Inorganic Chemistry

Photochemical Water-Splitting with Organomanganese Complexes

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Supporting Information

ABSTRACT: Certain organometallic chromophores with water-derived ligands, such as the known $[Mn(CO)_3(\mu_3 - OH)]_4$ (1) tetramer, drew our attention as possible platforms to study water-splitting reactions. Herein, we investigate the UV irradiation of various tricarbonyl organomanganese complexes, including 1, and demonstrate that dihydrogen, CO, and hydrogen peroxide form as products in a photochemical water-splitting decomposition reaction. The organic and manganese-containing side products are also characterized. Labeling studies with ¹⁸O-1 suggest that the source of



oxygen atoms in H_2O_2 originates from free water that interacts with 1 after photochemical dissociation of CO (1-CO) constituting the oxidative half-reaction of water splitting mediated by 1. Hydrogen production from 1 is the result of several different processes, one of which involves the protons derived from the hydroxido ligands in 1 constituting the reductive half-reaction of water splitting mediated by 1. Other processes that generate H_2 are also operative and are described. Collectively the results from the photochemical decomposition of 1 provide an opportunity to propose a mechanism, and it is discussed within the context of developing new strategies for water-splitting reactions with organomanganese complexes.

INTRODUCTION

Organometallic compounds and their reactions have been the focus of many successful mechanistic investigations leading to industrially practiced chemistry. It follows that efforts in solar energy storage by means of water-splitting technology could benefit from the strategic application of organometallic catalysts.^{1,2} In particular, a small class of organometallic chromophores that contain water-derived ligands mediate light-driven water-splitting transformations producing both a reduced and oxidized water-derived product. Milstein and coworkers discovered one of the first of these water-splitting systems using light and a ruthenium pincer pyridine complex.³ At the same time, Kunkely and Vogler uncovered two isolated oxidation/reduction pathways to produce O2 and H2 from water using osmocene and light.^{5,6} Additionally, Beweries and Rosenthal and co-workers reported a water-splitting half reaction⁷ with titanocene and subsequently improved the system to a fully realized water-splitting cycle.⁸ Finally, Fan and co-workers have demonstrated that cymantrene (CpMn(CO)₃) is capable of photochemically transforming water into H₂ and H_2O_2

These examples constitute a rare class of organometallic compounds that photochemically split water into H_2 and an oxidized water equivalent (Chart 1). These systems are distinct from other important catalysts^{10,11} in that both half reactions nominally occur at a single site, and sacrificial reagents or sensitizers are not needed. A thorough knowledge of the mechanism whereby H_2 and H_2O_2 forms by irradiation of the said class of compounds is of paramount importance for developing catalytic water-splitting technologies that utilize





organometallic complexes. Generally, the ligand plays an important role in the reaction mechanism of organometallic complexes. For instance, the mixed phosphine/amine pyridine pincer complex that Milstein used for ruthenium-mediated water-splitting plays a functional role in transporting redox equivalence in the form of a transferable hydride. In another example, Beweries showed that the hydrogen production half-reaction with titanocene can combine with an oxidative half-reaction if the Cp ligands are tied together in an *ansa*-titanocene complex.

Unfortunately, of these four examples all but osmocene suffer from the fact that H_2O_2 (or HO·), rather than O_2 , is the initial product of water oxidation. In addition to this, the apparent lack of catalysis is perhaps the greatest drawback of these transformations. However, Fan and co-workers demonstrated catalytic production of H_2 from thiols with concomitant disulfide production using Mn^I -carbonyl compounds.^{12,13} If the mechanisms with water splitting and "thiol splitting" are similar, they differ primarily in the calamitous effects of

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hydrogen peroxide. This latter point may indeed curtail the scope of organometallic catalyzed water-splitting systems without a tandem catalyst to convert H_2O_2 into O_2 to prevent back reactions.

Despite the disadvantages to H_2O_2 as a product in water splitting, H₂O is the ideal donor in photochemical hydrogen production. Proton reduction to H₂ is a two-electron process, thereby restricting the oxidation reactions on the donor side in traditional three-component photochemical reactors (water oxidation to O_2 is a four-electron process). To circumvent this dilemma, Nocera has pioneered the strategy of coupling the two-electron H₂ evolution reaction with other two-electron oxidations such as X_2 formation (e.g., Cl₂).^{10,14} Hydrogen peroxide derived from water constitutes a suitable two-electron redox partner to couple hydrogen evolution, but only if a catalase is present to circumvent the back-reaction. To this end, it is important to recognize that Milstein's ruthenium complex appears to behave as a dual catalyst; in one cycle it splits water, while in another it behaves as a catalase producing O_2 as a final product. Therefore, additional efforts to understand this organometallic catalase activity may provide the necessary advancement to application.

Progress in this area is impeded, because there is less known about the photochemistry of organometallic centers containing water-derived ligands in comparison to anhydrous systems within the established field of organometallic photochemistry.¹⁵ Thus, we are interested in probing the reactivity of organometallic chromophores with water-derived ligands on earthabundant metal centers. We recently reported our exploration of the formation mechanism of the tetrameric complex $[Mn(CO)_3(\mu_3-OH)]_4$ (1) and briefly stated that irradiation of this complex with UV light resulted in the formation of H₂ and H₂O₂ along with additional products.¹⁶ Herein we describe these findings in detail. The results indicate 1 produces H₂ with and without added water, and H_2O_2 forms only when water is present. In addition to our mechanistic investigation with 1, we screened several other L₂XMn(CO)₃ complexes for comparative purposes (L = neutral ligand; X = anionic ligand). Certain observations from these studies in addition to the ones with 1 help elucidate a plausible mechanism.

EXPERIMENTAL SECTION

Physical Methods. NMR experiments were performed on Varian Mercury 300 MHz, Inova 400 MHz, and Inova 500 MHz spectrometers. Headspace analysis was obtained using a PerkinElmer Clarus 580 GC (thermal conductivity detector, Ar carrier gas). Gas chromatography-mass spectrometry (GCMS) analysis of reaction mixtures was performed using an HP 5890 Series II GC coupled with a HP 5972 Series Mass Selective Detector. Mass spectral analysis of isotopically labeled dihydrogen was performed on a Thermo Finnigan MAT95 XL high-resolution mass spectrometer equipped with an electron impact ionizer. Transmission and attenuated total reflectance (ATR)-Fourier transform infrared (FTIR) spectra were collected inside of a VAC Atmospheres Omni glovebox using a Bruker Alpha IR spectrometer with ALPHA-T Universal sampling module and ALPHA-P Platinum ATR module (diamond crystal), respectively. UV-vis spectra were collected using an 8154 Agilent Spectrophotometer. CHN combustion analyses were performed by Robertson Microlit Laboratories, NJ. X-band electron paramagnetic resonance (EPR) spectra were collected using a Bruker EMX EPR spectrometer.

Synthetic Methods. All reagents were obtained from commercial vendors and used as received unless otherwise noted. Unless otherwise stated, all manipulations were performed in a nitrogen-filled Genesis VAC glovebox or under argon using typical Schlenk line techniques. Solvents were dried and obtained from a PPT solvent purification

system and stored over 3 Å molecule sieves inside of a glovebox. Molecular sieves were activated at 200 °C under vacuum (<100 mTorr) for 2-3 d prior to use. Solvents dried by this method contained ~10 ppm water. Dryer solvent was required for certain experiments and was obtained by passing predried solvent through freshly activated alumina (<100 mTorr, 300 °C, 18 h); these experiments are explicitly defined in the Results Section. Deuterated solvents were degassed by freeze-pump-thaw methods and stored inside a glovebox over 3 Å sieves. The lithium salts LiCp^{tet} and LiCp* were prepared by addition of 1 equiv of *n*-BuLi (0.25 M in hexane) to 1 M solution of Cp^{tet}H (1 g, 0.008 mol) or Cp*H (5 mL, 0.0319 mol, distilled prior to use) in hexane at -78 °C, stirred overnight, and subsequently filtered and washed with hexane in a glovebox and dried (80% yield both cases). The following compounds were prepared according to literature: $1 \cdot (C_6 H_6)_{23}^{16}$ (Tp)Mn(CO)₃ (Tp = trispyrazolyl borate), $Cp^{tet}Mn(CO)_3$, and $Cp^*Mn(CO)_3$ were prepared using $(py)_2Mn(CO)_3Br$ as the manganese synthon; tris(1pyrazolyl)methane (Tpm), tris(3,5-dimethyl-1-pyrazoyl)methane (Tpm*), $[(Tpm)Mn(CO)_3]OTf$, and $[(Tpm*)Mn(CO)_3]OTf$;¹⁸ (bipy)Mn(CO)₃Br and (phen)Mn(CO)₃Br and (phen)Mn- $(CO)_{3}Br.^{19}$

Synthesis of $[Ph_3PO]_2 \cdot H_2O_2$. Open to air, Ph_3P (2 g, 0.0076 mol) was dissolved in 150 mL of toluene in a Schlenk flask, which was cooled to 0 $^\circ\text{C}$ and blanketed with argon. $H_2\text{O}_2$ (10 equiv; 30% in H_2O_1 9 mL, 0.076 mol H_2O_2) was added dropwise via syringe with vigorous stirring. The reaction mixture was stirred overnight under argon and allowed to slowly warm to room temperature. After 12 h, the solution was filtered open to the air through a fritted glass funnel to obtain a white precipitate; the material was subsequently dried under vacuum (room temperature (RT)) for 18 h and brought into a glovebox. The ATR-FTIR and ¹H NMR spectra of the white precipitate showed Ph₃PO·H₂O₂·H₂O adduct according to literature.² The Ph₃PO·H₂O₂·H₂O adduct was further dried by dissolving in dry acetonitrile, freezing the solution, and removing solvent at RT in vacuo. Anhydrous [Ph3PO]2·H2O2 was thus obtained as a white crystalline solid and showed no trace of H₂O in the ATR-FTIR or ¹H NMR spectra (Figure S1; 1.1 g, 49% based on Ph₃P). ATR-FTIR: (cm⁻¹) 3235, 1436, 1169, 1154, 1118, 1092, 1068, 1029, 996, 764, 750, 720, 692, 535, 506, 463,442. ¹H NMR (MeCN-*d*₃, 300 MHz, 298 K): δ 7.63 (30H, m, C₆H₅), δ 8.78 (2H, s, H₂O₂). ³¹P NMR (MeCN d_{3} , 300 MHz, 298 K): δ 26.25. Caution! Although we never encountered any explosions, care should be taken when manipulating anhydrous sources of H_2O_2 .

Photochemistry Methods. Conditions for Photochemical Experiments. Irradiations were performed using a Newport Corporation APEX2-Xe 100 W xenon arc lamp. Irradiations of L₂XMn(CO)₃ complexes were conducted in degassed n-hexane/water biphasic solutions. Because of solubility, the irradiations of 1 were conducted in benzene or toluene rather than hexane. Various filters were employed with the xenon arc lamp: no filter (broadband), UV bandpass filter (50% Abs Cutoff = 382 nm; %
 $T_{\rm avg} \geq 70\%$ = 300–375 nm; % $T_{\rm avg} \leq 1\%$ = 400–635 nm; $\% T_{\rm avg} \leq 10\%$ = 280–290 nm), a 345 nm cutoff filter ($\lambda \ge 345$ nm), and a 420 nm cutoff filter ($\lambda \ge 420$ nm). Samples of L₂XMn(CO)₃ or 1 in appropriate solvent were prepared inside of a N2-filled glovebox, and the Schlenk tube was sealed with an unpunctured Suba-Seal septum that was secured to the flask with electrical tape. For irradiations containing water, the water was degassed by three freeze-pump-thaw cycles and carefully transferred to the Schenk tube with a gastight syringe. GC headspace analysis prior to photolyses were occasionally checked and reproducibly do not contain O2. On the rare occasion that O2 was observed in GC traces (either before or after a photolysis), the samples were discarded and not included in our analyses. Samples were positioned 5 cm from the aperture of the lamp housing, and the stir rate was always the same for each reaction. For gas quantification, a sample of gas (3 mL) was obtained with a 10 mL gastight syringe; the puncture was sealed with a dollop of grease if subsequent sampling was desired. For quantification of organic products, the flask was open to the air, and 500 μ L of the organic phase was removed and diluted with 500 μ L of hexane

containing 0.001 M dodecane. Calibration curves were prepared for each analyte (e.g., see Figure S2).

Characterization of White Solid (2) Obtained from Irradiations in Dry Toluene. The white precipitate (2) formed during an overnight photolysis of $1 \cdot (C_6H_6)_2$ (100 mg, 0.13 mmol) in 30 mL of toluene was isolated on a fritted glass funnel inside of a nitrogen-filled glovebox (exposure of this solid to air results in rapid color change to dark brown) and subsequently washed with toluene and dried in vacuo (40 mg). The ATR-FTIR spectrum of the solid was obtained inside of a glovebox: (IR(cm⁻¹)) ν (OH) = 3650, ν (OD) = 2700, ν (CO) = 1850 (Figure S3). CHN analysis Anal. Calcd (found) for [Mn₃(CO)₂(OH)₃(O)]: %C 8.35 (8.17); %H 1.05 (1.14); %N < 0.02 (0). EPR samples of the pure material and 1% in NaHCO₃ were prepared in the glovebox and covered in mineral oil.

Conversion of Hydrogen Peroxide into Dioxygen after Irradiation of **1** in Wet Solvents. Irradiation of compound $1 \cdot (C_6 H_6)_2$ (3.9 mM) in a biphasic solution of benzene/water or toluene/water (9:1 mL) in a sealed 25 mL Pyrex Schlenk tube using the 300-375 nm band-pass filter for 5 min resulted in the formation of H2O2 and a white precipitate suspended in the aqueous layer. After irradiation, 1 mL of degassed sodium phosphate buffer solution (pH 7, 0.1M) was added to the reaction mixture through the septum with a syringe, followed by removal of 10 mL of headspace gas to depressurize the closed system; it is imperative to exclude oxygen from these experiments. A solution of catalase (1 mg/10 mL) in sodium phosphate buffer (pH 7, 0.1M) was degassed, and addition of 200 μ L of this solution directly into the aqueous layer using a long needle resulted in formation of tiny bubbles from the aqueous layer-it is critical that the catalase not come into contact with the organic phase, as the catalase immediately precipitates if contact is made. The reaction mixture was allowed to stir at a very low rate for 10 min before analyzing the headspace for O2. The headspace was analyzed before and after the addition of catalase; O₂ was only observed after bubble formation upon catalase addition. The headspace was also analyzed by GCMS when ¹⁸O-1 isotopologues were used and ³⁴O₂ analyzed for.

Synthesis of Ph_3P -Oxide by Reacting Ph_3P with Photogenerated H_2O_2 from 1. Irradiation of compound $1 \cdot (C_6H_6)_2$ (1.3 mM) in a biphasic solution of toluene/water (9:1 mL) in a sealed 25 mL Pyrex Schlenk tube using the band-pass filter for 5 min resulted in the formation of H_2O_2 and a white precipitate suspended in the aqueous layer. The liquid portions were separated from solids via Schlenk filtration into a flask containing premassed Ph_3P and allowed to stir overnight. The sample was then lyophilized to remove volatiles. GCMS samples were prepared in the glovebox under a nitrogen atmosphere and subsequently analyzed.

Hydrogen Peroxide Quantification. The technique used here for hydrogen peroxide detection is a modified version of published methods.²² A reaction mixture containing a known amount of 1 (~1 mM in 10 mL of dry toluene) was subjected to UV irradiation for a specified time. After photolysis an equal volume of water (10 mL) was added to the reaction mixture under sealed conditions via a syringe. After it was stirred for 5 min, the aqueous portion was separated. This aqueous portion (5 mL) was then treated with equal volume (5 mL) of 1 M KI solution in 0.05 M H_2SO_4 , and the solution was allowed to rest for 5 min. A 1 mL aliquot was diluted with water to 10 mL and directly analyzed by UV-vis spectroscopy in a 1 cm quartz cuvette. After 5 min the absorption of I_3^- at 353 nm ($\varepsilon = 26\ 000\ M^{-1}\ cm^{-1}$)²² was determined, and the yield of H2O2 from photolysis experiment was calculated (Figure S4). Ammonium molybdate (two drops, 3% aqueous) can be added to accelerate the formation of I_3^- and was necessary when concentrations of H2O2 were very low. Addition of ammonium molybdate was not necessary in experiments with 1, as the concentration of H2O2 was sufficiently high for I3- to fully develop within the first 5 min. When photolyses of 1 were conducted in the presence of water (1 mM 1 in 9 mL of toluene +1 mL of water), 9 mL of water was added to the mixture instead of 10 mL and subsequently worked up as describe above. Note: the I3- will continue to develop over time due to a slow background oxidation from air; therefore, it is important to ensure that samples do not develop for much longer than 5 min.

Observation of $[Cp^{tet}Mn(CO)_2]_2(\mu$ -CO) from Photolysis of Cp^{tet}Mn(CO)₃. Cp^{tet}Mn(CO)₃ (0.0212 g, 0.08 mmol) was dissolved in 5 mL of dry benzene and photolyzed for 1 h under an argon atmosphere to obtain a green solution (the same green species is generated in wet or dry hydrocarbon solvent). Headspace analysis by GC confirmed 0.5 equiv of CO. In situ UV-vis monitoring was performed in a gastight cuvette. Removal of the solvent in vacuo resulted in a green oil. UV–vis (in situ or isolated oil in benzene): λ_{max} (benzene, nm) 320, 450, 680. ATR-FTIR (thin film, cm⁻¹): 2002, 1904, 1772. In situ monitoring with ¹H NMR: 0.005 g of $Cp^{tet}Mn(CO)_3$ was photolyzed in C_6D_6 for 2 h in J-young NMR tube. ¹H NMR (400 MHz, C₆D₆, ppm): δ 3.68 (s, 1H, CMe₄H), δ 1.43 & δ 1.38 (s, s, 6H, 6H, CMe₄H) for Cp^{tet}Mn(CO)₃; δ 4.22 (s, 1H, CMe₄H), δ 1.67 & δ 1.59 (s, s, 6H, 6H, CMe₄H) for [Cp^{tet}Mn- $(CO)_2]_2(\mu$ -CO). The UV-vis and FTIR data of the green species is tentatively assigned as $[Cp^{tet}Mn(CO)_2]_2(\mu$ -CO) due to similarity with the previously described FTIR and UV-vis data for [CpMn- $(CO)_{2}]_{2}(\mu - CO).^{2}$

Observation of $Mn_2(bipy)_2(CO)_6$ from Photolysis of $(bipy)Mn_{(CO)_3Br}$. A 30 min irradiation of $(bipy)Mn(CO)_3Br$ (17 mg, 0.05 mmol) in wet or dry hydrocarbon solvent resulted in the formation of a purple solution (the purple solution decolorized upon exposure to water or air). When the irradiation was performed in dry solvent, it was possible to isolate a purple solid by removal of the volatiles in vacuo. UV–vis, λ_{max} (benzene, nm): 294, 853. ATR-FTIR: (cm⁻¹) 3101, 3069, 3024, 2022, 1953, 1913, 1888, 1860, 1836. The data matches those for the known dimeric species $Mn_2(bipy)_2(CO)_6^{.25}$

Observation of $MnTp_2$ from Photolysis of $TpMn(CO)_3$. A 5 mL toluene solution containing 0.012 M TpMn(CO)₃ (21 mg, 0.06 mmol) was treated with 100 μ L of H₂O and degassed with three freeze–pump–thaw cycles. The solution was subjected to 1 h of broadband irradiation, and water was removed in vacuo; the colorless solution was filtered and analyzed with thin-film ATR-FTIR. ATR-FTIR: (cm⁻¹) 2468 ν (BH), 1500, 1400, 1388, 1297, 1202, 1111, 1046, 971, 875, 756, 716, 656, 616. These features are identical to those published for MnTp₂.²⁶

Actinometry. The intensity of the irradiating light (I_0) just outside the front window of the photolysis cell was measured by a chemical actinometry method employing potassium ferrioxalate $(K_3Fe(C_2O_4)_3)$. 3H₂O) to calculate the quantum yield.²⁷ A solution of 0.006 M K₃Fe(C₂O₄)₃·3H₂O in 1.0 N H₂SO₄ was prepared, and 10 mL of this solution was used for each irradiation. Irradiation conditions such as the reaction flask, distance from the aperture of the lamp, filter, and stir rate were identical to the standard photolysis conditions used for irradiation experiments of compound 1. The irradiations were done for 5, 10, and 15 s. Then 1 mL of photolyzed solution (V_1) was mixed with 0.5 mL of HOAc (0.6 N, pH 4.6) and 2.0 mL of 0.1% 1,10phenanthroline and then diluted to 10 mL(V) with water. An identical sample with unphotolyzed solution was also prepared and used as the blank for UV-vis. The mixed solutions were then allowed to stand for 1 h in the dark before analysis by UV-vis. The absorption spectra were collected, and the absorbance at 510 nm of the solution was measured. All preparation and manipulation of the ferrioxalate solution were performed in a dark room, using a red photographic safelight. Finally, the light intensity of the examined light source (I_0) was determined by eqs 1 and 2, where A is absorbance, V is the final volume (10 mL), V_1 is the volume of irradiated actinometer solution used to prepare V (1 mL), ε is extinction coefficient ($\varepsilon = 11100 \text{ M}^{-1}$ cm⁻¹), *t* is irradiation time in seconds, $\Phi_{Fe(II)} = 1.28$, and f = 1. The final I_0 value (1.69 \pm 0.05 \times 10⁻⁶ einstein s⁻¹) was determined by averaging the I_0 for all three irradiation times. This process was performed in duplicate.

moles of Fe(II) =
$$\frac{V \times 10 \times A}{1000 \times \varepsilon \times V_1}$$
 (1)

$$I_0 = \frac{\text{moles of Fe(II)}}{\phi_{\text{Fe(II)}} \times t \times f}$$
(2)

Table 1.	Yields of	of H_2 as	nd H_2O_2	Produced from	1 h of Irradiations	of L ₂ XMn($(CO)_3$	Complexes"
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entry	complex	conditions	light ^b source	$molar^{c}$ equiv of CO	% yield ^c H ₂	% yield H ₂ O ₂
1	1	toluene/H ₂ O (9:1)	300-375 nm	8.0 ± 1	79 ± 14	22 ± 2
2	1	toluene/ H_2O^d (9:1)	300-375 nm	4.2 ± 1	28 ± 5	40 ± 4
3	1	benzene/ H_2O^e (9:1)	300-375 nm	7.0 ± 1	84 ± 5	10 ± 1
4	1	toluene ^f	300-375 nm	7.7	45	0
5	1	benzene ^f	300-375 nm	4.0	24	0
6	$CpMn(CO)_3$	toluene/H ₂ O (9:1)	300-375 nm	2.0	21	0.8
7	$CpMn(CO)_3$	hexane/H ₂ O (5:1)	broadband	2.8	24	12
8	$Mn_2(CO)_{10}$	toluene/H ₂ O (9:1)	300-375 nm	0.67	03	0
9	$Mn_2(CO)_{10}$	hexane/ H_2O (5:1)	broadband	2.7	33	0
10	[TpMn(CO) ₃]	hexane/ H_2O (5:1)	broadband	2.9	29	0.5
11	(bipy)Mn(CO) ₃ Br	toluene/H ₂ O (9:1)	300-375 nm	2.9	33	0.8
12	no complex	hexane/ $H_2O(5:1)$	broadband	0	0	0

^{*a*}See Tables S1 and S2 for additional data. ^{*b*}Irradiations were conducted in Pyrex glass Schlenk flasks using a Newport Corporation APEX2-Xe 100 W xenon arc lamp as the light source: 300-375 nm = UV-band-pass filter ($\%T_{avg} \ge 70\% = 300-375$ nm), broadband = no filter, $\lambda \ge 345$ nm = 345 nm cutoff filter, $\lambda \ge 420$ nm = 420 nm cutoff filter. ^{*c*}Entries 6–12 did not produce H₂ when water was excluded. ^{*d*}5 min. ^{*e*}120 min. ^{*f*}Solvent was dried with freshly activated alumina.

Quantum yield of product (Φ_p) was determined using eq 3, where *P* is the product:

$$\phi_{\rm p} = \frac{\rm mol \ P}{I_0 \times t \times f} \tag{3}$$

RESULTS

Photochemical Water-Splitting Studies with L₂XMn-(**CO**)₃ **Complexes.** We explored a variety of manganese carbonyl compounds within the context of Fan's original discovery of water splitting with cymantrene and hydrogen production from water with $Mn_2(CO)_{10}$ for comparative purposes with 1 (Table 1, entries 6–9).^{9,28} Generally, our results are consistent with those found by Fan and co-workers. Solvents such as MeCN, tetrahydrofuran (THF), benzene, and toluene retard H₂ formation, and a majority of the compounds studied here produce H₂O₂ in yields below 1% regardless of solvent. In the few cases that did produce appreciable yields of H₂O₂ (12% Table 1, entry 7), only broadband irradiation was sufficient. Despite the intriguing reaction mediated by cymantrene, the overall water-splitting chemistry with the L₂XMn(CO)₃ complexes is unimpressive, and there are no obvious trends from varying the ancillary ligand (Table S2).

Although not the focus of this report, we briefly describe some notable observations from studies with complexes other than 1, because they aid in the interpretation of the photochemical water-splitting reaction mediated by 1 (Scheme 1 and Figure S5). For example, irradiation of $Cp^{tet}Mn(CO)_3$ in wet or dry hydrocarbon solvent produced 0.5 equiv of CO and a metastable green species with spectroscopic features strikingly similar to the known dimer $[CpMn(CO)_2]_2(\mu$ -CO).²⁴ Use of $Cp*Mn(CO)_3$ gave essentially the same result and in both cases produced almost no hydrogen. Thus, we propose that photolysis of Cp^{tet}Mn(CO)₃ and Cp*Mn(CO)₃ forms the dimeric $[Cp^{R}Mn(CO)_{2}]_{2}(\mu$ -CO) complex and that the absence of H₂ suggests that water binding is too slow for productive water-splitting chemistry, perhaps due to steric effects. The only tractable product we obtained from the photolysis of (bipy)Mn(CO)₃Br in wet or dry hydrocarbon solvent was the dimer $[(bipy)Mn^{0}(CO)_{3}]_{2}$ (Table 1, entry 11); we obtained $\sim 30\%$ H₂ when water was present in photolyses. Irradiation of $TpMn(CO)_3$ in wet hydrocarbon solvent produced the $Mn^{II}Tp_2$ species along with H_2 and 3 equiv of Scheme 1. Notable Observations from Photochemical Experiments with Monomeric $L_2XMn(CO)_3$ Complexes



CO (Table 1, entry 10). The presence of Mn^0 and Mn^{II} species after photolysis of the $L_2XMn^{I}(CO)_3$ complexes indicates that a disproportionation reaction might be operative and is consistent with observations made in the photolysis of 1 and $[Mn^{I}(CO)_3(OH_2)_3]^+$ (vide infra).

Photochemical Decomposition of 1. While hexane/ water mixtures proved the best for producing H_2 with the $L_2XMn(CO)_3$ compounds, complex 1 is insoluble in hexane and is only sparingly soluble in benzene. Also note that 1 is completely insoluble in water. Therefore, we conducted the majority of our photochemical experiments with 1 in dry or biphasic water/toluene solutions; a recent investigation discusses some of the advantages to using biphasic mixtures in photochemical water-splitting reactions.²⁹ Our interest in 1 stems not only from the fact that 1 already contains waterderived ligands and produced the highest yields of H_2 and H_2O_2 compared to the $L_2XMn(CO)_3$ complexes but also because of its interesting structure. Moreover, our broadly

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stated hypothesis that organometallic chromophores with water-derived ligands mediate photochemical water-splitting reactions is testable with **1**. Therefore, we sought to obtain enough data to construct a mass-balanced photochemical reaction for mechanistic purposes.

Broadband irradiation of a homogeneous solution of 0.001 M 1 in benzene/water or toluene/water biphasic mixture in a gastight Pyrex Schlenk tube with a Xe-arc lamp causes immediate formation of an off-white precipitate, carbon monoxide, dihydrogen gas, 0.5% *o*- and 0.3% *p*-methyldiphenylmethane (in the case of toluene only), and H_2O_2 (Schemes 2

Scheme 2. Summary of Products Obtained from a 5 min UV Irradiation of 1 in Anhydrous Toluene



and 4). No set of conditions produced hydroxylated organic products or CO_2 . We obtained different yields of H_2O_2 and H_2 depending on the filter used and irradiation times (Table 2).

Table 2. Effect of Irradiation Time and Filters on H_2 and CO Yields with 1^a

filter ^b	% H ₂	% CO	$\% H_2O_2$	Φ_{co}^{c}	<i>t</i> (s)
300-375	0.2	39		0.23	13
300-375	0.4	78		0.20	30
300-375	1.0	158		0.20	60
300-375	23	220	28	0.14	120
300-375	33	480	$40\% \pm 4$	0.12	300
≥420	18	520	2	0.13	300
≥345	23	540	2	0.14	300
none ^d	35	630	34	0.16	300

^{*a*}Conditions: toluene/water (9:1), 0.001 M 1. ^{*b*}See text for details on filter. ^{*c*}See actinometry in Experimental Section, quantum yields for other products are 2 orders of magnitude smaller (e.g., ≤ 0.006). ^{*d*}No filter = broadband irradiation.

The highest yield of H_2O_2 is produced with a UV band-pass filter ($\% T_{avg} \ge 70\% = 300-375$ nm) and unless otherwise stated was used for most the experiments described below. The yield of dihydrogen produced reaches as high as $79\% \pm 14$ relative to the initial concentration of **1**. A time course (Figure 1 and Table S1) reveals that H_2 forms slowly, indicating that it is not arising directly from the primary photochemical reaction ($\Phi_{H2} = 0.006$ at 5 min). Moreover, dihydrogen and CO do not continue to form in the dark. The ratio of carbon monoxide maintains 8:1 over 60 min of irradiation with an end point of 8 mol equiv (765% \pm 98). The yields of CO vary from overnight photolyses but often exceed 11 equiv.

Characterization of the Precipitates. Some of the carbon is sequestered by the manganese in the form of $Mn^{II}(bi)$ -carbonate salts as indicated from the EPR and ATR-FTIR characterization of the precipitates. However, if water is excluded, a different "anhydrous" precipitate forms (2). The rapidity at which 2 decomposes in air has complicated its



Figure 1. Yield of gaseous products from photolysis of 1 as a function of time in toluene/ H_2O 9:1 (top) and dry toluene (bottom) using the 300–375 nm filter.

identification and is an ongoing effort in our laboratory. Nevertheless, a combination of FTIR, EPR, and CHN analysis proved informative and beneficial for mass-balance purposes. For example, the ATR-FTIR spectrum of 2 reveals the presence of OH (ν (OH) = 3650 cm⁻¹) and metallo-carbonyl (ν (CO) = 1850 cm^{-1}) groups (Figure S3). The former is derived from the μ_3 -OH moieties in 1 evidenced by the shift to 2700 cm⁻¹ when d_4 -1 is used for photolysis. An EPR spectrum of 2 at room temperature indicates that this material contains paramagnetic centers, but they lack hyperfine structure even if diluted 100-fold in NaHCO₃ (Figure S3). A CHN analysis of 2 reveals an empirical composition consistent with $[Mn_3(\mu CO_2(OH)_3(O)$], which essentially corresponds to 1 minus a H atom and a Mn⁰ center and 10 CO ligands; however, this assignment is only one possibility, as it could just as easily be a mixture of various compounds. As will be discussed below, both H atoms and Mn⁰ are present at various stages of the photochemical decomposition reaction.

We speculate that 2 is an arrested manganese(I/II)-carbonyl material en route to a similarly ill-defined $Mn^{II}(bi)$ carbonate species that is observed when water is included in photochemical reactions with 1 or $L_2XMn(CO)_3$. For instance, when 2 is treated with air-free water it produces a different material with an ATR-FTIR spectrum closely resembling the white material that is obtained when 1, cymantrene, or $Mn_2(CO)_{10}$ is irradiated in hydrocarbon/water biphasic mixtures; these ill-defined white species are not the same, but they all contain stretches in the region associated with inorganic carbonates and hydroxides moieties (Figure S3).³⁰ Fan and co-workers

described the solids as $Mn(CO_3)$,²⁸ but we believe they are complicated mixtures of ill-defined manganese salts that possibly contain OH and/or CO₃ groups.

Investigating the Source of H_2 in Irradiation of 1. Unlike the other complexes used in Table 1, complex 1 does not need added water for H_2 production (Scheme 2). For instance, if water is rigorously excluded from irradiations in benzene or toluene H_2 is produced in 24% and 45% yields, respectively. Higher yields of H_2 can be obtained for longer irradiation times and are affected by different solvents such as THF and MeCN.³¹ No HD or D_2 is observed by mass spectrometry when 1 is irradiated in d_8 -toluene. We attempted similar experiments with d_4 -1 and mixtures of 1 and d_4 -1 in nondeuterated solvents and obtained inconsistent ratios of H_2 , D_2 , and HD (Figure 2). We note that during the



Figure 2. Mass spectra of dihydrogen produced from photolysis of 1 and d_4 -1 in dry toluene or d_8 -toluene. The two bottom spectra are representative examples of the same experiment repeated with different but identically prepared samples demonstrating the difficulty in reproducing isotopic ratios when d_4 -1 was used.

preparation of d_4 -1 it is imperative to use solvent that has been dried with freshly activated alumina; otherwise, the ATR-FTIR spectrum of d_4 -1 contain peaks associated with unlabeled 1. Furthermore, it appears that d_4 -1 scrambles deuterium with protons of aromatic solvents like toluene. For example, a ν (OH) slowly appears in the transmission FTIR spectrum when d_4 -1 dissolved in toluene dried with alumina (Figure S6). Additionally, ²H NMR spectroscopy reveals the presence of deuterated toluene when d_4 -1 is dissolved in toluene. It is known that 1 forms H-bonds with aromatic solvent molecules and may facilitate such scrambling (Scheme 3).³² Taking all this into consideration, we posit that the inconsistent ratio of labeled dihydrogen isotopes arises from scrambling with trace





water despite our best efforts to exclude it from certain experiments in addition to scrambling with toluene solvent.

After the first 60 s, the quantum yield of CO begins to drop substantially. At this stage, photons are no longer a limiting reagent, and the reaction mechanism can no longer be reliably interpreted. Nevertheless, the continued production of gaseous products during prolonged irradiation suggests to us that after initial loss of CO (forming 1-CO), secondary photochemical and/or thermal processes begin (sustained irradiation is required to reach the maximum yields of CO, H2O2, 2, and H_2). We therefore probed the solution contents after a 10 min broadband irradiation to gain insight into these processes and found that 1 is completely consumed and $Mn_2(CO)_{10}$ is the only manganese-containing soluble compound obtained in $8.1\% \pm 1.6$ yield (Figure S7). The formation of Mn₂(CO)₁₀ upon photolysis of 1 is not so unlike the results obtained by Bamford, who found that $Mn_2(CO)_{10}$ is produced upon photolysis of $[Mn^{I}(CO)_{3}(OH_{2})_{3}]^{+}$ in aqueous solutions and proposed a disproportionation reaction.³³ Moreover, we obtained Mn⁰ and Mn^{II} compounds in the photolysis of (bipy)Mn(CO)₃ and TpMn(CO)₃, respectively, as described above. Although it may only be a minor component of the reaction, a disproportionation of 1-CO accounts for our observation of Mn⁰ compounds and the presence of paramagnetic centers in 2 that form in the photolysis of 1 in anhydrous conditions.

The presence of $Mn_2(CO)_{10}$ from photolysis of 1 caused us to consider the possibility that $Mn_2(CO)_{10}$, and not 1, was responsible for the formation of H_2 and H_2O_2 . However, no H_2 is produced when $Mn_2(CO)_{10}$ is irradiated in dry solvents, nor does H_2O_2 form when $Mn_2(CO)_{10}$ is irradiated in wet solvent thus confirming that species derived uniquely from 1 are responsible for the observed photochemical products. We did, however, confirm Fan and co-workers findings that H₂ is produced by the photochemical reaction between $Mn_2(CO)_{10}$ and water in hexane (30% yield, entry 9, Table 1).²⁸ However, the yield of H_2 in wet toluene is small (3% yield, entry 8, Table 1). In another control reaction we demonstrated that Mn₂(CO)₁₀ and anhydrous [Ph₃PO]₂·H₂O₂ in benzene or toluene produce H_2 in a photochemical reaction (31% yield) providing an explanation for the steady decrease of H_2O_2 in photochemical reactions with 1 despite the stability of $[Ph_3PO]_2 \cdot H_2O_2$ under irradiation by itself (vide infra). In conclusion, the presence of $Mn_2(CO)_{10}$ shows that Mn^0 species form during the photolysis of 1 and implicates a possible third process for H₂ production, namely, a photochemical process that involves H_2O_x (x = 1,2) and Mn^0 species derived from 1.

Investigating the Source of Oxygen in H_2O_2 from Irradiation of 1. Following H_2O_2 yield as a function of time in photolyses of 1 with water indicates that it rapidly increases at first and then steadily decreases as the yield of H_2 increases (Figure 1). Samples analyzed after 5 min of irradiation of 1 in rigorously dried toluene or benzene contain only trace amounts of H_2O_2 (\ll 1%). For these experiments, the solvent was dried by passing it through a column of freshly activated alumina. If the freshly activated alumina was not used to dry the solvent prior to photolysis, hydrogen peroxide was detected in slightly higher yields in benzene or toluene (max 2%, $\Phi_{H2O2} = 0.0013$, t = 5 min). If water is purposefully added, the yield of hydrogen peroxide jumps to 40% \pm 4 (max 45%, $\Phi_{H2O2} = 0.007$, t = 5 min). We also emphasize that the yields of H_2O_2 are consistent; irregular yields might indicate O_2 leakage and subsequent reduction to H_2O_2 .

To determine the source of O atoms in the H_2O_2 product we analyzed O_2 and phosphine oxides generated from the synthesized H_2O_2 . For instance, anaerobic treatment of postirradiation aqueous portions with catalase liberates O_2 from the H_2O_2 generated from water in photolyses with 1. GCMS of the gas when ¹⁸O isotopologues of 1 is used includes an m/z for ³⁴O₂ with intensity only slightly above the background of naturally occurring ³⁴O₂. Similarly, when the photogenerated hydrogen peroxide is used to prepare Ph₃PO, only trace label incorporation from ¹⁸O-1 is achieved. Taken together, these experiments show that water is necessary for the formation of H_2O_2 and that the hydroxido oxygen atoms in 1 are not predominantly incorporated into product (Scheme 4).

Scheme 4. Summary of Products From a 5 min UV Irradiation of 1 in Wet Toluene and Subsequent Reactions with Water-Derived H_2O_2



Radical Trapping Experiments with 1. Methane is a product when 1 is irradiated in MeCN (16%) and o- and pmethyldiphenylmethane (<1%) in toluene. Although difficult to reproduce, biphenyl was observed in some cases when 1 was irradiated in benzene. Despite the low yields of these products, their presence suggested possible radical processes in the photochemical decomposition of 1. Moreover, we wanted to test for hydroxyl radicals as a possible source of the H₂O₂. When (2,2,6,6-tetramethylpiperidin-1-yl)oxidanyl (TEMPO), 5,5-dimethyl-1-pyrroline N-oxide (DMPO), or Ph₃P is included in photochemical reactions with 1, the production of H₂ is completely suppressed. Of these reagents, only TEMPO is a radical, and thus the suppression of H₂ production may arise from a coordination of the reagent after CO loss with a rate that is competitive for the process that produces H₂. In fact, various soluble manganese-carbonyl compounds are produced when TEMPO and Ph₃P are included, but these compounds have not been characterized beyond ATR-FTIR spectroscopy.

When DMPO was added to a solution of **1** in dry toluene after a 5 min photolysis, no radical species were observed via EPR spectroscopy except for those associated with the precipitates (vide supra). Thus, there are no long-lived radicals that form during the irradiation experiments. Additionally, no radicals were observed when an anhydrous solution of DMPO and $[Ph_3PO]_2 \cdot H_2O_2$ was photolyzed in the absence of 1. This experiment confirms that we are not irradiating with photons energetic enough to homolyze H_2O_2 .³⁴

When DMPO and 1 were irradiated together in dry toluene, EPR spectroscopy confirmed the presence of two radicals consistent with the {DMPO-benzyl}· and {DMPO-H}· radicals (Figure 3).^{35,36} When benzene was used, the {DMPO-H}· was



Figure 3. RT X-band EPR spectra (black) were collected immediately after a 5 min photolysis of 1 in toluene (top) or benzene (bottom) in the presence of 4-5 molar equiv of DMPO. See Table S3 for simulation (red) parameters.

the major radical species with a minor radical component consistent with {DMPO-phenyl}. For the irradiations in anhydrous solvent, there was no indication of {DMPO-OH} or {DMPO-OOH} radicals. The EPR spectra obtained from irradiations with 1 and DMPO in toluene/water were essentially silent with radicals barely perceptible above the baseline. Unfortunately the noise level is too great to accurately model the radicals generated in wet solvent, and their identity remains uncertain.

DISCUSSION

The water-splitting systems studied by Milstein and Beweries contain water-derived ligands prior to photon absorption. Additionally, the O-O bond-forming step is the photochemical step. Compare this to water splitting with cymantrene, which involves photochemical ligand dissociation prior to substrate

water binding. Currently, the proposed mechanism for cymantrene water splitting is purely thermal after initial photochemical loss of CO. As unlikely it is that endergonic catalytic water splitting can be driven thermally, we confirmed Fan's observation of photochemical H₂ and H₂O₂ formation using cymantrene and $Mn_2(CO)_{10}$ in addition to using several other L₂XMn(CO)₃ variants. An immediate conclusion from our photochemical reactions (Table 1 and Table S2) is that the water-splitting reaction is affected by supporting ligand, but there are no obvious trends. The highest yields of H₂ and H₂O₂ are from irradiations of 1. One potential reason for the higher overall yield is that water-derived ligands in 1 are present prior to photolysis in contrast to the other manganese complexes described above, and this hypothesis guided our efforts toward understanding the photo-decomposition of 1.

Hydrogen Peroxide Quantification Methodology. One of our primary goals was to understand the mechanism of photochemical water splitting using **1**, which thus necessitated a reliable methodology to quantify H_2O_2 generated under the conditions studied here. The need arose specifically because interpretation of results from the traditional methods were complicated by the fact that manganese-containing compounds after photolysis interfered with the absorption of colorimetric indicators giving false positives and erroneously high yields.³⁷ Of the several methodologies we considered, the most attractive was quantitative iodometric determination with UV–vis spectrophotometry.^{22,23} Use of this method enables reliable determination of H_2O_2 concentration in aqueous solutions prepared with 30% aqueous H_2O_2 .

However, quantification of H_2O_2 generated in organic solvents, such as toluene, required additional validation. For this, we synthesized an anhydrous form of H_2O_2 following the lead of Blümel and co-workers.²¹ They prepared various hydrated phosphine oxide—hydrogen peroxide adducts including $[Ph_3PO] \cdot H_2O_2 \cdot H_2O$, from which we modified their procedure to obtain the anhydrous $[Ph_3PO]_2 \cdot H_2O_2$ form (Scheme 5). Thus, our method was also validated for

Scheme 5. Synthesis of an Anhydrous Source of H_2O_2 PPh₃ $\xrightarrow{xs H_2O_2 (aq)}$ [Ph₃PO]·H₂O₂·H₂O \longrightarrow 0.5 [Ph₃PO]₂·H₂O₂

0 °C to RT

vacuum

quantifying H_2O_2 extracted from toluene solutions containing a known amount of pure $[Ph_3PO]_2$ · H_2O_2 ; subsequent analysis of the aqueous portion revealed that 91% (±3) H_2O_2 was extracted into the water.

Proposed Mechanism for H₂O₂ and H₂ Production from 1. The light-driven formation of H₂ and H₂O₂ mediated with 1 is complicated as evident from our investigation. Reflecting upon the results from photo-decomposition of 1, we cautiously speculate a mechanism (Scheme 6). First, on the basis of the high quantum yield of CO compared to other products, the initial photochemical step ($h\nu$) is loss of CO ligand, forming 1-CO in the process. Species 1-CO may react with CO (k_{-1}) but most likely is carried forward by means of relaxing from hot vibrational states. The result of this relaxation is uncertain and could result in complete destruction of the cluster or loss of several CO ligands. More likely it results in a disproportionation ($k_{disprop}$) into a [(Mn¹)₂Mn^{II}] species (3) and Mn⁰ species. Scheme 6. Proposed Mechanism for Photochemical Water Splitting Mediated by 1



This premise is supported by the presence of $Mn_2(CO)_{10}$ and paramagnetic Mn^{II} centers in 2 that form under anhydrous conditions. Furthermore, the stoichiometry of 2, $[Mn_3(CO)_2(OH)_3(O)]$, is such that all oxygen atoms originating from the hydroxido ligands in 1 are accounted for along with the three manganese centers. The dihydrogen and simultaneous precipitation of 2 is thus proposed to form by bimolecular coupling of 3. In part, this is supported by the presence of HD, D₂, and H₂ in experiments where d_4 -1 was irradiated in the presence of 1. Additionally, the formation of ${DMPO-H}$ · instead of H₂ when DMPO is included in photolysis further supports this hypothesis. While at this stage our mechanistic proposal for the formation of H_2 via 3 is only speculative, there is ample evidence that indicates a species uniquely derived from 1 forms dihydrogen in a thermal (k_{H2}) or photochemical step $(h\nu_2)$ under anhydrous conditions. Finally, since solvent is not directly involved in the H-H forming step and the hydroxide ligands in 1 are derived from water, this H_2 production reaction represents the reduction half reaction in water splitting by **1**.

The oxidative side of water splitting occurs only when water is included. For example, the H_2O_2 product appears to originate from free water, since label incorporation from ¹⁸O-1 is not found in the oxidized product. This was demonstrated by analyzing O_2 liberated from the synthesized H_2O_2 with catalase by GCMS or using the H_2O_2 to generate phosphine oxides. Moreover, H_2O_2 is only formed when water is included in photolyses. Since the complex 1 does not exchange with free $H_2^{18}O$ in MeCN, water must interact (k_2/k_{-2}) with 1-CO or a species resulting from it, such as 3.¹⁶ This proposal is reasonable considering the rapid exchange of water with the known complex $[Mn^1(CO)_3(OH_2)_3]^+$, which is among the fastest for d⁶ transition-metal carbonyl aqua compounds.³⁸

Another convincing argument in support of H_2O_2 forming from interaction of water with **1-CO** or **3** is that the photons used in this experiment are not energetic enough to split water alone. Specifically, to photochemically split water directly one requires more than 6.5 eV photons;³⁹ it is unlikely that such a process is occurring given that our lamp provides less energetic photons less than 4.4 eV. While this is not energetic enough to homolyze water via direct sensitization, the various filters we used in photochemical decomposition of **1** have the largest impact on H_2O_2 yield; H_2 and CO are produced regardless of filter, but H_2O_2 is only produced when $\lambda < 345$ nm is used (Table 2). Therefore, the amount of energy provided by the lamp directly influences the water-splitting reaction, the oxidation half-reaction requiring the most energy, but it is not directly splitting water.

To understand this phenomenon in more detail, we investigated the electronic structure of **1**. The UV–vis spectrum of **1** in MeCN and toluene contains an intense band at 388 nm (4800 M^{-1} cm⁻¹) and 392 nm (4600 M^{-1} cm⁻¹), respectively (Figure 4).¹⁶ Density functional theory



Figure 4. (top) UV-vis spectrum of 1 in MeCN with overlaid TDDFT predicted vertical transitions (solid red vertical lines).

(DFT) calculations of 1 reveal a Kohn–Sham orbital splitting that closely resembles the cluster orbitals in other organometallic chalcogenide cubane complexes with a triply degenerate lowest unoccupied molecular orbital (LUMO) being the last three of the thirty-two cluster orbitals (Figure S8 and Table S4).⁴⁰ For discussion purposes, these cluster orbitals serve as the ligand-field equivalent of monomeric organometallics. We performed time-dependent (TD) DFT calculations and obtained three allowed vertical transitions that agree with the experimental UV-vis features, the most intense being 3.01 eV and the most energetic being at 4.1 eV. Historically, these transitions were attributed to ligand-field $d\pi - \sigma^*$ to explain photodissociation of CO ligands from organometallic carbonyl compounds.¹⁵ However, the bands in the UV-vis spectrum of 1 shift in different solvents and are likely cluster orbital to $CO\pi^*$ charge transfer in nature, which is similar to the forbidden $d\pi$ -CO π^* metal-to-ligand charge transfer (MLCT) transitions in monomeric carbonyl compounds as described in contemporary literature.⁴¹ Different excitation energy may have varying CO dissociation outcomes and affect subsequent water-splitting reactions. Such a phenomenon has been observed with $Fe(CO)_5$ in gas phase and solution whereby a different number of CO ligands are dissociated depending on the energy of photons provided, despite the fact that only one photon is absorbed.⁴² Hence, the higher-energy photons used to drive the water-oxidation halfreaction mediated by 1 may enable the dissociation of multiple carbonyl ligands from 1 within a time frame appropriate for H_2O_2 to form.

While the exact nature of the O–O bond-forming step is not certain, we cast doubt on the formation of free hydroxide radicals, because hydroxylated organics and {DMPO–OH} are not observed.^{43,34} Both 1 and water are necessary for H_2O_2 formation. Hence, species uniquely derived from complex 1 are

involved in the oxidative half-reaction for water splitting in a rapid chemical (k_3) or photochemical $(h\nu_3)$ step. We considered the possibility that compounds similar to the known cation $[Mn^{I}(CO)_{3}(OH_2)_{3}]^{+}$ might form upon interaction of **1-CO** or **3** and water and subsequently promote water splitting. To test this, we independently synthesized and photolyzed $[Mn(CO)_{3}(OH_2)_{3}]^{+}$ but found that no dihydrogen or hydrogen peroxide was formed (Scheme 7). However,





 $[Mn^{\rm I}(\rm CO)_3(\rm OH_2)_3]^+$ does not contain hydroxido ions that are likely present in 1-CO or 3. The $[Mn^{\rm I}(\rm CO)_3(\rm OH_2)_3]^+$ ion is known to be unstable toward base (decomposing into 1), so it remains for a future endeavor to test these water-soluble manganese carbonyl compounds for water splitting. 38

Finally, an additional process forms dihydrogen $(h\nu_4)$ that involves the interaction of H_2O_x (x = 1,2) and Mn^0 species derived from the disproportionation of **1-CO** that are reminiscent of, if not identical to, the photochemical reactions between $Mn_2(CO)_{10}$ and H_2O or $Mn_2(CO)_{10}$ and $[Ph_3PO]_2$. H_2O_2 (Scheme 8). In addition to the known spontaneous

Scheme 8. Photochemical H₂ Production From $Mn_2(CO)_{10}$



reactions between H_2O_2 and $Mn_2(CO)_{10}$,⁴⁴ the latter process partially accounts for the disappearance of H_2O_2 in extended irradiations of 1, since $[Ph_3PO]_2 \cdot H_2O_2$ is not decomposed into OH· by the light source. Albeit, the formation of Mn^0 species is only a minor component of the mechanism, as the yield of $Mn_2(CO)_{10}$ is less than 10%.

We have demonstrated that complex 1 is capable of mediating a water-splitting reaction and that the yields of H₂ and H₂O₂ with 1 are the highest compared to other monomeric $L_2XMn(CO)_3$ complexes, possibly because 1 contains water-derived ligands prior to photolysis. After photolysis of a CO from 1, we propose that 1-CO undergoes disproportionation to yield Mn⁰ and 3. The former is responsible for the observed $Mn_2(CO)_{10}$ in post-irradiated solutions of 1. One H₂ production pathway does not require water that we hypothesize originates from H. release from 3 to form 2 and one-half H₂. Labeling studies confirm that H_2 is derived from 1, but the distribution of dihydrogen isotopes obtained when d_4 -1 is used suggests that 1 can exchange protons with water and possibly toluene, and we are currently investigating the scrambling chemistry. The Mn⁰ species undergo a separate set of photochemical or thermal reactions with H_2O_x (x = 1,2) that also form H_2 . The lack of incorporation of label into H_2O_2 when ¹⁸O-1 is used

demonstrates that the water-oxidation half-reaction occurs from a species derived from 1-CO (or 3) reacting with water. Therefore, it may not be necessary to install water-derived ligands prior to photon absorption for the water-oxidation step. Specific details surrounding the O–O bond-forming step remains elusive, but we cast doubt on the viability of pathways involving free hydroxide radicals by the lack of {DMPO–OH}and hydroxylated organic products.

Together with the results from photochemical water-splitting with $L_2XMn(CO)_3$ complexes, the mechanism we propose suggests the necessary formation of unsaturated $\{L_2Mn(CO)_2$ hydroxido $_n$ species to accommodate additional water ligands for the water-oxidation reaction. The relatively high yield of H₂O₂ from species that contain Brønsted-Lowry basic ligands, such as cyclopentadienide, compared to nonbasic ligands supports this premise. Complex 1 already contains hydroxido moieties and hence is uniquely suited for the formation of these $L_2Mn(CO)_2$ -hydroxido units and produces the most H_2O_2 . Additionally, disproportionation of photolyzed Mn^I compounds is a recurring outcome for a variety of $L_2XMn(CO)_3$ complexes, including 1, and appears to be important for the waterreduction half reaction. Thus, future investigations will focus on developing ligands that facilitate or inhibit disproportionation and also proton transfer as to arrive at metastable L2Mn- $(CO)_2$ -hydroxido complexes. Finally, the H₂O₂ product in the photochemical reaction of 1 is destroyed by the Mn⁰ species that result from the disproportionation indicating the need for a more robust system or organometallic catalase-like molecules to achieve turnover conditions, and we are actively pursuing these strategies in our laboratory.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01483.

Spectra obtained by NMR, UV–vis, IR, and EPR; tabulated data including results from photochemical experiments, yields produced from UV–vis irradiations, comparison of selected experimental bond lengths, EPR parameters from literature and simulation, and calculated excited states; additional references, input file for TDDFT calculations, qualitative calculated frontier molecular orbital splitting diagram (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Piers, W. E. Future Trends in Organometallic Chemistry: Organometallic Approaches to Water Splitting. *Organometallics* **2011**, 30, 13–16.

(2) Klahn, M.; Beweries, T. Organometallic water splitting-from coordination chemistry to catalysis. *Rev. Inorg. Chem.* **2014**, *34*, 177–198.

(3) Kohl, S. W.; Weiner, L.; Schwartsburd, L.; Konstantinovski, L.; Shimon, L. J. W.; Ben-David, Y.; Iron, M. A.; Milstein, D. Consecutive Thermal H_2 and Light-Induced O_2 Evolution from Water Promoted by a Metal Complex. *Science* **2009**, *324*, 74–77.

(4) Yang, X.; Hall, M. B. Mechanism of Water Splitting and Oxygen– Oxygen Bond Formation by a Mononuclear Ruthenium Complex. J. Am. Chem. Soc. 2010, 132, 120–130.

(5) Kunkely, H.; Vogler, A. Water Splitting by Light with Osmocene as Photocatalyst. *Angew. Chem., Int. Ed.* **2009**, *48*, 1685–1687.

(6) Chen, Y.; Han, J.; Fang, W.-H. Mechanism of Water Oxidation to Molecular Oxygen with Osmocene as Photocatalyst: A Theoretical Study. *Inorg. Chem.* **2012**, *51*, 4938–4946.

(7) Kessler, M.; Hansen, S.; Hollmann, D.; Klahn, M.; Beweries, T.; Spannenberg, A.; Brückner, A.; Rosenthal, U. Synthesis of $Cp_2^{*}Ti-(OTf)$ and Its Reaction with Water. *Eur. J. Inorg. Chem.* **2011**, 2011, 627–631.

(8) Godemann, C.; Hollmann, D.; Kessler, M.; Jiao, H.; Spannenberg, A.; Brückner, A.; Beweries, T. A Model of a Closed Cycle of Water Splitting Using ansa-Titanocene(III/IV) Triflate Complexes. J. Am. Chem. Soc. **2015**, *137*, 16187–16195.

(9) Kee, J. W.; Tan, Y. Y.; Swennenhuis, B. H. G.; Bengali, A. A.; Fan, W. Y. Hydrogen Generation from Water upon $CpMn(CO)_3$ Irradiation in a Hexane/Water Biphasic System. *Organometallics* **2011**, *30*, 2154–2159.

(10) Esswein, A. J.; Nocera, G. D. Hydrogen Production by Molecular Photocatalysis. *Chem. Rev.* 2007, 107, 4022–4047.

(11) Selected reviews: (a) Blakemore, J. D.; Crabtree, R. H.; Brudvig, G. W. Molecular Catalysts for Water Oxidation. *Chem. Rev.* 2015, *115*, 12974–13005. (b) Kärkäs, M. D.; Verho, O.; Johnston, E. V.; Åkermark, B. Artificial Photosynthesis: Molecular Systems for Catalytic Water Oxidation. *Chem. Rev.* 2014, *114*, 11863–12001. (c) Najafpour, M. M.; Renger, G.; Holynska, M.; Moghaddam, A. N.; Aro, E.-M.; Carpentier, R.; Nishihara, H.; Eaton-Rye, J. J.; Shen, J.-R.; Allakhverdiev, S. I. Manganese Compounds as Water-Oxidizing Catalysts: From the Natural Water-Oxidizing Complex to Nanosized Manganese Oxide Structures. *Chem. Rev.* 2016, *116*, 2886–2936.

(12) (a) Tan, K. Y. D.; Kee, J. W.; Fan, W. Y. CpMn(CO)₃-Catalyzed Photoconversion of Thiols into Disulfides and Dihydrogen. *Organometallics* **2010**, *29*, 4459–4463. (b) Tan, K. Y. D.; Teng, G. F.; Fan, W. Y. Photocatalytic Transformation of Organic and Water-Soluble Thiols into Disulfides and Hydrogen under Aerobic Conditions Using $Mn(CO)_{c}Br. Organometallics$ **2011**, *30*, 4136–4143.

(13) Zhang, Z.; Li, W.; Liu, J.; Chen, X.; Bu, Y. DFT studies on the mechanism of the conversion of thiols into disulfides and dihydrogen catalyzed by $CpMn(CO)_3$ complex. *J. Organomet. Chem.* **2012**, 706–707, 89–98.

(14) Examples of X_2 elimination: (a) Cook, T. R.; Surendranath, Y.; Nocera, D. G. Chlorine Photoelimination from a Diplatinum Core: Circumventing the Back Reaction. J. Am. Chem. Soc. **2009**, 131, 28–29. (b) Teets, T. S.; Nocera, D. G. Halogen Photoreductive Elimination from Gold(III) Centers. J. Am. Chem. Soc. **2009**, 131, 7411–7420. (c) Powers, D. C.; Hwang, S. J.; Anderson, B. L.; Yang, H.; Zheng, S.-L.; Chen, Y.-S.; Cook, T. R.; Gabbaï, F. P.; Nocera, D. G. Stereoelectronic Effects in Cl₂ Elimination from Binuclear Pt(III) Complexes. Inorg. Chem. **2016**, 55, 11815–11820. Examples of H₂ elimination from similar platforms: (d) Heyduk, A. F.; Nocera, D. G. Hydrogen Produced from Hydrohalic Acid Solutions by a Two-Electron Mixed-Valence Photocatalyst. Science **2001**, 293, 1639–1641. (15) Geoffroy, G. L.; Wrighton, M. S. Organometallic Photochemistry; Academic Press: New York, 1979.

(16) Kadassery, K. J.; Dey, S. K.; Friedman, A. E.; Lacy, D. C. Exploring the Role of Carbonate in the Formation of an Organo-

manganese Tetramer. Inorg. Chem. DOI: 201710.1021/acs.inorg-chem.7b01438.

(17) For $(py)_2MnBr(CO)_3$ synthesis: Pons, M.; Herberich, G. E. Inorg. Synth. **2014**, 36, 148–149. For synthesis of $(Tp)Mn(CO)_3$ (trispyrazolyl borate = Tp), Cp^{tet}Mn(CO)₃, and Cp*Mn(CO)₃: Kirk, P.; Castellani, M. P. Inorg. Synth. **2014**, 36, 62–64.

(18) Reger, D. L.; Grattan, T. C.; Brown, K. J.; Little, C. A.; Lamba, J. J. S.; Rheingold, A. L.; Sommer, R. D. Syntheses of tris(pyrazolyl)methane ligands and {[tris(pyrazolyl)methane] $Mn(CO)_3$ }SO₃CF₃ complexes: comparison of ligand donor properties. *J. Organomet. Chem.* **2000**, 607, 120–128.

(19) Bourrez, M.; Molton, F.; Chardon-Noblat, S.; Deronzier, A. $[Mn(bipyridyl)(CO)_3Br]$: An Abundant Metal Carbonyl Complex as Efficient Electrocatalyst for CO₂ Reduction. *Angew. Chem., Int. Ed.* **2011**, *50*, 9903–9906.

(20) Kurtz, D. A.; Dhakal, B.; Hulme, R. J.; Nichol, G. S.; Felton, G. A. N. Correlations between photophysical and electrochemical properties for a series of new Mn carbonyl complexes containing substituted phenanthroline ligands. *Inorg. Chim. Acta* **2015**, 427, 22–26.

(21) Hilliard, C. R.; Bhuvanesh, N.; Gladysz, J. A.; Blümel, J. Synthesis, purification, and characterization of phosphine oxides and their hydrogen peroxide adducts. *Dalton Trans.* **2012**, *41*, 1742–1754.

(22) (a) Monzani, E.; Quinti, L.; Perotti, A.; Casella, L.; Gullotti, M.; Randaccio, L.; Geremia, S.; Nardin, G.; Faleschini, P.; Tabbi, G. Tyrosinase Models. Synthesis, Structure, Catechol Oxidase Activity, and Phenol Monooxygenase Activity of a Dinuclear Copper Complex Derived from a Triamino Pentabenzimidazole Ligand. *Inorg. Chem.* **1998**, 37, 553–562. (b) Ackermann, J.; Meyer, F.; Kaifer, E.; Pritzkow, H. Tuning the Activity of Catechol Oxidase Model Complexes by Geometric Changes of the Dicopper Core. *Chem. - Eur. J.* **2002**, 8, 247.

(23) (a) Ramette, R. W.; Sandford, R. W. Thermodynamics of Iodine Solubility and Triiodide Ion Formation in Water and in Deuterium Oxide. J. Am. Chem. Soc. **1965**, 87, 5001–5005. (b) Burgess, A. E.; Davidson, J. C. A Kinetic–Equilibrium Study of a Triiodide Concentration Maximum Formed by the Persulfate–Iodide Reaction. J. Chem. Educ. **2012**, 89, 814–816. (c) Kim, K.; Yabushita, A.; Okumura, M.; Saiz-Lopez, A.; Cuevas, C. A.; Blaszczak-Boxe, C. S.; Min, D. W.; Yoon, H.-I.; Choi, W. Production of Molecular Iodine and Tri-iodide in the Frozen Solution of Iodide: Implication for Polar Atmosphere. Environ. Sci. Technol. **2016**, 50, 1280–1287.

(24) Creaven, B. S.; Dixon, A. J.; Kelly, J. M.; Long, C.; Poliakoff, M. Structure and reactivity of $(\eta^{5}-C_{5}H_{5})Mn(CO)_{2}$ in room-temperature solution. Evidence for formation of a dinuclear intermediate detected by flash photolysis and time-resolved infrared spectroscopy. *Organometallics* **1987**, *6*, 2600–2605.

(25) Stor, G. J.; Morrison, S. L.; Stufkens, D. J.; Oskam, A. The Remarkable Photochemistry of fac-XMn(CO)₃(α -diimine) (X = Halide): Formation of Mn₂(CO)₆(α -diimine)₂ via the mer Isomer and Photocatalytic Substitution of X- in the Presence of PR₃. Organometallics **1994**, 13, 2641–2650.

(26) Xing, Y. H.; Aoki, K.; Bai, F. Y. Synthesis and Structure of the Mn(II) Complexes with Tripyrazolylborate Ligands: Mn[HB(pz)₃]₂ and Mn[HB(3,5-Me₂-pz)₃]₂. Synth. React. Inorg. Met.-Org. Chem. **2004**, 34, 1149–1163.

(27) (a) Bolton, J. R.; Stefan, M. I.; Shaw, P.-S.; Lykke, K. R. Determination of the quantum yields of the potassium ferrioxalate and potassium iodide–iodate actinometers and a method for the calibration of radiometer detectors. *J. Photochem. Photobiol., A* **2011**, 222, 166–169. (b) Demas, J. N.; Bowman, W. D.; Zalewski, E. F.; Velapoldi, R. A. Determination of the quantum yield of the ferrioxalate actinometer with electrically calibrated radiometers. *J. Phys. Chem.* **1981**, 85, 2766–2771.

(28) Kee, J. W.; Chong, C. C.; Toh, C. K.; Chong, Y. Y.; Fan, W. Y. Stoichiometric H_2 production from H_2O upon $Mn_2(CO)_{10}$ photolysis. *J. Organomet. Chem.* **2013**, 724, 1–6.

(29) Kagalwala, H. N.; Chirdon, D. N.; Mills, I. N.; Budwal, N.; Bernhard, S. Light-Driven Hydrogen Generation from Microemulsions Using Metallosurfactant Catalysts and Oxalic Acid. Inorg. Chem. 2017, DOI: 10.1021/acs.inorgchem.7b00463.

(30) Nakamoto, K. Infrared Spectra of Inorganic and Coordination Compounds, 2nd ed.; Wiley-Interscience: New York, 1970.

(31) THF (60 min) = 35% H₂ + 7.1 equiv of CO; MeCN (18 h) = 6% H₂ + 16% CH₄ (no ethane); toluene (120 min to 18 h, broadband) = $85\% \pm 21$ H₂ + 9.3 ± 2 equiv of CO; benzene (120 min, broadband or 300-375 nm) = $52\% \pm 12$ H₂ + 7.7 ± 1 equiv of CO.

(32) Holman, K. T.; Zaworotko, M. J. Crystal and molecular structure of $[Mn(CO)_3(\mu_3-OH)]_4$. J. Chem. Crystallogr. 1995, 25, 93–95.

(33) Bamford, C. H.; Coldbeck, M. Evidence for the formation of the triaquatricarbonylmanganese(I) cation and related derivatives from pentacarbonylchloromanganese. *J. Chem. Soc., Dalton Trans.* **1978**, 4–8.

(34) Grela, M. A.; Coronel, M. E. J.; Colussi, A. J. Quantitative Spin-Trapping Studies of Weakly Illuminated Titanium Dioxide Sols. Implications for the Mechanism of Photocatalysis. *J. Phys. Chem.* **1996**, *100*, 16940–16946.

(35) Buettner, G. R. Spin Trapping: ESR Parameters of Spin Adducts. *Free Radical Biol. Med.* **1987**, *3*, 259–303.

(36) When DMPO is not included under the normal set of conditions studied here, benzyl radicals that form are oxidized and subsequently produce diaryl methanes via Friedel–Crafts alkylation. This indicates that small amounts of high-valent (O.S. ≥ 2) manganese are formed in photolyses of 1: (a) Lockwood, M. A.; Wang, K.; Mayer, J. M. Oxidation of Toluene by $[(phen)_2Mn(\mu-O)_2Mn(phen)_2]^{4+}$ via Initial Hydride Abstraction. J. Am. Chem. Soc. 1999, 121, 11894–11895. (b) Bryant, J. R.; Taves, J. E.; Mayer, J. M. Oxidations of Hydrocarbons by Manganese(III) Tris(hexafluoroacetylacetonate). Inorg. Chem. 2002, 41, 2769–2776. (c) Larsen, A. S.; Wang, K.; Lockwood, M. A.; Rice, G. L.; Won, T.-J.; Lovell, S.; Sadílek, M.; Tureček, F.; Mayer, J. M. Hydrocarbon Oxidation by Bis- μ -oxo Manganese Dimers: Electron Transfer, Hydride Transfer, and Hydrogen Atom Transfer Mechanisms. J. Am. Chem. Soc. 2002, 124, 10112–10123.

(37) Several methods for the quantification of H_2O_2 are summarized in ref 9 and include alkaline potassium hexacyanoferrate, acidified potassium chromate, acidified potassium iodide, and Fenton reagent test. In our hands, these methods gave false positives due to manganese-containing oxidants present in analyte solutions.

(38) (a) Prinz, U.; Koelle, U.; Ulrich, S.; Merbach, A. E. The Organometallic fac-[(CO)₃Mn(H₂O)₃]⁺ Aquaion: Base-Hydrolysis and Kinetics of H₂O-Substitution. *Inorg. Chem.* **2004**, *43*, 2387–2391. (b) Grundler, P. V.; Helm, L.; Alberto, R.; Merbach, A. E. Relevance of the Ligand Exchange Rate and Mechanism of fac-[(CO)₃M(H₂O)₃]⁺ (M = Mn, Tc, Re) Complexes for New Radiopharmaceuticals. *Inorg. Chem.* **2006**, *45*, 10378–10390.

(39) Gligorovski, S.; Strekowski, R.; Barbati, S.; Vione, D. Environmental Implications of Hydroxyl Radicals (·OH). *Chem. Rev.* **2015**, *115*, 13051–13092.

(40) McGrady, J. E. Periodic trends in metal-metal bonding in cubane clusters, $(C_5H_5)_4M_4E_4$ [M = Cr, Mo, E = O, S]. J. Chem. Soc., Dalton Trans. 1999, 1393–1399.

(41) (a) Hummel, P.; Oxgaard, J.; Goddard, W. A., III; Gray, H. B. Ligand-Field Excited States of Metal Hexacarbonyls. *Inorg. Chem.* **2005**, *44*, 2454–2458. (b) Hartwig, J. F. *Organotransition Metal Chemistry, From Bonding to Catalysis;* University Science Books: Mill Valley, CA, 2010.

(42) (a) Yardley, J. T.; Gitlin, B.; Nathanson, G.; Rosan, A. M. Fragmentation and molecular dynamics in the laser photodissociation of iron pentacarbonyl. *J. Chem. Phys.* **1981**, *74*, 370–378. (b) Leadbeater, N. Enlightening organometallic chemistry: the photochemistry of $Fe(CO)_5$ and the reaction chemistry of unsaturated iron carbonyl fragments. *Coord. Chem. Rev.* **1999**, *188*, 35–70.

(43) Hatipoglu, A.; Vione, D.; Yalçin, Y.; Minero, C.; Çinar, Z. Photo-oxidative degradation of toluene in aqueous media by hydroxyl radicals. *J. Photochem. Photobiol.*, A **2010**, 215, 59–68.

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(44) Jin, Z.; Wen, Y.; Xiong, L.; Yang, T.; Zhao, P.; Tan, L.; Wang, T.; Qian, Z.; Su, B.-L.; He, Q. Intratumoral H2O2-triggered release of CO from a metal carbonyl-based nanomedicine for efficient CO therapy. *Chem. Commun.* **2017**, *53*, 5557–5560.