample of NO showed that the only impurity was a trace of $\mathrm{N_2O}$. The isotopic compositions of the cis complexes so prepared are shown in Table I. For experiments using ^{15}N labeled complexes all solutions were prepared in a glovebox under dry $\mathrm{N_2}$ and degassed on the vacuum line. Reactions between *cis*-$\mathrm{Mo(R_2dtc)_2(NO)_2}$ and azide or cyanate were completed by heating the dimethyl sulfoxide solutions at 60 °C for 12–14 h. The gaseous products were transferred using vacuum line techniques into a vessel cooled to −196 °C. Mass spectra were recorded with an AEI MS10-C2 mass spectrometer. Prior to measurement the gas vessel was cooled at −76 °C to remove traces of dimethyl sulfoxide.

Gas Volume Measurements. The volume of gas evolved has been measured using a thermostated gas buret system. In a typical experiment *cis*-$\mathrm{Mo(Et_2dtc)_2(NO)_2}$ (0.2 g; 4.42×10^{-4} mol) and KNCO (0.073 g; 8.95×10^{-4} mol) were dissolved in dimethyl sulfoxide (5 cm^3). The solution was degassed on the vacuum line and then heated at 60 °C for 13 h. The gas evolved was transferred into a measuring

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