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Inorganica Chimica Acta 300–302 (2000) 102–112

Inorganica Chimica Acta

Photoactivation of water by Cp'_2Mo and photochemical studies of Cp_2MoO. Investigation of a proposed water-splitting cycle and preparation of a water-soluble molybdocene dihydride

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Received 15 July 1999; accepted 27 October 1999

Abstract

Irradiation ($\lambda > 350$ nm) of Cp'_2MoH_2 ($Cp' = \eta^5$-$C_5H_4CH_3$) dissolved in 3:5 H_2O–CH_3CN (v/v) results in the quantitative formation of Cp'_2MoO and 2 equiv. of H_2. In light of this result, the photochemistry of the Cp'_2MoO and Cp_2MoO complexes was re-examined to determine the feasibility of using these molybdocene complexes as sensitizers in a photochemical water-splitting scheme. The metal-containing products formed by irradiation of Cp_2MoO were $[Cp_2MoO_2(MoO_2)]_2$, $\{(\eta$-$C_5H_5)(\mu$-$[\eta^1:\eta^5$-$C_5H_4])Mo\}_2$ ($C_{20}H_{18}Mo_2$) and Cp_2MoPPh_3 (in the presence of PPh_3), but gas chromatographic and mass spectroscopic analyses showed that free O_2 was not a product. Variations in the temperature, pH of the solution, and wavelength of the irradiating light did not yield any O_2. Experiments showed that O_2 reacted with Cp_2MoO to form $[Cp_2MoO_2(MoO_2)]_2$. A sensitive apparatus was therefore built to remove and quantitate any O_2 generated in solution (as little as 0.02 μmol of O_2) before it could react with Cp_2MoO, but no O_2 was detected in experiments using this apparatus. It is concluded that O_2 is not produced by irradiation of Cp_2MoO. Electron spin resonance experiments in the presence of α-phenyl-tert-butylnitrone, a radical spin trap, demonstrated that $Cp^{\bullet}$ radicals form when Cp_2MoO is irradiated, and it is proposed that this photoprocess may be responsible for the observed photochemistry. © 2000 Elsevier Science S.A. All rights reserved.

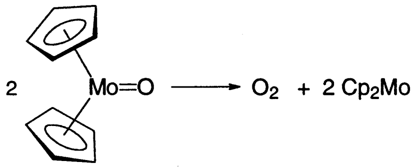
Keywords: Photochemistry; Molybdocene complexes; Water activation

1. Introduction

A vast majority of the published research working toward photochemical water-splitting has focused on systems based on outer-sphere electron transfer [1,2]. An alternative route for the activation of water involves oxidative addition to an organometallic complex. There are, however, relatively few examples of this type of activation, presumably due to the strength of the H–OH bond (≈ 119 kcal mol^{-1}) [3]. In a recent paper, we reported that irradiation of $Cp^*_2WH_2$ ($Cp^* = \eta^5$-$C_5(CH_3)_5$) in aqueous media results in the activation of water and the subsequent formation of H_2 via an oxidative addition route (Eq. (1)) [4]. Two equivalents of H_2 are formed in this reaction because the initial photoprocess is loss of H_2 to form Cp^*_2W.

$$Cp^*_2WH_2 \xrightarrow[-H_2]{h\nu} Cp^*_2W \xrightarrow{H_2O} Cp^*_2WH(OH) \rightarrow Cp^*_2WO + H_2 \quad (1)$$

What made this finding especially intriguing was that, in 1988, we reported that the closely-related Cp_2MoO molecule gave some O_2 on irradiation (Eq. (2)) [5]. The Cp_2M-based molecules (M = Mo or W) thus appear to be likely candidates for water-splitting catalysts. We therefore decided to re-examine the photochemistry of Cp_2MoO and Cp'_2MoO ($Cp' = \eta^5$-$C_5H_4CH_3$) with the goals of quantifying the amount of O_2 produced and of determining if O_2 and H_2 can be photochemically generated from water using the same catalyst. This paper



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PII: S0020-1693(99)00541-1

details our reinvestigation of the photochemistry of the Cp_2MoO and Cp'_2MoO complexes.

2. Results and discussion

2.1. Activation of water by Cp'_2MoH_2

A reaction analogous to Eq. (1) occurred with Cp'_2MoH_2 in aqueous solution (Eq. (3)). Thus, irradiation of Cp'_2MoH_2 ($\lambda > 350$ nm) in 3:5 H_2O–CH_3CN (v/v) formed Cp'_2MoO in quantitative yield (as determined by NMR) and 2 equiv. of H_2 (as determined by gas manometric measurements). The rates of H_2 and Cp'_2MoO formation were monitored as a function of time, and H_2 was produced at twice the rate of Cp'_2MoO.

$$Cp'_2MoH_2 \xrightarrow[H_2O]{h\nu} Cp'_2MoO + 2H_2 \qquad (3)$$

2.2. Irradiation of Cp_2MoO in nonaqueous solvents

To determine the feasibility of completing the water-splitting cycle started in Eq. (3), we reinvestigated the photochemistry of Cp_2MoO and Cp'_2MoO. Unless specifically noted, the results obtained with each complex were identical, and therefore the abbreviation Cp will be used throughout to indicate both the Cp and Cp′ ligands. Our initial goal was to quantify the amount of O_2 generated in reaction 2 because the original detection of O_2 by mass spectroscopy was only qualitative. For the quantitative analyses, gas chromatography (GC) was used to analyze the headspace gases above irradiated solutions of Cp_2MoO. In a typical experiment, a 0.39 M deoxygenated benzene solution of Cp_2MoO was placed in a septum-sealed 5-ml flask and irradiated ($\lambda > 350$ nm) for 15 h[1]. During this time the solution turned from green to brown, accompanied by the formation of a reddish–brown precipitate (previously identified as $[Cp_2MoO_2(MoO_2)]_2^5$) that was insoluble in common organic solvents. A gas tight syringe[2] was used to withdraw 250 μl of the headspace gases, which were immediately analyzed by GC. Peak areas corresponding to O_2 were calculated to represent 0.3 μmol, or a 0.1% yield. Repeated experiments (with both Cp'_2MoO and Cp_2MoO) showed that the apparent yield of O_2 (approximately 0.1% with 200 mg Cp_2MoO) could not be distinguished from the amount of O_2 found in control experiments conducted in the dark without Cp_2MoO. It is reasonable to assume that the minute amounts of O_2 observed in these experiments were due to air leakage through the septa or into the syringe needle.

As detailed in Section 4, mass spectroscopic analysis of the samples did not detect the presence of O_2.

2.3. Irradiation of Cp_2MoO in aqueous solution

If Cp_2MoO were acting as a catalyst for the water-splitting reaction then the amount of O_2 produced in an aqueous solvent system should be greater than the amount of O_2 produced in a dry organic solvent. To test this theory, Cp_2MoO (0.04 M) in 5:2 CH_3CN–H_2O[3] was irradiated ($\lambda > 350$ nm) for 26 h. In these experiments, a brown precipitate of $[Cp_2MoO_2(MoO_2)]_2$ formed and the solution color changed from green to brown. Again, however, no O_2 above background levels was detected. The headspace gases were analyzed by GC and the peak area for O_2 was calculated to represent 3 μmol of O_2 (a 3% yield), similar to that found (3.8 μmol) in a control sample that was stored in the dark.

2.4. The effect of wavelength

The effect of decreasing wavelength on the photochemistry of Cp_2MoO was explored by irradiating with light ($\lambda > 200$ nm). By extending the wavelength to 200 nm, a higher energy absorption band with λ_{max} at 250 nm also absorbed the radiation. The electronic absorption spectrum of Cp_2MoO shows bands at approximately 650, 430 (sh) and 250 nm [5]. In this experiment, a 5:2 CH_3CN–H_2O solution of Cp_2MoO (0.04 M) was irradiated ($\lambda > 200$ nm) for 18 h, and the headspace gases were analyzed by GC. The peak area corresponding to O_2 was calculated to be identical to that found in a control sample.

2.5. Analysis of O_2 with the sweeping-gas apparatus

There are few compelling arguments that explain the discrepancy between our current results and the earlier experiment [5] in which O_2 was apparently formed. One reason might be that our earlier mass spectrometer had a lower detection limit than our current instrument. However, even if this were the case, the O_2 would be forming in such small yields as to make the reaction useless in a solar conversion process. Alternatively, it is noteworthy that Cp_2MoO is oxygen sensitive, reacting with O_2 to yield $[Cp_2MoO_2(MoO_2)]_2$ as one of several oxygenated molybdocene products (Eq. (4)) [5,6][4].

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[1] The original experiment in which O_2 was detected was conducted by irradiating Cp_2MoO at $\lambda > 350$ nm. The photoreaction was attributed to the lowest energy electronic excited state, which has a broad absorption centered with λ_{max} at 650 nm [5].

[2] A syringe with a small needle dead volume (Alltech catalog number 010031), designed especially for gas sampling and analysis, was purged with the appropriate inert gas prior to use in an effort to reduce atmospheric contamination.

[3] A mixed solvent system was used due to the low solubility (≈ 10 mM) of Cp_2MoO in pure H_2O.

[4] (a) IR absorption bands of $[Cp_2MoO_2(MoO_2)]_2$ are assigned at 911, 881 and 850 cm^{-1}. (b) A crystal structure of the (n-Bu)Cp derivative of $[Cp_2MoO_2(MoO_2)]_2$ has been determined; this complex has similar IR bands in the parent complex (see Ref. [6]).

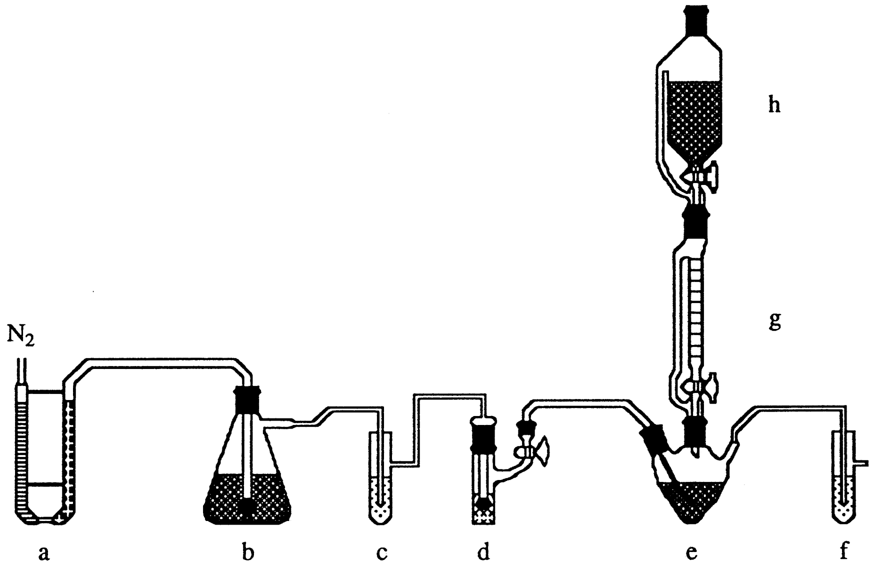
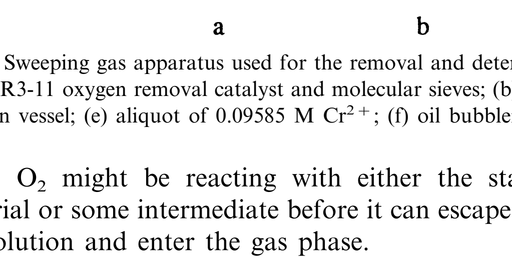


Fig. 1. Sweeping gas apparatus used for the removal and determination of O_2 from solution. The components are: (a) N_2 purification column of BASF R3-11 oxygen removal catalyst and molecular sieves; (b) gas washing bottle with 10% Cr^{2+} and Hg/Zn amalgam; (c) benzene bubbler; (d) reaction vessel; (e) aliquot of 0.09585 M Cr^{2+}; (f) oil bubbler; (g) Cr^{2+} dispensing buret; (h) storage vessel for 0.09585 M Cr^{2+} solution.

Thus, O_2 might be reacting with either the starting material or some intermediate before it can escape from the solution and enter the gas phase.



(4)

A method for circumventing both the sensitivity and reactivity problems was developed by combining a sensitive method for the detection of O_2 in inert gas streams with a method for separating O_2 from the starting materials and other products [7]. In this method (Fig. 1), solutions of Cp_2MoO were sparged with a strong flow of purified N_2 during irradiation. This gas stream was subsequently bubbled through an aliquot of Cr^{2+}, which is rapidly oxidized by O_2 (Eq. (5)). Each equivalent of O_2 oxidizes 4 equiv. of Cr^{2+}, providing for a very sensitive method of detection. Any remaining Cr^{2+} is oxidized by the addition of Fe^{3+} (Eq. (6)), and the resulting Fe^{2+} is titrated with Ce^{4+} (Eq. (7)), allowing the amount of Cr^{2+} oxidized by O_2 to be calculated.

$$4CrCl_2 + 4HCl + O_2 \rightarrow 4CrCl_3 + 2H_2O \tag{5}$$

$$2CrCl_2 + Fe_2(SO_4)_3 + 2HCl \rightarrow 2CrCl_3 + 2FeSO_4 + H_2SO_4 \tag{6}$$

$$Ce^{4+} + Fe^{2+} \rightarrow Ce^{3+} + Fe^{3+} \tag{7}$$

With this device, the plan was to sweep away molecular oxygen from the reaction solution with the flow of inert gas before it could react with any species in solution. In a typical experiment, a 4:1 benzene–pyridine solution of Cp_2MoO (0.24 M) was syringed under nitrogen into the sparging vessel of the N_2 purging apparatus. The solution was cooled to 10°C in a water bath to reduce evaporation of the solvent. The solution was simultaneously purged with N_2 and irradiated ($\lambda > 350$ nm) for 4 h. The Cr^{2+} solution was treated with deoxygenated Fe^{3+} solution and then titrated with Ce^{4+}. However, in none of the experiments was O_2 detected above the level of uncertainty in the concentration of the Cr^{2+} solution (0.09585 ± 0.00002 M)[5]. This uncertainty corresponds to 1 μmol of O_2, or a 0.2% yield. In summary, these experiments confirm the GC and MS results: free O_2 is not a photoproduct in the irradiation of Cp_2MoO.

2.6. Effect of temperature increases on the reactivity of Cp_2MoO

Our earlier study [5] reported that Cp_2MoPPh_3 formed when Cp_2MoO was irradiated in the presence of PPh_3 (Eq. (8)), from which it was inferred that Cp_2Mo was an intermediate in the photochemical reaction.

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[5] Control experiments showed that the system was effective in trapping 50% of the O_2 in 10 ml of air (0.09 mmol O_2) injected via syringe into the sparging vessel over a period of 30 seconds, and 80% was trapped during a 3 min injection. The photochemical reactions would likely form O_2 at a much slower rate than these air injections, so the apparatus should be capable of detecting all of the O_2 produced in a photoreaction.

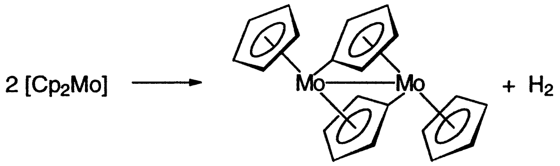
Table 1
Selected spectroscopic data

Complex	^{1}H NMR (δ) [a]	^{31}P NMR (δ) [a]	IR (cm^{-1}) [b]	Reference
Cp_2MoO	5.11 (s)		800 [ν(Mo=O)]	[5a]
Cp_2MoPPh_3	7.86 (m, 6H), 7.0 (m, 9H), 3.88 (m, Cp, 10H, 4.2 Hz)	80.2 (s)		this work, [5a,10]
$[Cp_2MoO_2(MoO_2)]_2$			911, 881, 850	[5a,6]
$C_{20}H_{18}Mo_2$	5.40 (m, 2H), 4.84 (m, 2H), 4.54 (s, 10H), 4.05 (m, 2H), 3.02 (m, 2H)			[5a]
I	4.55 (t, 2H, Cp), 4.25 (t, 2H, Cp), 2.41 (m, 2H), 2.14 (m, 2H), 2.09 (m, 6H), −8.4 (s, Mo–H)			this work
II [c]	4.88 (t, Cp), 4.74 (t, Cp), 3.3–3.0 (m, br)			this work

[a] Benzene-d_6.
[b] Mineral oil mull.
[c] D_2O.

$$Cp_2MoO + PPh_3 \rightarrow Cp_2MoPPh_3 \quad (8)$$

These trapping experiments were repeated in order to quantify the amount of Cp_2MoPPh_3 formed. ^{1}H NMR spectra of the soluble products formed during a 12 h irradiation ($\lambda > 350$ nm) of a benzene-d_6 solution of Cp_2MoO (0.02 M) and PPh_3 (0.03 M) at 22°C showed a 5% conversion to Cp_2MoPPh_3 ($\delta = 3.88$ ppm, Table 1). A small amount of $[Cp_2MoO_2(MoO_2)]_2$ was also formed. The reaction to form Cp_2MoPPh_3 was thermally enhanced, as shown by irradiating ($\lambda > 350$ nm) a solution of Cp_2MoO (0.02 M) and PPh_3 (0.03 M) at 40°C. In this case, the yield of Cp_2MoPPh_3 increased to 33% (10 h). The other major soluble product (21%) of this reaction was $\{(\eta\text{-}C_5H_5)(\mu\text{-}[\eta^1{:}\eta^5\text{-}C_5H_4])Mo\}_2$ (henceforth abbreviated as $C_{20}H_{18}Mo_2$ in this paper), which is known to form from the reactive Cp_2Mo species (Eq. (9)) [8]. Control reactions held at 40°C in the dark showed ^{1}H NMR resonances for Cp_2MoPPh_3 (35%), with minimal $C_{20}H_{18}Mo_2$ (< 5%, 24 h).



(9)

The larger yields of Cp_2MoPPh_3 at higher temperatures suggested that elevated temperatures might facilitate the photochemical reactions of Cp_2MoO. To check this possibility, the photochemical experiments to detect O_2 were all repeated at 50–60°C. The control experiments were likewise repeated at higher temperature. However, as was the case at room temperature, no O_2 was detected by GC, MS, or the sweeping-gas apparatus in any of these photochemical experiments. Similarly, no O_2 was detected above background levels in experiments run at 50°C in the dark. In these experiments ^{1}H NMR analysis of the benzene-d_6-soluble products showed only resonances for Cp_2MoPPh_3. Thus, all of the Cp_2MoO had reacted without forming any detectable O_2, from which it is concluded that O_2 does not form thermally from Cp_2MoO. The fate of the oxo ligand is discussed in Section 2.7.

2.7. Fate of the oxo ligand

No molecular oxygen was detected in the head space gas or in the swept-gas under any conditions in any of the photochemical or thermal reactions of Cp_2MoO described above. Clearly, however, Cp_2MoO did react to form non-oxygenated products (Cp_2MoPPh_3 and $C_{20}H_{18}Mo_2$) in its thermal reactions, and the question was, therefore, where did the oxygen atom go? In all cases where Cp_2MoO reacted to a reasonable extent, a red–brown precipitate of $[Cp_2MoO_2(MoO_2)]_2$ formed (Table 1) [6], and it is reasonable to propose that this compound is the oxo-ligand sink[6].

Triphenylphosphine oxide is known to form from PPh_3 and O_2 under UV irradiation, and the reaction is catalyzed in the presence of certain transition metals [9]. An interesting finding is that $O{=}PPh_3$ was not observed by infrared or NMR spectroscopy in any of the photochemical or thermal experiments. Prolonged heating of Cp_2MoO (0.04 M) in benzene-d_6 with 1–3 equiv. of PPh_3 revealed no $O{=}PPh_3$ resonances in the ^{31}P NMR spectra recorded after 4, 10, 20 and 70 h[7]. No reactions

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[6] The loss of Cp in forming the tetrameric oxo species photochemically may be explained by an excited state that has partial Cp-to-metal charge-transfer character [5]. This is discussed in a later section of the paper.

[7] In these experiments, the free PPh_3 ($\delta = -5.6$) and Cp_2MoPPh_3 ($\delta = 80.2$) resonances were the only two phosphorus-containing species present in solution. The chemical shift observed for Cp_2MoPPh_3 in this study (80.2 ppm) differed significantly from the value reported in the literature [10]. However, preparation of the complex by the same route reported in the literature gave an identical spectrum to the one obtained in the photochemical and thermal experiments reported herein.

Table 2
Assorted ESR data and hyperfine coupling constants

$^{\bullet}$R	Source	a(N) (G)	a(H) (G)	g	Ref.
$^{\bullet}C_5H_5$	Cp_2MoO [a]	14.67	3.90	2.007	this work
$^{\bullet}C_5H_5$	Cp_2MoO [a]	14.62	3.90	2.007	this work
$^{\bullet}C_5H_5$	Cp_2MoO [b]	14.6	3.4	2.006	this work
$^{\bullet}C_5H_5$	$HgCp_2$ [a]	14.68	3.98	2.007	this work
$^{\bullet}C_5H_5$	$HgCp_2$ [c]	14.5	5.7	2.007	[12]
$^{\bullet}C_6H_5$	$Sn(C_6H_5)Cl_2$ [a]	13.81	2.12	NA	[11b]

[a] In C_6H_6.
[b] In THF.
[c] In toluene.

occurred (as monitored by ^{1}H or ^{31}P NMR) when C_6H_6 solutions of Cp_2MoO or Cp_2MoH_2 were either heated or irradiated in the presence of O=PPh_3, demonstrating that [Cp_2Mo] does not abstract the oxo group from O=PPh_3.

An additional point to note is the dissociation of two generally strongly bonded Cp ligands from Cp_2MoO to form $[Cp_2MoO_2(MoO_2)]_2$. No cyclopentadiene was detected by ^{1}H NMR in any of the experiments described above. To investigate the mechanism of Cp loss, irradiated solutions of Cp_2MoO were monitored by ESR for the formation of stable free radical species (i.e. Cp$^{\bullet}$). No radical signals were observed during irradiation ($\lambda > 340$ nm) of Cp_2MoO (0.1 M in C_6H_6) in the ESR cavity over a period of 0.5–22 h, but this was not surprising considering the low quantum yields (0.01–0.05) [5]. However, in the presence of the spin trap α-phenyl tert-butyl nitrone (PBN, 0.13M), a solution of Cp_2MoO (0.013 M) in C_6H_6 that was irradiated ($\lambda >$ 350 nm) directly in the ESR cavity for 55 min gave an ESR spectrum consistent with that of other Cp–PBN adducts (Table 2). Note that PBN is reportedly stable towards photolysis in C_6H_6 [12]; this observation was confirmed during this investigation by irradiating C_6H_6 solutions of PBN in the ESR cavity. No radicals were detected over a time period of 5–120 min. Unfortunately, the spin trapping technique with PBN is unavailable for use in the thermolysis studies due to substantial spontaneous nitroxide radical formation when solutions of PBN are heated [11]. Note that PBN showed no signs of reactivity with Cp_2MoO in C_6H_6 after 3 days at 23°C in the dark as monitored by UV–Vis and ^{1}H NMR.

The β-^{1}H and [9] N hyperfine splitting constants (Table 2) for the observed radical species formed during the irradiation of Cp_2MoO are similar to those reported for the Cp–PBN nitroxide radical in toluene [12] (the solvent polarity has a large effect on the hyperfine splitting) [13]. Spectra obtained during the irradiation of mercurocene ($HgCp_2$) with PBN in C_6H_6 had nearly identical hyperfine splitting to those found during the irradiation of Cp_2MoO with PBN. $HgCp_2$ undergoes facile photo-cleavage of Cp$^{\bullet}$, and this radical has been trapped with numerous nitroso- and nitrone-functionalized spin traps [11].

2.8. Interpretation of the photochemical and thermal reactions

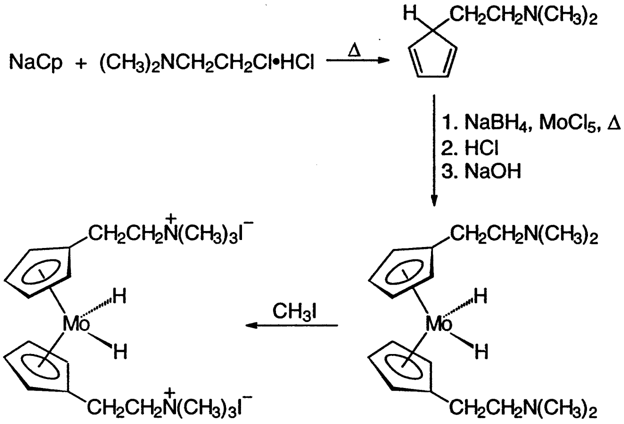
Although free O_2 is not a product of Cp_2MoO irradiation, it might be argued that, because $[Cp_2MoO_2(MoO_2)]_2$ forms by reaction of Cp_2MoO with O_2 and because $[Cp_2MoO_2(MoO_2)]_2$ is a product of all the photoreactions, the O_2 photoproduct reacts rapidly with Cp_2MoO before it can be detected. However, two points suggest this explanation is unlikely. First, it would be necessary to stipulate that all of the O_2 is reacting with the Cp_2MoO before it can be swept out of the reaction solution. The strong flow of the nitrogen purge gas and the sensitivity of the detection apparatus suggest that, were any O_2 to form, some of it would be swept from the solution and detected by the apparatus. Second, only low yields of products were obtained that can be construed as forming from the Cp_2Mo intermediate that would result from Mo–O bond cleavage. We recall, only small amounts of $Cp_2Mo(PPh_3)$ and $C_{20}H_{18}Mo_2$ formed in the photochemical reactions. Higher yields of these products were formed in the thermal reactions of Cp_2MoO, which suggests that Mo–O bond cleavage is a thermal process.

The results in Section 2.7 suggest that $[Cp_2MoO_2(MoO_2)]_2$ is formed in a pathway involving photoinduced Mo–Cp bond cleavage. The photoinduced loss of Cp$^{\bullet}$ may be explained by low-energy ligand-to-metal charge-transfer (LMCT) bands predicted by molecular orbital calculations ($\lambda_{max} = 640–665$ nm, $\varepsilon =$ 140–200 M^{-1} cm^{-1}) [5]. This type of reactivity is not uncommon; several Group IV metallocenes [14] and $CpReO_3$ [15] have been shown to undergo photolytic cleavage of Cp$^{\bullet}$ using the spin-trapping technique. $CpReO_3$ has also been shown to undergo thermal cleavage to yield Cp$^{\bullet}$ [16]. A low energy

LMCT band was suggested to be responsible for the photo-cleavage of Cp$^\bullet$ from $CpReO_3$, [15,16], which is similar to the mechanism proposed here for Cp_2MoO. Subsequent reaction steps that lead to $[Cp_2MoO.2(MoO_2)]_2$ remain unknown, but in this system it is reasonable to propose that this oxidized species is a thermodynamic sink, and its formation therefore inevitable.

2.9. Preparation and photochemistry of $[\{(CH_3)_3NCH_2CH_2Cp\}_2MoH_2][I]_2$ (II)

One of the long term goals in studying the Cp_2MoO molecule is to probe the effect that water has as a solvent on organometallic reactions. While many water-soluble organometallic complexes have been reported, the vast majority of these must incorporate hydrophilic phosphines [17]. This approach is of limited scope in metallocene chemistry, and it was necessary therefore to develop routes to provide water-soluble cyclopentadienyl complexes. As an example of a water-soluble metallocene complex, the derivatized Cp_2MoH_2 complex with structure **II** was prepared. The synthetic route is shown in Eq. (10). This scheme is analogous to that using unsubstituted Cp ligands, albeit in a lower yield (18%).



(10)

The ^1H NMR chemical shifts of the Cp ring protons in **I** (4.55 and 4.25) and Cp'_2MoH_2 (4.45 and 4.20 ppm) are essentially identical, which implies that the incorporation of the amine onto the Cp ring has minimal impact on the electronic properties of complex **I** compared to Cp'_2MoH_2. This conclusion is consistent with previous studies. For example, the electronic and spectroscopic properties of Cp′ and fluoroalkyl–Cp complexes are very similar if two or more methylene groups separate the Cp ring from any electron withdrawing groups on the fluoroalkyl chain [18]. In addition, we recently showed that phosphines with at least three methylene units between the P atom and an electron withdrawing group (e.g. OH, SO_3^-) have coordination and spectroscopic properties similar to phosphines without the electronegative groups [19].

The ammonium complex (**II**) is highly water soluble but only slightly soluble in CH_3OH and CH_3CN. Note that only 0.8 equiv. of either dimethyl sulfate or CH_3I is used for the conversion of **I** to **II**. An excess of dimethyl sulfate or of CH_3I gives products that have additional hydride resonances in the ^1H NMR spectrum. These products may be methylated metal species, possibly molybdocene methyl hydrides [20][8]. Addition of CH_3I was done dropwise at 0°C, and the precipitate immediately filtered and washed to avoid the replacement of hydrido ligands by iodide.

3. Summary

If O_2 is produced by irradiation of Cp'_2MoO, it is either at a level below our detection limits (approximately 1 μmol of O_2) or it is reacting too rapidly with other species in solution to be observe by these methods. However, neither of these explanations seems valid in view of the sensitivity of the O_2-detection apparatus and the nature of the products that form in the photoreaction. ESR spin-trapping experiments showed that irradiation of Cp_2MoO homolytically cleaves the Mo–Cp bonds to produce Cp$^\bullet$, and it is suggested that this process is responsible for the observed photochemistry.

The water soluble $[\{CpCH_2CH_2N(CH_3)_3\}_2MoH_2][I]_2$ complex was prepared and its photochemistry is similar to the parent dihydride. While this particular complex is difficult to prepare and purify, the dimethylaminoethyl cyclopentadiene ligand is a convenient ligand to prepare. It is readily converted to the quaternary ammonium salt, in which form it renders complexes water soluble. Use of this derivatized cyclopentadiene ligand should allow for more extensive development of water-soluble metallocene-type complexes.

4. Experimental

All manipulations of air-sensitive materials were carried out in an inert (N_2 or Ar) atmosphere by using standard Schlenk or vacuum line techniques or by handling the materials and solutions in a Vacuum Atmospheres glove-box.

4.1. Materials

Cp_2MoO [$Cp = \eta^5\text{-}C_5H_5$] and Cp'_2MoO [$Cp' = \eta^5\text{-}C_5H_4(CH_3)$] were prepared and purified according to

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[8] $Cp_2W(CH_3)H$ and $Cp^*{}_2W(CH_3)H$ are known complexes.

literature methods [21]. Solvents were purified and rigorously deoxygenated by standard methods [22]. Molybdenum(V) chloride (Johnson–Matthey Electronics) and other chemicals were used as received.

4.2. Instrumentation

^{1}H NMR spectra were collected either on GE QE-300 (300.15 MHz) or Varian Unity/Inova 300 (299.95 MHz) spectrometers. ^{13}C (75.43 MHz) and ^{31}P (121.42 MHz) spectra were both collected using the Varian instrument. Signals were referenced to TMS, DSS, or 1% H_3PO_4 in D_2O. Infrared (IR) spectra were obtained on a Nicolet Magna IR 550 spectrometer with 0.03-mm path length sodium chloride sealed cells or with mineral oil mulls on NaCl plates. Mass spectra were obtained by electron impact (EI) or fast atom bombardment (FABS) on a VG-ZAB 2F-HF instrument. Electronic absorption spectra (UV–Vis) were acquired using a Perkin–Elmer Lambda 6 spectrophotometer and quartz cells especially designed for air sensitive work. Potentiometric titrations were conducted with Corning 105 pH meter (in mV mode), with Pt and saturated calomel reference electrodes, and pH titrations were conducted with a Corning 220 pH meter.

ESR spectra were obtained on a Bruker ESP 300e operating at 9.6 GHz with a Hewlett–Packard frequency counter. Typical analyses were conducted with a 50 G sweep width (center field 3430 G), a modulation frequency of 50–100 KHz, modulation amplitude 1–5 G, conversion time 20.5 ms, time constant 2.56 ms and a field resolution of 1024 bits. Solid diphenyl picryl hydrazine (DPPH) was used as an external standard for the measurement of g tensors.

Gas chromatographs were obtained on a Shimadzu GC-9A equipped with a thermal conductivity detector and a CR-3A integrator. A 12 ft × 1/8″ stainless steel column was packed with 80/100 mesh molecular sieves (5 Å) and pretreated at 360°C for 24 h under an Ar flow to remove residual water [23]. The GC was operated under the following conditions: Ar or He carrier gas (flow rate 18 ml min^{-1}), detector temperature 120°C, oven temperature 50°C and detector current 80 mA.

4.3. General irradiation procedure

Irradiations were conducted using an Oriel 200 W high pressure Hg arc lamp equipped with a Corning Glass 0-52 UV cutoff filter ($\lambda > 350$ nm). Irradiations in the UV region ($\lambda > 200$ nm) were carried out in quartz cells without the filter. Prolonged irradiation of Cp_2MoO or Cp'_2MoO solutions produced a color change in the solution from green to brown along with the formation of a red–brown precipitate. The solutions were filtered before ^{1}H NMR analysis.

4.4. Calibration of McLeod gauge and measurements of hydrogen gas

A linear-scale McLeod compression gauge connected with a high vacuum manifold and a standard 25-ml Schlenk tube was calibrated by determining the total enclosed volume (V_1), with deionized water. Prior to irradiation, the entire system was evacuated (with the reaction solution in a Schlenk tube frozen in liquid N_2) < 1 μm Hg, the system was sealed under static vacuum, and the initial pressure was measured (P_1). After allowing the solution to return to room temperature, it was irradiated for a specific amount of time, and the solution was again frozen in N_2. The pressure of the system was then measured (P_2), any increase in pressure was due to evolved headspace gases. The amount of gas generated (V_2) was determined using Boyle's Law ($P_1V_1 = P_2V_2$).

4.5. Molecular oxygen detection

For mass spectrometric analyses, solutions of Cp_2MoO or Cp'_2MoO were degassed by three freeze–pump–thaw cycles on a high vacuum line in the dark and were left under static vacuum during irradiation. Mass spectra of head space gases were obtained by first evacuating a small glass tube with Teflon valves at either end on a high vacuum line. Head space gases were then collected in the tube by opening it to the irradiated sample after freezing the sample at −78°C. The trapped gases were directly introduced into the mass spectrometer. Samples for GC analyses were prepared in special round-bottom Schlenk-type flasks under N_2 or Ar gas. The flasks had stopcock-sealed side arms that were double-sealed with two septa. Headspace gases were sampled by opening the stopcock and inserting a gas tight syringe through the septa and the stopcock tap. Quantification of GC peak areas was based on calibration curves made from the appropriate gas.

A third method of oxygen detection involved the continuous purging of Cp_2MoO solutions with purified N_2 gas (see Fig. 1). Any generated O_2 contained in the sweeping gas would react with a measured amount of Cr^{2+}, and a subsequent potentiometric titration determined the amount of O_2 [7]. The N_2 stream was purified by passing it over activated R3-11 (BASF) catalyst and 5 Å molecular sieves (Fig. 1(a)) and then sparging it through a 10% Cr^{2+} solution in 1 M H_2SO_4 over 20 g of amalgamated zinc (Fig. 1(b), used to reduce Cr^{3+}). The N_2 was then bubbled through 20 ml of benzene (Fig. 1(c), to prevent evaporation of the reaction solution). Solutions of Cp_2MoO were syringed under N_2 into a 10-ml glass bottle fitted with a fritted-glass sparging tube (Fig. 1(d)). The bottle was placed in a thermostated oil or H_2O bath that was in a position for irradiation. The purified, benzene-saturated N_2 gas purged solutions of Cp_2MoO at rates of either 20 or 50 ml min^{-1}. The N_2 stream (containing any generated O_2) was then bubbled through an aliquot of 0.09585 M $CrCl_2$ (15.00 ml, 1.438 mmol, the Cr^{2+} solution had been acidified to pH 1 with HCl), which was dispensed from a buret (Fig. 1(g)) under a blanket of N_2 into a 100-ml pear-shaped flask (Fig. 1(e)). Any O_2 passed through this solution would oxidize 4 equiv. of Cr^{2+}. Unreacted Cr^{2+} was oxidized by the addition of 0.3 M $Fe_2(SO_4)_3$ (5 ml, 1.5 mmol). The air-stable Fe^{2+} was then titrated potentiometrically in air with 0.04985 M $(NH_4)_2Ce(NO_3)_6$. Blank determinations were conducted in order to both standardize the Cr^{2+} solutions and to test for leaks. The solutions of Cr^{2+} were stored over several grams of amalgamated zinc to prevent or reverse oxidation to Cr^{3+} (Fig. 1(h)).

4.6. Irradiation of Cp'_2MoH_2 in H_2O/CH_3CN

A solution of Cp'_2MoH_2 (22 mg, 0.087 mmol) in 4 ml of 3–5 water–acetonitrile (v/v) was degassed by three freeze–pump–thaw cycles and irradiated ($\lambda > 350$ nm). Electronic absorption spectra were collected and manometric measurements were performed every hour for the first 6 h of irradiation and at the 24 h mark. After 24 h, the ^1H NMR spectrum (in benzene-d_6 after removal of the solvent in vacuo) showed only Cp'_2MoO. Analysis by UV–Vis indicated a 94% yield of Cp'_2MoO from Cp'_2MoH_2. Manometric measurements showed that 2.2 equiv. of H_2 were generated. EI MS of the headspace gas showed a parent ion for hydrogen [M^+] at m/z 2. No reaction occurred with an identically prepared sample stored in the dark for 24 h.

4.7. Irradiation of Cp'_2MoH_2 in $D_2O–CD_3CN$

A solution of Cp'_2MoH_2 (20.0 mg, 0.078 mmol) in 4 ml of 3:5 deuterium oxide–acetone-d_3 (v/v) was irradiated ($\lambda > 350$ nm) for 24 h. The color of the solution turned from golden-yellow to brown. Electronic absorption spectra were collected every hour for the first 6 h of irradiation and then at the 24 h mark. After 24 h, the ^1H NMR spectrum (in benzene-d_6 after removal of the solvent in vacuo) showed mostly the deuterated starting material Cp'_2MoD_2 and a small amount ($< 5\%$) of $C_{22}H_{24}Mo_2$. An identical sample stored in the dark also showed that the hydrides exchanged in D_2O.

4.8. Irradiation of Cp'_2MoO: analysis for O_2 by GC

A 0.39 M solution of Cp'_2MoO (105 mg, 0.39 mmol) in 1 ml of benzene was placed in a septum-sealed 5-ml round-bottom flask. The solution was irradiated ($\lambda >$ 350 nm) for 15 h, and 250 μl of the headspace gases were sampled with a gas tight syringe and analyzed by GC. The peak area corresponding to O_2 was calculated to represent 0.3 μmol of the gas, or a 0.1% yield of O_2. The amount of O_2 observed in the irradiated sample was similar to that found in an identically prepared sample that was stored in the dark.

4.9. Irradiation of Cp'_2MoO in aqueous solutions: analysis for O_2 by GC

A 0.04 M solution of Cp'_2MoO (57 mg, 0.2 mmol) in 5 ml of 5:2 $CH_3CN–H_2O$ was placed in a septum-sealed 10-ml round-bottom flask. The solution was irradiated ($\lambda > 350$nm), and the headspace gases were sampled and analyzed by GC after 0.5, 6.5 and 26 h of irradiation. After 26 h, the peak area corresponding to O_2 was calculated to represent 3 μmol of the gas, or a 3% yield of O_2. The amount of O_2 observed in the irradiated sample was similar to that found (3.8 μmol) in an identically prepared sample that was stored in the dark.

A 0.04 M solution of Cp'_2MoO (90 mg, 0.33 mmol) in 8 ml of 5:2 $CH_3CN–H_2O$ was placed in a septum-sealed 12-ml quartz cuvette. The solution was irradiated ($\lambda > 200$ nm) for 18 h, and 500 μl of the headspace gases were analyzed by GC. The peak area corresponding to O_2 was calculated to represent 6 μmol of the gas, or a 3.6% yield of O_2. The amount of O_2 observed in the irradiated sample was identical to that found (6 μmol) in an identically prepared sample that was stored in the dark.

4.10. Irradiation of Cp_2MoO in aqueous solutions: analysis of O_2 by GC

A 0.10 M solution of Cp_2MoO (125 mg, 0.52 mmol) in 5 ml of 3:2 $CH_3CN–H_2O$ was placed in a septum-sealed 10-ml round-bottom flask. The N_2 atmosphere in the cuvette was exchanged with Ar. The solution was irradiated ($\lambda > 350$ nm) for 14 h, and GC analysis of the headspace gases showed no O_2 present above background levels (< 0.02 μmol).

A 0.16 M solution of Cp_2MoO (154 mg, 0.64 mmol) in 4 ml of 4:1 $CH_3CN–H_2O$ that had been adjusted to pH 12 with 6 M NaOH was placed in a septum-sealed 20-ml quartz cuvette. The N_2 atmosphere in the cuvette was exchanged with Ar. The solution was irradiated ($\lambda > 200$ nm) for 10 h, and analysis of the headspace gases showed no O_2 present above background levels (< 0.02 μmol). A similar experiment adjusted to pH 3 with 1 M HCl also yielded no O_2.

4.11. Irradiation of Cp_2MoO at elevated temperatures: analysis of O_2 by GC

A 0.20 M solution of Cp_2MoO (455 mg, 1.9 mmol) in 9.5 ml of 4:1 benzene–pyridine was placed in a septum-sealed 25-ml Schlenk tube. The tube was warmed to 60°C in an oil bath and irradiated ($\lambda > 350$ nm) for 5 h. Analysis of the headspace gases showed O_2 to be present in 0.1% yield (1.3 μmol), similar to that found (0.5 μmol) in an identically prepared sample that was stored in the dark.

4.12. Analysis of O_2 by GC in non-irradiated solutions at elevated temperatures

A 0.29 M solution of Cp_2MoO (210 mg, 0.87 mmol) in 3 ml of 4:1 benzene–pyridine was placed along with PPh_3 (260 mg, 1 mmol) in a septum-sealed 25-ml Schlenk tube. The N_2 atmosphere in the tube was exchanged with Ar. The tube was warmed to 50°C in an oil bath in the dark for 12 h. Analysis of the headspace gases showed no O_2 present above background levels (< 0.02 μmol).

4.13. Irradiation of Cp'_2MoO: analysis of O_2 by MS

A 0.12 M solution of Cp'_2MoO (81 mg, 0.3 mmol) in 2 ml of benzene and 0.5 ml of pyridine in a 25-ml Schlenk tube was degassed by three freeze–pump–thaw cycles. The solution was irradiated ($\lambda > 350$ nm) for 15 h under static vacuum, and the headspace gases were collected and analyzed by MS as described above. Intensities of the *m*/*z* 28 and 32 peaks were identical to those recorded by the spectrometer prior to exposure of the headspace gases. Similarly, a 0.24 M solution of Cp'_2MoO (600 mg, 2.2 mmol in 8 ml benzene and 1 ml pyridine) also resulted in no observable increase in O_2 after 65 h.

4.14. Irradiation of Cp_2MoO: analysis of O_2 by MS

A 0.17 M solution of Cp_2MoO (750 mg, 3.1 mmol) in 15 ml of benzene and 3 ml of pyridine in a 25-ml Schlenk tube was degassed by three freeze–pump–thaw cycles. The solution was irradiated ($\lambda > 350$ nm) for 4.5 h under static vacuum, and the headspace gases were collected and analyzed by MS. Intensities of the *m*/*z* 28 and 32 peaks were identical to those recorded by the spectrometer prior to exposure of the headspace gases.

4.15. Irradiation of Cp_2MoO at elevated temperatures: analysis of O_2 by MS

A 0.25 M solution of Cp_2MoO (500 mg, 2.4 mmol) in 8 ml of benzene and 1.5 ml of pyridine was placed along with PPh_3 (200 mg, 0.8 mmol) in a 25-ml Schlenk tube. The solution was degassed by three freeze–pump–thaw cycles and then placed in an oil bath held at 55°C and irradiated ($\lambda > 350$ nm) for 3 h under static vacuum. The headspace gases were collected and analyzed by MS. Intensities of the *m*/*z* 28 and 32 peaks were identical to those recorded by the spectrometer prior to exposure of the headspace gases.

A 0.25 M solution of Cp_2MoO (500 mg, 2.4 mmol) in 8 ml of benzene and 1.5 ml of pyridine was placed along with PPh_3 (630 mg, 2.4 mmol) in a 25-ml Schlenk tube, which was then placed in a 55°C oil bath in the dark. MS analysis showed no significant O_2 production. The solvent from this reaction was removed in vacuo and a portion of the brown residue was redissolved in benzene-d_6. ^1H NMR analysis showed resonances due to Cp_2MoPPh_3 (d, $\delta = 3.88$, 95%) and $C_{20}H_{18}Mo_2$ (5%, Table 1). No Cp_2MoO or $O{=}PPh_3$ was observed in ^1H, ^{31}P NMR or IR spectra.

4.16. Analysis of O_2 with purging/potentiometric titration apparatus

A 0.24 M solution of Cp_2MoO (290 mg, 1.2 mmol) in 5 ml of 4:1 benzene–pyridine was syringed under nitrogen into the sparging vessel in the N_2 purging apparatus. The sparging vessel was cooled to 10°C in a water bath. The solution was simultaneously purged with N_2 and irradiated ($\lambda > 350$ nm) for 4 h. The Cr^{2+} solution was then titrated with Ce^{4+}. O_2 was not detected above the level of uncertainty in the concentration of the Cr^{2+} solution (corresponding to 1 μmol of O_2, or a 0.2% yield).

A 0.24 M solution of Cp_2MoO (230 mg, 0.95 mmol), along with PPh_3 (400 mg, 1.5 mmol) in 4 ml of 4:1 benzene–pyridine was syringed under N_2 into the sparging vessel in the N_2 purging apparatus. The sparging vessel was warmed to 50°C in an oil bath while the solution was simultaneously purged with N_2 for 3 h. A water-cooled cold trap was used to condense solvent vapors that had evaporated from the heated solution of Cp_2MoO. The Cr^{2+} O_2 trapping solution was then titrated with Ce^{4+}. O_2 was not detected above the level of uncertainty in the concentration of the Cr^{2+} solution (1 μmol of O_2, or a 0.2% yield). Analysis of the benzene-d_6-soluble products in the purging vessel by ^1H NMR showed only Cp_2MoPPh_3.

4.17. Irradiation of Cp_2MoO: formation of Cp_2MoPPh_3 and $(Cp_2Mo)_2$

A solution of Cp_2MoO (10 mg, 0.041 mmol) and PPh_3 (15 mg, 0.057 mmol) in 2 ml of benzene-d_6 was irradiated ($\lambda > 350$ nm) for 12 h. ^1H NMR analysis of the filtered solution showed Cp_2MoPPh_3 (5%, δ 3.88), Cp_2MoO (95%), and a minor amount of $C_{10}H_{18}Mo_2$ ($< 5\%$). The relative amounts of Cp_2MoPPh_3 and Cp_2MoO did not change when the amounts of Cp_2MoO and PPh_3 were doubled to 50 (0.21 mmol) and 100 mg (0.38 mmol) in the same volume of solvent.

4.18. Reaction of Cp_2MoO at elevated temperatures

A solution of Cp_2MoO (25 mg, 0.10 mmol) and PPh_3 (22 mg, 0.10 mmol) in 2 ml of benzene-d_6 in a 10-ml Schlenk tube was placed in a constant-temperature oil bath at 60°C in the dark for 10 h. ^1H NMR analysis of the filtered solution showed Cp_2MoPPh_3 (50%), Cp_2MoO (48%) and $C_{10}H_{18}Mo_2$ (2%). The IR spectrum (mineral oil mull) of the red–brown precipitate formed in the above reaction consisted of bands at 912 (s), 881 (m), and 842 (w) cm^{-1}, consistent with the formation of the oxygenated product $[Cp_2MoO_2(MoO_2)]_2$ [6].

No triphenyl phosphine oxide was detected by ^1H or ^{31}P NMR or by IR. Cp_2MoPPh_3 has a singlet in the ^{31}P NMR spectrum at 80.2 ppm. The identity of this species was confirmed by preparing Cp_2MoPPh_3 via the irradiation ($\lambda > 350$ nm, 10 h) of Cp_2MoH_2 (15 mg, 0.07 mmol) in the presence of PPh_3 (17 mg, 0.07 mmol) in 1 ml benzene-d_6.

A solution of Cp_2MoO (25 mg, 0.10 mmol) and PPh_3 (22 mg, 0.10 mmol) in 2 ml of benzene-d_6 in a 10-ml Schlenk tube was placed in a 60°C oil bath and irradiated ($\lambda > 350$ nm) for 10 h. ^1H NMR analysis of the filtered solution showed product ratios of Cp_2MoPPh_3 (33%), Cp_2MoO (46%) and $C_{10}H_{18}Mo_2$ (21%).

4.19. Irradiation of Cp_2MoPPh_3

Cp_2MoPPh_3 (50 mg, 0.10 mmol) was isolated via silica gel column chromatography from the above reaction and dissolved in 2 ml of benzene in a 10-ml Schlenk tube. The solution was irradiated ($\lambda > 350$ nm) for 16 h in an oil bath at 60°C. ^1H NMR analysis of the solution indicated a 45% conversion of Cp_2MoPPh_3 to $C_{10}H_{18}Mo_2$, with 55% of the starting material remaining. An identically prepared sample showed no reaction when heated to 60°C in the dark.

4.20. Analysis of irradiated solutions of Cp_2MoO by ESR

Cp_2MoO (10 mg, 0.041 mmol) in 1 ml C_6H_6 contained in a quartz ESR tube was irradiated ($\lambda > 350$ nm) in the ESR cavity. ESR spectra (64–128 scans) obtained at 15, 30 and 60 min, and at 4, 8, and 22 h showed no radical signals in the 3100–3700 G range (where carbon centered radicals are typically located).

Cp_2MoO (10 mg, 0.041 mmol) and α-phenyl tert-butyl nitrone (PBN, 73 mg, 0.41 mmol) in 1 ml C_6H_6 contained in a quartz ESR tube were irradiated ($\lambda > 350$ nm) in the ESR cavity. ESR spectra (64 scans) collected after 55 min showed a triplet of doublets, centered at $g = 2.007$, with $a(N) = 14.67$ G and $a(H) = 3.90$ G. An identical experiment performed in THF solution provides a similar signal, with $g = 2.006$, $a(N) = 14.6$ G and $a(H) = 3.4$ G.

A control reaction with PBN (24 mg, 0.13 mmol) in 1 ml C_6H_6 was irradiated ($\lambda > 340$ nm) in the ESR cavity for 60 min. No radical signals were observed from this solution. After heating the solution for 30 min at 50°C, a complex series of lines were observed in the ESR spectrum, none of which showed the characteristic triplet of doublets pattern seen when Cp_2MoO was present.

4.21. Synthesis of $[(CH_3)_2NCH_2CH_2Cp]_2MoH_2$ (**I**)

Dimethylaminoethyl cyclopentadiene was prepared according to a literature procedure [24], modified by the use of 1,3-dimethyl-2-imidazolidinone instead of HMPA. A solution of 9.0 g (0.066 mol) of the above in 150 ml of THF was deprotonated at 0°C with 27 ml of n-butyl lithium (2.5 M in pentane), added in 9 ml portions. A mixture of 35 ml of hexanes, 4.5 g $MoCl_5$ and 2.9 g of $NaBH_4$ was cooled to −78°C. The deprotonated Cp was added to this mixture via an addition funnel over a period of 1 h. The mixture was allowed to warm to room temperature and was then refluxed for 4.5 h. The rest of the synthesis was completed as reported, except that the last filtration must be stopped before any oily brown–yellow residue passes through the frit. After benzene extraction, the product was concentrated in vacuo to 2.8 g of a yellow brown oil (46%). The product was purified by loading 0.5 g in 5 ml of benzene on a 1 × 6″ in long column of specially treated alumina [5], with the modification of eluting the column with benzene. The collected fractions were concentrated in vacuo to yield 0.2 g of purified material. Yield: 18%. ^1H NMR (C_6D_6): δ 4.55, 4.25 (t, H–$CpCH_2CH_2N(CH_3)_2$), 2.41 (m, $CpCH_2CH_2N(CH_3)_2$), 2.14 (m, $CpCH_2CH_2N(CH_3)_2$), 2.09 (m, $CpCH_2CH_2N(CH_3)_2$), −8.4 (s, Mo–H). $^{13}C\{H\}$ NMR (C_6D_6): δ 101.87 (s, $CpCH_2CH_2N(CH_3)_2$), 78.89, 74.01 (s, H–$CpCH_2CH_2N(CH_3)_2$), 62.42 (s, $CpCH_2CH_2N(CH_3)_2$), 45.97 (m, $CpCH_2CH_2N(CH_3)_2$), 29.67 (s, $CpCH_2CH_2N(CH_3)_2$). Mass spectra (EI) analysis shows the parent ion at 370 m/z.

4.22. Synthesis of $[\{(CH_3)_3NCH_2CH_2Cp\}_2MoH_2][I]_2$ (**II**)

A total of 180 mg (0.49 mmol) of **I** was dissolved in 10 ml of THF. Addition of 0.4 mmol CH_3I dropwise via syringe to the above solution produced a yellow precipitate. The product was immediately filtered through a sintered glass frit, rinsed with THF and dried in vacuo to yield 0.15 g of a pale yellow solid. Yield: 58%. ^1H NMR (D_2O): δ 4.88, 4.74 (t, H–$CpCH_2CH_2N(CH_3)_3$), 3.3–3.0 (m br, $CpCH_2CH_2N(CH_3)_2$). Mass spectra (FABS) analysis shows the parent ion at 654 m/z.

4.23. Irradiation of $[\{(CH_3)_3NCH_2CH_2Cp\}_2MoH_2][I]_2$ *(**II**)*

A 3.5 ml CH_3OH solution of **II** (95 mg, 0.15 mmol) was placed in a quartz cuvette. The yellow solution was irradiated ($\lambda > 200$ nm) for 48 h, and a 250 μl sample of the headspace gas was withdrawn with a syringe. Analysis by GC showed that 0.034 mmol of H_2 was produced (23%).

Acknowledgements

Acknowledgement is made to the DOE for the support of this work through grant DE-FG06-94ER14406.

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