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Hydrogen gas formation from the photolysis of rhenium hydrides – mechanistic and computational studies†‡

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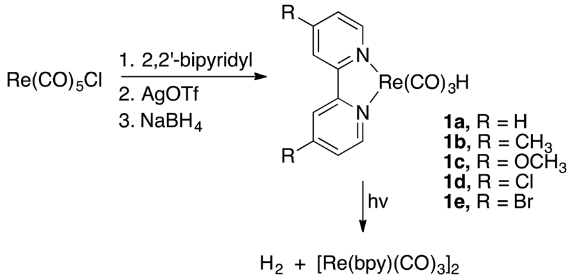
The photolysis of 4,4′-disubstituted, 2,2′-bipyridine *fac*-Re(bpy)(CO)$_3$H derivatives produces stoichiometric H$_2$ gas. The rate of production varies greatly depending on the electronic nature of the disubstituted bipyridine (bpy) with halogenated substituents increasing the rate. Isotope labeling studies along with B3LYP geometry optimization DFT modeling studies indicate a mechanism involving a Re–H–Re bridging complex that leads to a dimeric Re–Re(η^2-H$_2$) state prior to dissociating H$_2$ gas.

Rising carbon dioxide (CO$_2$) levels as a result of burning fossil fuels continue to necessitate the development of alternative carbon neutral energy sources.[1,2] Efficient sources of carbon neutral fuels, such as hydrogen gas (H$_2$), could provide the energy required to meet the rising global energy demands.

Rhenium(I) metal complexes have been investigated for their role in the photocatalytic reduction of CO$_2$ to CO,[3–8] and for the role they play as photosensitizers and photocatalysts in the solar energy conversion of water to H$_2$.[9] The advantages of utilizing rhenium(I) metal catalysts lie in their relative stability and the ease of excited state studies performed at room temperature.[10–15] For example, the use of *fac*-Re(bpy)(CO)$_3$Cl (bpy = 2,2′-bipyridine) as an efficient homogeneous catalyst for the selective, sustained photochemical, or electrochemical reduction of CO$_2$ to CO has been reported.[3,16,17] The corresponding rhenium(I) bipyridine carbonyl hydride analogues have also been reported,[18–20] in which electrocatalytic CO$_2$ reduction and insertion and photodissociation of Re–H have been investigated. Modifications to the bipyridine ligand have also provided some insight into the properties and photoreactivity of rhenium(I) hydrides during photolysis.[21,22] Recently, a three component system involving select rhenium hydrides, cobalt complexes and triethanolamine (TEA) has been reported for photocatalytic H$_2$ production.[9] Intermolecular hydrogen bonding of rhenium hydrides with proton donors has also been studied lending insight into the formation of ReH⋯HX bonds.[23] Perhaps most closely related to this work is the use of thermally unstable [Re(η^2-H$_2$)(CO)$_n$(L)$_m$]$^+$ complexes to form [Re(CO)$_n$(L)$_m$]BPh$_4$ complexes *via* the evolution of H$_2$.[24] However given the extensive investigations with Re(bpy)CO$_3$X, where X = H or halides, an in-depth study on the mechanism of X$_2$ formation has not been conducted. In this communication, the photochemical production of H$_2$ from bipyridyl tricarbonyl rhenium(I) hydrides is presented, along with a mechanism based on computational studies.

Although there has been an extensive amount of studies on Re(I) complexes, remarkably, the photochemical production of H$_2$ from *fac*-Re(bpy)(CO)$_3$H does not appear to have been reported.[25] Given that the synthesis of 2,2′-bipyridine *fac*-Re(bpy)(CO)$_3$H is known, Scheme 1,[26,27] and its 4,4′-disubstituted derivatives are all accomplished by facile, high yielding reactions, this system is ideal for studying this important reaction.

Photolysis, using a 200 W mercury–xenon lamp (*λ* = 380–750 nm), was initially performed in air on Re(bpy)(CO)$_3$H in a variety of solvents (CD$_3$CN, THF-d^8, acetone-d^6 and CD$_2$Cl$_2$) and monitored by ^{1}H NMR, Fig. 1. Consistent results were observed in all cases with the appearance of the H$_2$ resonance and the disappearance of the Re–H resonance. The dis-



Scheme 1 The reaction pathway for the synthesis of substituted Re(bpy)(CO)$_3$H complexes and hydrogen formation.

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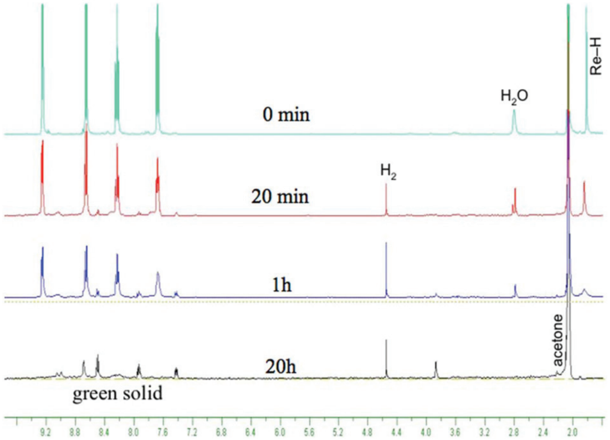


Fig. 1 ^1H NMR in acetone-d_6 of the photolysis of **1a**. Chemical shift in ppm.

appearance of the hydride resonance at 1.84 ppm along with the appearance of the H_2 resonance at 4.5 ppm is apparent. Interestingly, the spectrum also shows the disappearance of the water peak at 2.8 ppm and the degradation of the aromatic bipyridine peaks from 7.4–9.2 ppm. This degradation is attributed to the formation of the known solid $[Re(bpy)(CO)_3]_2$ dimer (see ESI Fig. S2‡),[4,28] which precipitates out of solution as a green solid upon exposure to light. UV-vis spectral data for the solid were consistent with previously published data.[4]

Given that no HD production was observed when using deuterated solvents, a crossover experiment was performed to identify the source of the H_2 gas. Photolysis of an approximately 1 : 1 mixture of $Re(bpy)(CO)_3H$ and $Re(bpy)(CO)_3D$ complexes resulted in the production of both HD and H_2 peaks as identified *via* ^1H NMR spectroscopy, Fig. 2. The HD peak was confirmed from both the chemical shift and the coupling constant ($\delta = 4.54$ ppm and $J_{HD} = 42.5$ Hz).[29,30] This indicates that hydrogen production is directly related to the reaction of rhenium hydride or rhenium deuteride with only each other and not with the solvent.

2,2′-Disubstituted bipyridines containing electron withdrawing groups **1d** and **1e** (R = Cl and Br) showed the fast disappearance of the hydride resonance, 10 and 8 minutes respectively, whereas complexes **1a–c** needed appreciably longer times of 20 (**1a**), 35 (**1b**) and 40 (**1c**) minutes to completely degrade at identical concentrations. This decrease in electron density in the bipyridine ring system allows for electronic stabilization during the metal to ligand charge transfer occurring during photolysis, which has also been observed and reported for *fac*-$Re(bpy)(CO)_3Cl$ complexes.[13]

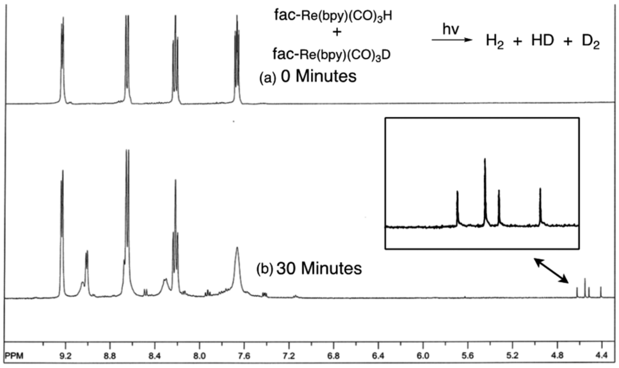
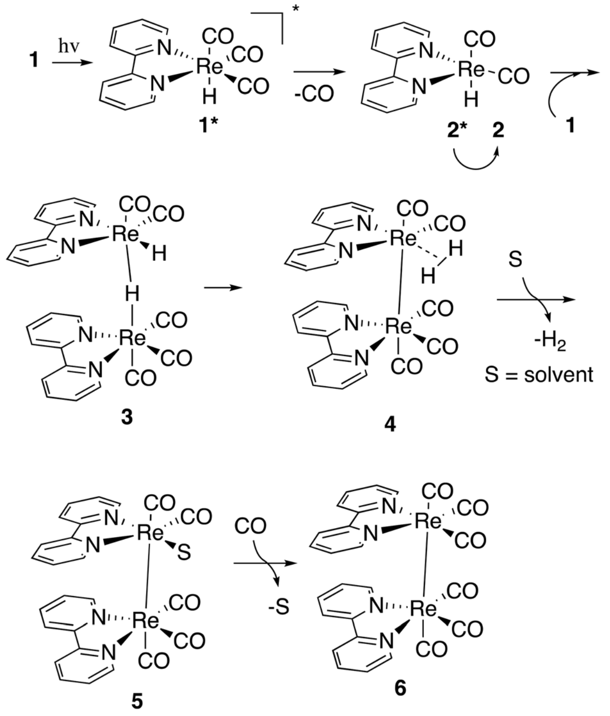


Fig. 2 The ^1H NMR crossover experiment of a 1 : 1 ReH/ReD mixture in acetone-d_6. (a) 0 minutes and (b) 30 minutes.

Photolysis was next carried out in an oxygen free environment, using **1e**, which showed an accelerated rate of formation of H_2. The initial degradation of Re–H was observed prior to photolysis; however, upon initiation of photolysis, the formation of the degradation product ceased and hydrogen formation began, also confirming the dependence of light. In the absence of light and O_2, degradation of the complex to an unknown product occurred without the production of H_2. Additional photolysis studies in both the presence and the absence of water were conducted in an effort to determine the role water plays in the reaction pathway. Thus, complex **1e** was dissolved in nearly dry d^6-acetone. Initial ^1H NMR was performed to determine the extent of water in the solvent, and photolysis was then performed until the water peak and the rhenium hydride resonances disappeared. Once the water peak disappeared, photolysis was continued until no additional H_2 was produced. Additional complex **1e** was added to the solution (only the Re–H singlet was visible in the NMR spectrum, with no H_2 or H_2O signals observed) and photolysis was resumed. The formation of new H_2 was again observed demonstrating that H_2 production is only dependent upon the presence of Re–H and light. Finally, a dry d^6-acetone/Re–H sample was spiked with D_2O and photolyzed, which produced only an H_2 signal and no HD triplet.

With these data in hand, the mechanism illustrated in Scheme 2 is proposed. An excited state $Re(bpy)(CO)_3H$ **1*** undergoes initial dissociation of CO to produce **2***. Photochemical dissociation of CO from *fac*-$Re(bpy)(CO)_3Cl$ has been shown to occur by Ishitani and co-workers.[8,31] In their report, loss of CO occurs followed by rearrangement and then re-coordination of CO to produce *mer*-$Re(bpy)(CO)_3Cl$ in both the presence and the absence of a CO atmosphere. Following CO dissociation **2*** relaxes to the ground (singlet) state **2**, which forms bridged Re–H–Re **3** with subsequent hydride transfer and Re–Re dimer formation to produce $Re(\eta^2\text{-}H_2)$ **4**. Dihydrogen transfer between $CpRe(PPh_3)_2H_3$ and $IrBr(CO)(dppe)$ has been reported,[32] and stable cationic η^2-H_2 rhenium complexes have been synthesized and characterized through the addition of H_2 to unsaturated rhenium complexes;[33] thus excellent precedence exists for this step. Loss of H_2 with concurrent solvent coordination, which could also be water, leads to the observed dimers **5** and/or **6**. Solvent coordination in these types of systems is also well precedented,[4,28] however, coordination of CO could also occur in this step.

The reaction pathway in Scheme 2, where after the initial CO dissociation (**1***→**2***) the reaction proceeds in the electronic ground states, is the most likely pathway, as the excited state lifetimes are on the order of tens to hundreds of



Scheme 2 The proposed mechanism for the formation of H_2 from the photolysis of $Re(bpy)(CO)_3H$.

nanoseconds,[4,25] which are presumably significantly shorter than the rate of the next (bimolecular) reaction step. However, it is possible that alternative pathways exist with additional steps in the excited (triplet) states, in particular since the reaction is performed under continuous illumination. As the computational modeling below demonstrates, all these pathways are energetically feasible (Fig. 3) and the singlet and triplet intermediate species are structurally very similar (ESI‡).

Support for the proposed mechanism was obtained from computational modeling using density functional theory (DFT). Previous computational studies found that the final dimeric complex $[Re(bpy)(CO)_3]_2$ **6** prefers a skewed *trans* arrangement (rotation about the Re–Re bond)[28] with the orientation of the stacked $Re(bpy)(CO)_3$ rotated by ∼140° over the skewed *cis* arrangement, with an ∼40° angle. We found this to be the case without the empirical correction for dispersion, however, inclusion of the dispersion interaction[34] reverses the order of stability with the skewed *cis* conformation preferred by ∼3 kcal mol^{-1}. The skewed *cis* arrangement is also consistent with the crystal structure of the manganese biphosphine analogue $[Mn(tmbp)CO_3]_2$ (tmpb = 4,4′-tetramethyl-2,2′-biphosphine).[35]

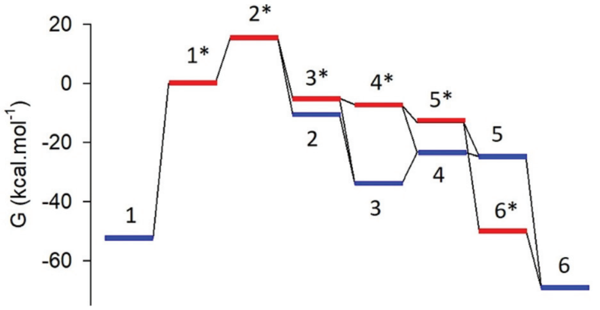


Fig. 3 The schematic energy diagram for the proposed reaction mechanism (in acetone). Gibbs free energy calculated using the corrected SMD method (see text for details) is plotted for each of the chemical species relative to the reactant species: **1** (singlet ground state $Re(bpy)(CO_2)_3H$), **1*** (triplet excited state $Re(bpy)(CO_2)_3H$) and solvent (acetone). The blue levels correspond to the singlet states and the red levels to triplet states. The numbering follows that in Scheme 2 text (see also Fig. S2 in the ESI‡).

The initial structures of intermediates **3**, **4** and **5** (Scheme 2) were therefore constructed to correspond to the skew *cis* final product. These were fully optimized at the DFT level, with the B3LYP density functional and the 6-31G(d) basis set for C and H, 6-31+G(d) for N and O, LANL2DZ for Re,[28] Grimme empirical dispersion correction[34] and the polarized continuum model for the solvent.[36,37] We also modeled the corresponding triplet excited states **3***, **4***, **5*** and **6***.

The optimized geometry parameters are summarized in Tables S1–S3 (ESI‡), along with the electronic energies and thermal free energies (at 298 K, 1 atm) of the individual species (Table S4‡). A schematic diagram of the Gibbs free energies computed using the corrected SMD method[36,37] for acetone solvent is plotted in Fig. 3. (The corresponding diagram for THF is shown in the ESI, Fig. S2.‡)

It is evident that multiple pathways with the triplet–singlet relaxation occurring at different steps are feasible. The triplet pathway (red in Fig. 3) is thermodynamically downhill after the dissociation of CO from **1***, which requires a total of ∼86 kcal mol^{-1} (the triplet state **1*** is about 56 kcal mol^{-1} higher in energy than the ground singlet state and the CO dissociation requires an additional ∼30 kcal mol^{-1}). By contrast, the singlet pathway (highlighted in blue in Fig. 3) has an uphill step of ∼10 kcal mol^{-1} in the rearrangement of the hydrogen bridged **3** to $Re(\eta^2\text{-}H_2)$ **4**. The final product singlet $[Re(bpy)(CO)_3]_2$ is thermodynamically more stable than the reactant singlet $Re(bpy)(CO_2)_3H$, by ∼20 kcal mol^{-1}.

Structurally, the triplet state of monomer **1*** is considerably distorted from the octahedral geometry around the Re atom (Table S2 and Fig. S2‡). **2*** has a rather regular trigonal bipyramidal arrangement, in contrast to the ground state **2**, which again resembles an octahedral structure, but with one equatorial coordination site vacant. For the remaining reaction intermediates (**3–5**) and the product complex (**6**) the singlet and triplet structures are very similar (Tables S2 and S3, and Fig. S2‡). The first proposed double-Re complex **3** has the two Re centers bridged by hydrogen, however, a Re–Re bond is also likely, since the Re–Re distance is less than 0.3 Å longer than that in the fully formed complex **6** (for the triplet states of **3*** the Re–Re distance is only 0.1 Å greater than that in **6***). Complexes **4** and **4*** have the shortest Re–Re distances for all the singlet and triplet species, respectively.

Note also that if only vibrational contributions to the free energy are considered (the rightmost column of Table S4‡), corresponding to the limit of no free translations or rotations which are generally significantly constrained in the condensed phase (solution), the differences between the individual species are more pronounced. For example, the overall ΔG for the reaction is about 30 kcal mol^{-1}.

Conclusions

Photocatalytic hydrogen formation using the energy from the sun may provide an alternative green energy source. In this work, we have shown that rhenium hydrides can produce H_2 *via* photolysis and have further elucidated a working mechanism for this process. An alternative mechanism to the proposed bridged monohydrogen Re–H–Re species would be a bridged dihydrogen complex (Re–H_2–Re), which has been postulated previously in both ruthenium and osmium systems.[38,39] However, modeling studies have indicated that an analogous bridged Re–H_2–Re intermediate is of considerably higher energy than the Re–H–Re species proposed herein. Thus, we propose that the rhenium system reported follows a discreetly different mechanism.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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