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Hydrogen Generation from Water upon $CpMn(CO)_3$ Irradiation in a Hexane/Water Biphasic System

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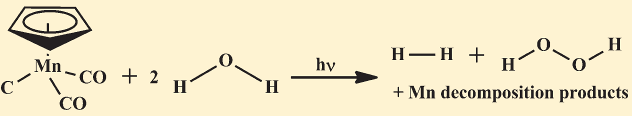
ABSTRACT: Photolysis of $CpMn(CO)_3$ in a hexane/water biphasic system has been shown to generate hydrogen peroxide and hydrogen in 40−50% yield. Photolysis of the title compound results in loss of a CO ligand followed by coordination of a water molecule. The initially formed $CpMn(CO)_2(H_2O)$ intermediate was detected using time-resolved IR spectroscopy. The cyclopentadiene (CpH) monomer is generated as the major product, formed by the transfer of an H atom from the coordinated H_2O solvent to the Cp ring. A simple mechanism for H_2 generation is proposed on the basis of deuteration studies which demonstrate the production of D_2 and CpD upon photolysis of $CpMn(CO)_3$ in a hexane/D_2O biphasic system.



INTRODUCTION

There has been considerable interest in the generation of hydrogen gas by the photoactivation of water using transition-metal complexes. A detailed understanding of the photoprocesses involved may further the "green" goal of using hydrogen as a major energy source, thereby reducing the dependence on fossil fuels. Several examples of metal complexes are known to activate water, and some of them contain platinum,[1,2] cobalt in cobaloximes,[3,4] and iron in hydrogenase mimics.[5−8] In addition, the discovery of a ruthenium metal complex which reacts with water leading to consecutive thermal H_2 and light-induced O_2 production from water has recently been reported by Kohl et al.[9] Iron carbonyl has been used together with an iridium photosensitizer and sacrificial reagents to generate hydrogen from proton sources.[10] Recently, a molybdenum−oxo catalyst has also been shown to generate hydrogen from water.[11] The mechanism behind water activation by metal complexes has been highlighted in a recent review.[12] In some instances, oxidative addition of water to a metal center may be part of the overall transformation for the reduction of H_2O to yield H_2. The importance of water photoactivation by transition-metal centers necessitates more extensive studies aimed at understanding the various photopathways that may lead to hydrogen generation from water, especially under ambient conditions. In this paper, we report the results of a study which demonstrates the production of hydrogen and hydrogen peroxide from water at room temperature by UV irradiation of $CpMn(CO)_3$ ($Cp = \eta^5\text{-}C_5H_5$) in a hexane/water biphasic system. A mechanism to account for this photoprocess is also proposed.

RESULTS

H_2 and H_2O_2 Production. Broad-band irradiation (300−800 nm) of $CpMn(CO)_3$ in a hexane/water two-phase system results in the disappearance of the parent ν_{CO} bands at 2029 and 1947 cm^{-1}. The solution was photolyzed until there were no further absorption changes in the IR spectrum. Mass spectrometric analysis of the headspace above the solution demonstrated the presence of hydrogen gas, as evidenced by a signal at m/e 2 (Figure 1). Since the photolyzed solution was frozen using liquid nitrogen prior to sampling, the signal is primarily due to H_2 gas produced as a result of the photoreaction and is not a result of hexane or water vapor sampled above the solution. Calibrating against a fixed pressure of pure H_2, the yield of H_2 produced from $CpMn(CO)_3$ irradiation was determined to be 47 ± 12% with respect to the initial mole quantity of $CpMn(CO)_3$. The time evolution of H_2 demonstrates that its production slows down considerably toward the end of irradiation, due to depletion of the parent tricarbonyl. When D_2O was used instead of H_2O, D_2 was the primary gaseous product, as evidenced by a peak at m/e 4 in the mass spectrum. The mass spectrum did not provide any evidence for the formation of O_2 and CO_2 as a result of this photoreaction.

In control experiments, photolysis of $CpMn(CO)_3$ in dried hexane yielded very small amounts of H_2 (<5% yield). No hydrogen was detected in the absence of photolysis or when the reaction mixture was photolyzed under air exposure. However, addition of water to the dried hexane solution restored the hydrogen signals upon irradiation. In addition, the H_2 yield remained unchanged upon addition of 1−5 mol equiv of various acids (HBF_4, CH_3COOH, HPF_6) to the solution. Together with the control experiments, the data lead to the important conclusion that both H_2O and $CpMn(CO)_3$ are necessary for the production of H_2 gas in this photoprocess.

In addition to H_2, hydrogen peroxide was also detected in the aqueous layer upon $CpMn(CO)_3$ photolysis. Three different assays, including the Fenton reagent test, were conducted to

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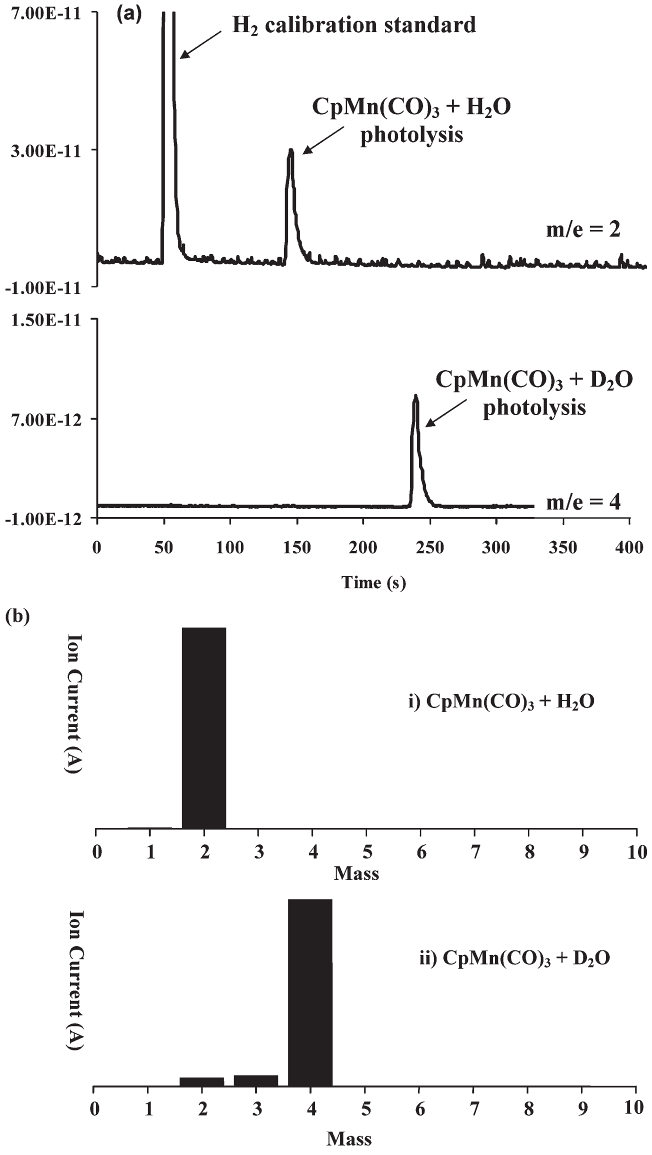

Figure 1. (a) Time-dependent mass spectra taken of the headspace content upon $CpMn(CO)_3$ photolysis in a hexane/H_2O or hexane/D_2O mixture. The *m*/*e* values of 2 and 4 corresponding to H_2 and D_2 were scanned over time during which the gases (H_2 standard, headspace contents of $CpMn(CO)_3/H_2O$ and $CpMn(CO)_3/D_2O$ after photolysis) were being injected into the mass spectrometer. (b) Gas-phase mass spectra showing the fragmentation pattern of the headspace obtained from the hexane photolysis of $CpMn(CO)_3$ with (i) H_2O and (ii) D_2O.

confirm the presence of H_2O_2 (see the Experimental Section).[13,14] The yield of H_2O_2 production was determined by titration with standardized acidified potassium hexacyanoferrate(III) (Figure 2) and the titrimetric analysis of iodine produced by the reaction of H_2O_2 with acidified potassium iodide. Yields of 36 ± 5% and 42 ± 4% were obtained using the $Fe(CN)_6^{3-}$ and I^- assays, respectively, resulting in an average yield of 39 ± 5% for H_2O_2 production relative to the initial amount of $CpMn(CO)_3$.

NMR and IR Spectroscopy. The ^1H NMR spectrum taken of the hexane layer following photolysis of $CpMn(CO)_3$ was consistent with the generation of cyclopentadiene monomer, C_5H_6 (CpH). Complete photolysis of $CpMn(CO)_3$ resulted in a >90% yield of CpH relative to the initial amount of $CpMn(CO)_3$. Partially deuterated C_5H_5D was the main product when $CpMn(CO)_3$ was photolyzed in a biphasic hexane/D_2O mixture. Importantly, the CpH signals decreased dramatically (<10% yield) when $CpMn(CO)_3$ photolysis was carried out in dried hexane, suggesting that the presence of water is necessary for the production of CpH.

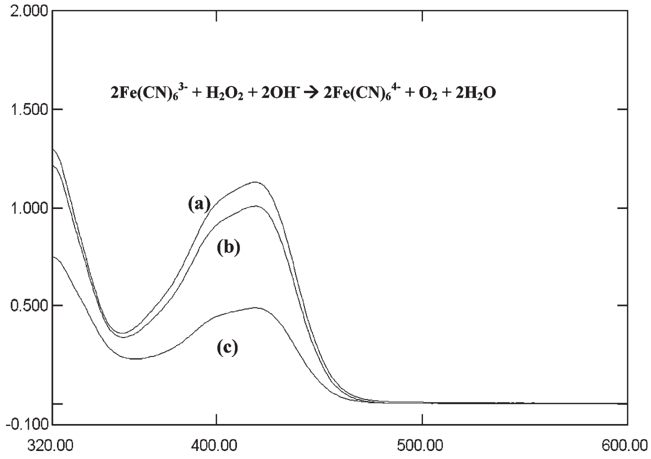

Figure 2. UV−vis spectra showing the absorption maximum at 420 nm of 9.29×10^{-4} M $K_3Fe(CN)_6$: (a) before addition; (b) after addition of H_2O_2 produced from 20 min of photolysis, corresponding to 0.95×10^{-4} M H_2O_2; (c) after addition of H_2O_2 from 360 min of photolysis corresponding to 2.95×10^{-4} M H_2O_2.

As shown in Figure 3, irradiation of the $CpMn(CO)_3$ hexane/water system resulted in the growth of four new IR-active bands, which are assigned to CO stretching absorbances of manganese carbonyl complexes formed upon photolysis. The intensities of all four peaks also decreased significantly when dried hexane was used. Since photolysis of $CpMn(CO)_3$ is known to result in the loss of a CO ligand,[15] and by analogy with several other characterized $CpMn(CO)_2L$ complexes, the position and the intensities of the four peaks suggest that they correspond to two $CpMn(CO)_2(\eta^2\text{-alkene})$ species,[16,17] one with CO bands at 1968 and 1910 cm^{-1} and the other at 1963 and 1905 cm^{-1}. The first dicarbonyl compound is identified as the $CpMn(CO)_2(\eta^2\text{-CpH})$ complex, since photolysis of $CpMn(CO)_3$ in neat CpH solvent yielded a species with identical CO stretching band positions. The second dicarbonyl species could be isolated as a yellow solid because of its poor solubility in hexane. The similar CO band positions for the second dicarbonyl species strongly suggest that it is also a η^2-bound alkene complex and hence has been assigned to the dimer complex $CpMn(CO)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-CpH})CpMn(CO)_2$, which was observed only when the ratio of $CpMn(CO)_3$ to CpH was increased significantly. In addition, the syntheses of these two manganese complexes have previously been reported.[18] In order to confirm the identities of the complexes, we have further obtained their NMR spectra and found very good agreement with the literature values.

As mentioned earlier, UV photolysis of $CpMn(CO)_3$ in the solution phase results in the dissociation of a CO ligand and coordination of a solvent molecule to the vacant site within picoseconds of CO loss.[15] For example, $CpMn(CO)_2(THF)$ is formed in high yield upon photolysis of $CpMn(CO)_3$ in the presence of THF.[19] The $CpMn(CO)_2(OHCH_3)$ complex has also been observed previously upon photolysis of the tricarbonyl

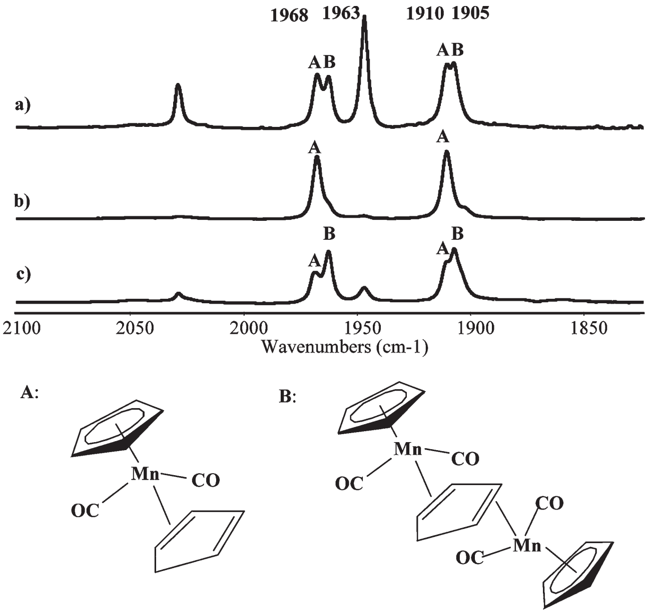

Figure 3. (a) Photolysis of $CpMn(CO)_3$ (1947, 2029 cm^{-1}) in wet hexane, producing two sets of product peaks: $CpMn(CO)_2(\eta^2\text{-}C_5H_6)$ (**A**, 1910, 1968 cm^{-1}) and $CpMn(CO)_2(\mu\text{-}\eta^2{:}\eta^2\text{-}CpH)CpMn(CO)_2$ (**B**, 1905, 1963 cm^{-1}). (b) Photolysis of $CpMn(CO)_3$ in neat cyclopentadiene, producing **A**. (c) Photolysis of $CpMn(CO)_3$ in hexane solution of cyclopentadiene ($CpMn(CO)_3$:CpH = 2:1), producing **A** and **B.** All spectra were recorded in hexane solvent.

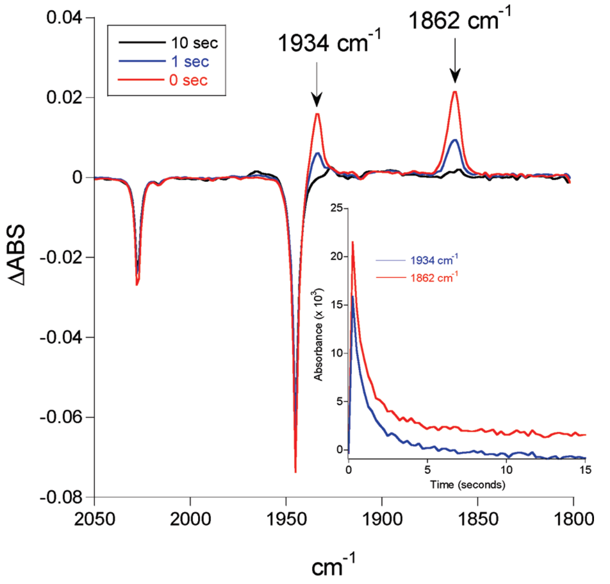

Figure 4. Difference FTIR spectrum obtained upon photolysis of $CpMn(CO)_3$ in a water-saturated hexane solution. The negative peaks are due to depletion of the parent tricarbonyl upon photolysis. The positive peaks are due to the $CpMn(CO)_2(H_2O)$ complex. The inset shows the decay of the CO stretching absorptions of the water complex at 293 K.

in the presence of methanol.[20] By analogy with these η^1-oxygen coordinated complexes, we were interested in determining whether the $CpMn(CO)_2(OH_2)$ complex was generated upon photolysis of $CpMn(CO)_3$ in the hexane/water system. The time-resolved IR spectrum obtained upon 355 nm laser photolysis of $CpMn(CO)_3$ in the hexane/water system (Figure 4), shows the formation of a short-lived complex with $\tau_{1/2}$ = 0.6 s at 293 K. The relative intensities and positions of the CO stretching absorbances for this species observed at 1862 and 1934 cm^{-1} are similar to those of the $CpMn(CO)_2(THF)$ complex in a cyclohexane solution at 1860 and 1931 cm^{-1}. This short-lived species is therefore identified as the $CpMn(CO)_2(OH_2)$ complex. It is interesting to note that while $CpMn(CO)_2(THF)$ has a relatively long lifetime of several minutes at room temperature, the water complex is significantly less stable. The lower stability of the water complex may be due to the weaker donor characteristics of the oxygen atom in water relative to those in THF. However, as discussed below, it may also be due to subsequent reactivity unique to the water complex.

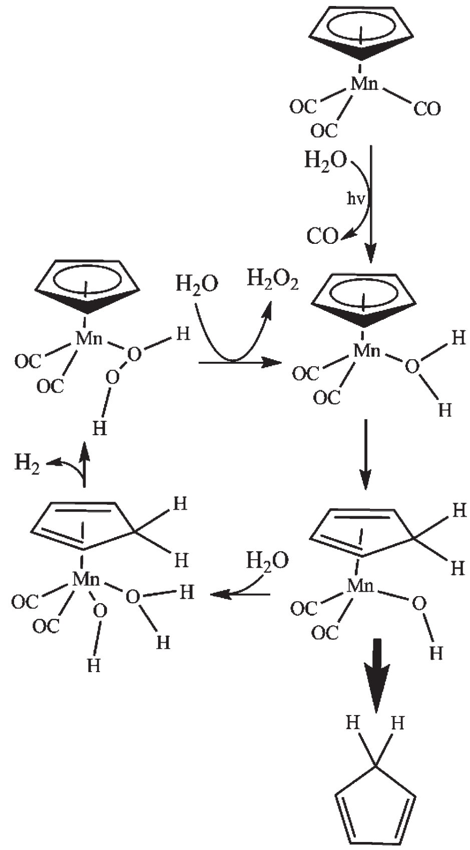

Figure 5. Proposed mechanism for the generation of H_2 and H_2O_2 from $CpMn(CO)_3$ photolysis in a hexane/water biphasic system.

The data presented above strongly suggest that water is intimately involved in the liberation of hydrogen upon photolysis of $CpMn(CO)_3$ in the hexane/water system. The proposed mechanism for this reaction has been illustrated in Figure 5. An important intermediate in this mechanism is the water-coordinated complex $CpMn(CO)_2(H_2O)$, which has been directly observed by time-resolved IR spectroscopy. In comparison to the more stable $CpMn(CO)_2(THF)$ complex, the shorter lifetime of $CpMn(CO)_2(H_2O)$ may be the result of a fast intramolecular proton transfer to the η^5-coordinated Cp ring. This type of H atom transfer is not without precedence in these systems. For example, Top et al. reported that photolysis of $CpMn(CO)_3$ derivatives in the presence of a proton source results in the formation of the appropriate solvate complex followed by intramolecular proton transfer to the Cp ring.[20] The resulting 16-electron diene manganese dicarbonyl intermediate can subsequently react via two pathways, with the first one being CpH ligand dissociation. This process accounts for the detection of free CpH in the ^{1}H NMR spectrum of the hexane layer and also for the presence of IR signals due to $CpMn(CO)_2(\eta^2\text{-}CpH)$. Interestingly, one of the main species detected in the hexane/D_2O two-phase system is CpD (C_5H_5D) together with D_2 liberation. As shown in the proposed mechanism, formation of these two major products is only possible through coordination of a second D_2O molecule to the $(\eta^4\text{-}CpD)Mn(CO)_2(OD)$ 16e intermediate. Thus, D_2 is formed when the *endo*-D of the η^4-CpD ligand combines with one of the D atoms of the coordinated D_2O molecule. The second D_2O molecule has to coordinate or at least undergo some stereospecific interaction with the diene intermediate; otherwise, the unlikely reaction of a free D_2O molecule with the intermediate via the *endo*-D or *exo*-H atom will lead to the production of both HD and D_2 in similar quantities, which is not observed. In a possibly concerted process, an intermediate peroxo complex is generated together with release of H_2 or D_2. The observed formation of H_2O_2 can then be accounted for as a product following dissociation from the postulated $CpMn(CO)_2(H_2O_2)$ complex into the aqueous layer. Interestingly, photolysis of a $M(OH)_2$ (M = Ru) complex was reported to yield O_2, also very likely by reductive elimination of H_2O_2 followed by disproportionation.[9] In a recent DFT study, the reductive elimination of H_2O_2 from this ruthenium complex has been shown to be a photolytic step because of the high endergonicity of the reaction.[21] The proposed mechanism therefore accounts for most of the experimental observations and involves species that are reasonable intermediates, including the $CpMn(CO)_2(OH_2)$ complex, which is directly observed.

According to the proposed mechanism, loss of the CpH ligand following proton transfer competes with H_2 production. Thus, addition of excess CpH to the photolysis mixture may lead to increased H_2 production. However, experiments conducted with added CpH resulted in higher yields of the $CpMn(CO)_2(\eta^2\text{-}CpH)$ complex. This observation is perhaps not unexpected, since the presence of free CpH competes with the binding of water for the vacant coordination site on the Mn center, yielding primarily $CpMn(CO)_2(\eta^2\text{-}CpH)$. Other attempts to improve the H_2 yield were also unsuccessful. For example, H_2 production remained unaffected when hexane was replaced by either nonpolar (e.g, cyclohexane, benzene, toluene) or polar solvents miscible with water (THF, DMSO, DMF, CH_3OH). Indeed, use of polar solvents resulted in reduced amounts of H_2 production, possibly due to strong binding of the polar solvent molecule to $CpMn(CO)_2$, thereby preventing H_2O coordination. Photolysis of $CpMn(CO)_3$ particles suspended in pure water also did not give better yields of H_2, while addition of CO (0.2−1 bar) into the headspace above the mixture slowed down the generation of H_2 considerably and did not lead to an increase in yield. Similarly, varying the pH of water (5−10) has little effect on the system.

The mechanism described is similar to that proposed for the formation of disulfides and H_2 from thiols following $CpMn(CO)_3$ irradiation.[22] In both cases, the manganese complex $CpMn(CO)_2(H_2O)$ or $CpMn(CO)_2(RSH)$ appears upon irradiation. In the disulfide case, however, the process can be made catalytic because of the more facile dissociation of the weaker S−H bond and formation of the stronger S−S bond in comparison to O−H and O−O bonds, respectively. We have also explored the possibility of the water-gas shift reaction occurring in the system. However, as carbon dioxide could not be detected in the mass spectrum, we have to rule out this reaction. At the end of irradiation, manganese deposits, possibly the oxides and hydroxides, were observed. In order to test whether the deposits were responsible for H_2 production, they were filtered, redispersed in fresh water, and irradiated. However, no hydrogen was detected in the mass spectrum.

We have proposed a mechanism that is able to explain the general features of our experimental data: namely the production of H_2 and H_2O_2, the detection of $CpMn(CO)_2(H_2O)$ by time-resolved IR spectroscopy, and the formation of CpH and its complex $CpMn(CO)_2(CpH)$ as one of the main loss reaction pathways followed by using NMR and cw IR spectroscopy, respectively. However, much detail about the mechanism has not yet been investigated. For example, it is possible that the subsequent steps suggested in Figure 5 may require further irradiation or a $Mn^{III}(OH)_2$ complex actually forms before H_2O_2 is expelled. We are also aware that some unknown low-concentration manganese species in the solution or even some insoluble deposits that have eluded detection may turn out to be the key intermediate after all. At present, it is difficult to ascertain the actual mechanism until much more work has been carried out on this system.

The data presented in this study demonstrate that $CpMn(CO)_3$ photolysis in a hexane/water two-phase mixture yields both hydrogen and hydrogen peroxide from water. No other metal complexes or proton sources are required. Since hydrogen peroxide can be catalytically decomposed into oxygen, the photolytic process described here can generate both H_2 and O_2 at room temperature. Although the process is not yet catalytic, we hope to stimulate interest into reviving the use of relatively inexpensive metal carbonyl complexes of strong Lewis acid character for photoactivating water in a stoichiometric or catalytic manner. Further work is being carried out in our laboratory to use $CpMn(CO)_3$ and $CpRe(CO)_3$ derivatives to improve the H_2 production.

■ EXPERIMENTAL SECTION

All chemicals were purchased from Sigma-Aldrich and used without further purification, unless otherwise noted. Anhydrous hexane was triply distilled from molecular sieves. Cyclopentadiene was obtained from the cracking of dicyclopentadiene at 150−160 °C and used immediately upon distillation. Chemicals used in the quantification were calibrated against their respective primary standards. UV−vis absorption spectra were recorded on a Shimadzu UV-2550 spectrometer.

Photolysis of $CpMn(CO)_3$ in Hexane/Water Mixture. In a typical experiment, the photolysis of $CpMn(CO)_3$ (0.030 g, 1.5×10^{-4} mol) in hexane (5 cm^3) and variable amounts of H_2O (up to 5 cm^3) was conducted in an evacuated quartz apparatus (25 cm^3 volume) employing a UV broad-band lamp (wavelength range 300−800 nm, typical power measured at 10 cm distance 0.85 W/cm^2). The photolysis was carried out over a 6 h period for completion. ^{1}H NMR spectra were recorded on Bruker ACF300 and AMX500 NMR spectrometers with chemical shifts referenced to residual solvent peaks in the respective deuterated solvents. Solution IR spectra were obtained on a Nexus 870 FT-IR spectrometer using a CaF_2 cell of 0.1 mm path length.

NMR Quantification of Cyclopentadiene. $CpMn(CO)_3$ (0.030 g, 1.5×10^{-4} mol) in 0.5 mL of isooctane and 0.5 mL of H_2O was photolyzed for 6 h before a 0.01 mL sample was transferred into a NMR tube containing 0.5 mL of $CDCl_3$. The NMR spectrum of the sample was obtained, and the quantification was performed using isooctane as an internal standard. CpH: ^1H NMR ($CDCl_3$) δ 6.57 m (2H), 6.46 m (2H), 2.98 m (2H).

Mass Spectrometric Determination of Hydrogen. Hydrogen gas was detected using a residual mass analyzer (Balzer Prisma QMS 220), where the signals at m/e 2, 3, and 4 were monitored over time. The headspace above the $CpMn(CO)_3$—hexane/water mixture (Figure 1) was sampled before and after photolysis. A 3 mL portion of the gas was injected directly into the residual gas analyzer using a syringe. A sample of pure hydrogen gas of known pressure was also injected for calibration and hence used to calculate the amount of hydrogen present in the photolytic mixture.

Deuteration Studies. $CpMn(CO)_3$ (0.030 g, 1.5×10^{-4} mol) in 0.5 mL of hexane and 0.5 mL of D_2O was photolyzed for 6 h before the headspace was studied using mass spectroscopy. HD and D_2 were observed as signals at m/e 3 and 4, respectively (Figure 1b). A 0.01 mL sample was transferred into an NMR tube containing 0.5 mL of $CDCl_3$. The NMR spectrum of the sample was obtained, and the integral ratio suggests the production of CpD. A similar experiment was conducted using 0.5 mL of d_{12}-cyclohexane and 0.5 mL of H_2O, giving only CpH and H_2 instead.

Analysis of Hydrogen Peroxide Production. $CpMn(CO)_3$ (0.030 g, 1.5×10^{-4} mol) in a mixture of 5.0 cm^3 of hexane and 5.0 cm^3 of H_2O was photolyzed for 6 h. The aqueous phase was removed and subjected to the analyses below.

Alkaline Potassium Hexacyanoferrate(III).

$$2Fe(CN)_6{}^{3-} + H_2O_2 + 2OH^- \rightarrow 2Fe(CN)_6{}^{4-} + O_2 + 2H_2O$$

Potassium hexacyanoferrate(III) solution (9.78×10^{-3} M) was prepared using literature procedures.[14] A 19.5 mL portion of alkaline potassium hexacyanoferrate(III) (9.78×10^{-4} M $K_3Fe(CN)_6$ in 0.4 M KOH solution) was added to 0.5 mL of the aqueous extract from the photolysis of $CpMn(CO)_3$. The resulting solution was then stirred and subjected to UV—vis absorption spectroscopy. The yield of H_2O_2 was determined to be 36 ± 5%.

Acidified Potassium Dichromate.

$$Cr_2O_7{}^{2-} + 3H_2O_2 + 8H^+ \rightarrow 2Cr^{3+} + 7H_2O + 3O_2$$

Potassium dichromate solution (4.08×10^{-3} M) was prepared using literature procedures.[13] A 19.5 mL portion of acidified potassium dichromate (4.08×10^{-4} M $K_2Cr_2O_7$ in 0.1 M HCl solution) was added to 0.5 mL of the aqueous extract from the photolysis of $CpMn(CO)_3$, and the resulting solution was then stirred and subjected to UV—vis absorption spectroscopy. The yield of H_2O_2 was determined to be 39 ± 5%.

Acidified Potassium Iodide.

$$2I^- + H_2O_2 + 2H^+ \rightarrow I_2 + 2H_2O$$

$$I_2 + 2Na_2SO_3 \rightarrow 2NaI + Na_2S_4O_6$$

Potassium iodide (5.19×10^{-2} M), sodium thiosulphate (5.16×10^{-4} M), and starch indicator solutions were prepared using literature procedures.[13] A 19.5 mL portion of acidified potassium iodide (5.19×10^{-3} M in 0.05 M H_2SO_4 solution) was added to 0.5 mL of the aqueous extract, and the resulting solution was left to stand in a glass-stoppered conical flask in the dark for 5 h until a brown coloration appeared. The solution was then titrated with sodium thiosulfate, and 1 drop of starch indicator was added toward the end point when the brown coloration became too faint to be observed accurately. The end point was defined as the point when the blue coloration of the starch—iodine complex disappears. The yield of H_2O_2 was determined to be 42 ± 4%.

Fenton Reagent Test.

$$2Fe^{2+} + 2H^+ + H_2O_2 \rightarrow 2Fe^{3+} + 2H_2O$$

A 5 mL portion of acidified iron sulfate solution (5.09×10^{-2} M $FeSO_4$ in 0.05 M H_2SO_4 solution) was added to 0.5 mL of the aqueous extract, and the presence of hydrogen peroxide is indicated by the immediate color change from pale green to yellow.

Photolysis of $CpMn(CO)_3$ under CO Pressurization. $CpMn(CO)_3$ (0.030 g, 1.5×10^{-4} mol) in a mixture of 5.0 cm^3 of hexane and 5.0 cm^3 of H_2O was photolyzed for 12 h under a CO atmosphere (between 0.2 and 1 bar). The headspace analysis and quantitative tests were performed subsequently.

Photolysis of $CpMn(CO)_3$ Suspended in Water. $CpMn(CO)_3$ (0.010 g, 5×10^{-4} mol) was ground into powder form before it was added to 5 g of water in a quartz apparatus. The suspended $CpMn(CO)_3$ was then subjected to UV photolysis for 6 h before the headspace above the mixture was analyzed using mass spectrometry.

Photolysis of $CpMn(CO)_3$ in Cyclopentadiene. $CpMn(CO)_3$ (0.048 g, 1.5×10^{-4} mol) in neat cyclopentadiene (2 mL) or cyclopentadiene in dried hexane solution (0.010 mL CpH in 2 mL of hexane) was photolyzed for 1 h in an evacuated quartz apparatus using a broad-band UV lamp. The solution was evaporated to dryness and the residue redissolved in hexane. The products were characterized using IR and NMR spectroscopy and identified to be $CpMn(CO)_2(\eta^2\text{-CpH})$ and $CpMn(CO)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-CpH})CpMn(CO)_2$, respectively.

$CpMn(CO)_2(\eta^2\text{-CpH})$: IR ($\nu$(CO)) 1968 s, 1910 s cm^{-1}; ^1H NMR (C_6D_6) δ 6.49 m (1H), 5.47 m (1H), 4.28 m (1H), 3.88s (5H), 3.76 m (1H), 2.95 m (2H).

$CpMn(CO)_2(\mu\text{-}\eta^2\text{:}\eta^2\text{-CpH})CpMn(CO)_2$: IR ($\nu$(CO)): 1963 s, 1905 s cm^{-1}; ^1H NMR (C_6D_6) δ 4.72 m (1H), 3.82 s (5H), 3.18 (1H), 3.07 m (1H).

Time-Resolved Infrared Spectroscopy. A Bruker Vertex 80 instrument operating in rapid scan mode was utilized to detect the presence of $CpMn(CO)_2(H_2O)$. To a 5 mL hexane solution of 2 mM $CpMn(CO)_3$ was added 1 mL of distilled water. The resulting mixture was shaken vigorously and then degassed by bubbling Ar for 5 min. After separation, the water-saturated organic layer was extracted and added to a 0.5 mm path length temperature controlled IR cell with CaF_2 windows (Harrick Scientific). The mixture was photolyzed with a single shot of 355 nm light from a Nd:YAG laser (Continuum Surelite I-10, 50 mJ/pulse) and the resulting spectrum acquired at 8 cm^{-1} resolution.

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