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Mechanistic basis for tuning iridium hydride photochemistry from H₂ evolution to hydride transfer hydrodechlorination†

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The photochemistry of metal hydride complexes is dominated by H₂ evolution, limiting access to reductive transformations based on photochemical hydride transfer. In this article, the innate H₂ evolution photochemistry of the iridium hydride complexes [Cp*Ir(bpy-OMe)H]⁺ (**1**, bpy-OMe = 4,4'-dimethoxy-2,2'-bipyridine) and [Cp*Ir(bpy)H]⁺ (**2**, bpy = 2,2'-bipyridine) is diverted towards photochemical hydrodechlorination. Net hydride transfer from **1** and **2** to dichloromethane produces chloromethane with high selectivity and exceptional photochemical quantum yield ($\Phi \leq 1.3$). Thermodynamic and kinetic mechanistic studies are consistent with a non-radical-chain reaction sequence initiated by "self-quenching" electron transfer between excited state and ground state hydride complexes, followed by proton-coupled electron transfer (PCET) hydrodechlorination that outcompetes H–H coupling. This unique photochemical mechanism provides a new hope for the development of light-driven hydride transfer reactions.

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Introduction

The photochemistry of transition metal complexes underpins a range of applications, including organic light-emitting diode (OLED) development,^{1,2} solar energy conversion,^{3–6} and photoredox catalysis.^{7–11} The photocatalysts in these systems usually operate *via* pathways that involve excited state single-electron transfer (SET), and careful photophysical and photochemical studies have established factors that give rise to photocatalysts with long excited-state lifetimes and good long-term stability.^{12–15} In terms of electronic structure, a large ligand field splitting (or a d¹⁰ configuration) is often critical. In terms of chemical structure, complexes that successfully engage in outer-sphere SET are typically supported by rigid chelating ligands that are completely inert towards chemical reactivity.

New opportunities can be imagined for photocatalysts that go beyond SET reactivity to tightly couple light absorption with bond-forming and bond-breaking chemical reactions. Photochemical ligand dissociation from transition metal complexes,

such as CO release from carbonyl complexes, has been the subject of intense study.^{16,17} Photodissociation can initiate thermal catalytic reactions *via* the generation of highly reactive coordinatively unsaturated intermediates.^{3,18–21} Other systems capable of photochemical bond-forming reactions include metal–halide complexes (*e.g.* dihalogen generation);^{3,4,22} metal–amide complexes (*e.g.* C–N cross-coupling reactions);^{23–29} and metal–aryl complexes (*e.g.* dual photoredox cross-coupling catalysis).^{10,30–32}

Complexes with metal–hydride bonds would appear to be ideal candidates for photocatalytic reductions involving net hydride transfer to an organic substrate, but examples of photochemical organic transformations utilizing metal hydride complexes are scarce.³³ The lack of development is likely due to a challenge that is unique to metal–hydride photocatalysts: there is an inherent competition between hydride transfer and H₂ evolution. Indeed, metal hydride complexes are quintessential H₂ evolution photocatalysts,³³ with particular application in the synthesis of solar fuels.³ Understanding how to tune the photochemical reactivity of metal hydride complexes between H₂ evolution and hydride transfer represents a fundamental challenge.

Iridium hydride complexes of the type [Cp*Ir(bpy-R)H]⁺ (bpy-R is 4,4'-disubstituted-2,2'-bipyridine) are promising candidates for exploring the photochemical activation of metal–hydride bonds.³⁴ Photoexcitation generates a weakly emissive metal–ligand charge transfer (MLCT) excited state.³⁵ The high degree of MLCT character derives from the strong σ -donor ability of the

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hydride ligand.³⁶ The photochemistry of these Ir hydride complexes is dominated by H₂ evolution (Scheme 1). Photocatalytic H₂ evolution was first reported in aqueous conditions,^{37–41} with subsequent research demonstrating photoelectrochemical H₂ production and photocatalytic formic acid dehydrogenation.^{42,43} In acetonitrile solvent, photolysis of [Cp*Ir(bpy)H]⁺ (either alone or with added acids) also produces H₂ in high yield.⁴⁴

Complex [Cp*Ir(bpy)H]⁺ undergoes H₂ evolution *via* a mechanism that is thus far unique amongst molecular hydrides. The MLCT excited state undergoes “self-quenching” electron transfer with a ground state hydride complex, followed by rapid bimolecular H–H coupling.⁴⁵ As such, the photochemical quantum yield for H₂ production approaches unity as the initial concentration of iridium complex is increased above 20 mM. Due to the bimolecular mechanism, H₂ is produced in good yield even in the absence of external proton sources.

While prior studies of [Cp*Ir(bpy-R)H]⁺ complexes have focused on photochemical H₂ evolution, we were surprised to observe net photochemical hydride transfer to a nicotinamide derivative in acetonitrile solvent (Scheme 1).⁴⁴ While promising as the first example of even a stoichiometric light-driven hydride transfer, this reaction suffered from low yields and competing H₂ evolution (even though no proton source was added). The reaction mechanism has not yet been explored. Nonetheless, the precedent for both H₂ evolution and hydride

transfer in the same iridium hydride complex led us to embark on further studies to elucidate the factors that control reactivity between H₂ evolution and hydride transfer.

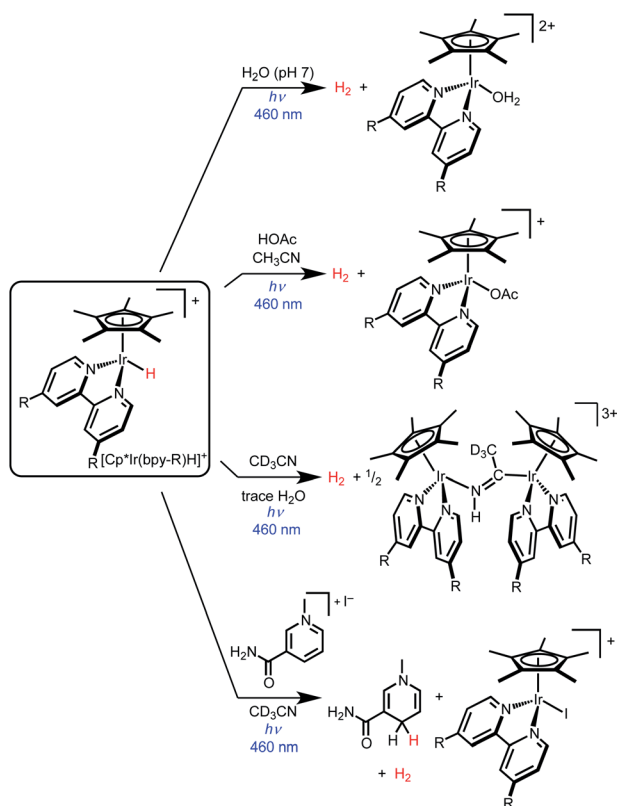
Here we report near-complete suppression of H₂ evolution and a switch to net hydride transfer in the presence of dichloromethane or other alkyl chlorides. Mechanistic studies of dichloromethane photoreduction elucidate a self-quenching electron transfer pathway that generates reactive organometallic intermediates capable of hydride transfer and hydrogen atom transfer reduction of CH₂Cl₂. Because a single photon absorption triggers the reactivity of two different metal centers, the maximum theoretical quantum yield is 2; experimental conditions were found that achieve $\Phi = 1.3$. The mechanistic insight into the factors that can suppress H₂ evolution and enable hydride transfer provides general guidance for future catalyst structures with photocontrolled reactivity.

Results and discussion

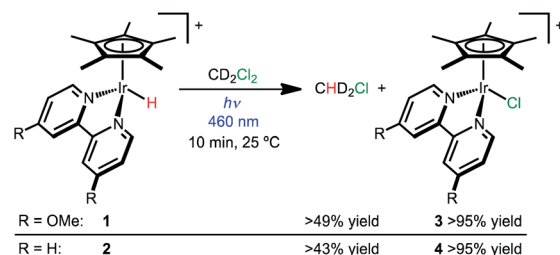
Photochemical hydrodechlorination of alkyl chlorides

Hydride complexes [Cp*Ir(bpy-OMe)H][OTf] (**1**) and [Cp*Ir(bpy)H][OTf] (**2**) were prepared following previously developed approaches.^{44,46} Hypothesizing that high concentrations of a hydride acceptor substrate could promote hydrodechlorination, dichloromethane was explored as both substrate and solvent.

Hydride **1** was dissolved in dichloromethane-*d*₂ (CD₂Cl₂) and monitored by NMR spectroscopy while protected from light, with only 3% conversion to [Cp*Ir(bpy-OMe)Cl]⁺ (**3**) observed after 2 h at 25 °C. Illumination of **1** in CD₂Cl₂ with a 460 nm LED lamp for 10 min produced chloride complex **3** quantitatively (Scheme 2). A diagnostic 1 : 2 : 3 : 2 : 1 pentet for dissolved chloromethane-*d*₂ gas (CHD₂Cl δ 2.99, $J_{\text{HD}} = 1.6$ Hz) was also observed (49% yield relative to **1** by ¹H NMR). The excitation wavelength was chosen to match the MLCT transition (λ_{max} ca. 420 nm, Fig. S23†).⁴³ When the same experiment was run in CH₂Cl₂, chloromethane (CH₃Cl) was produced in 69% yield relative to **1** (¹H NMR). Some of the volatile chloromethane product is lost to the headspace over time, so the solution yields are considered lower limits. Soluble H₂ was not detectable by ¹H NMR spectroscopy. The gas phase yield of H₂ was less than 4% relative to **1**, according to headspace analysis by gas chromatography (GC).



Scheme 1 Photochemical reactivity of iridium hydride complexes [Cp*Ir(bpy-R)H]⁺ (bpy-R is 4,4'-disubstituted-2,2'-bipyridine).



Scheme 2 Visible light photochemical hydrodechlorination of CD₂Cl₂.



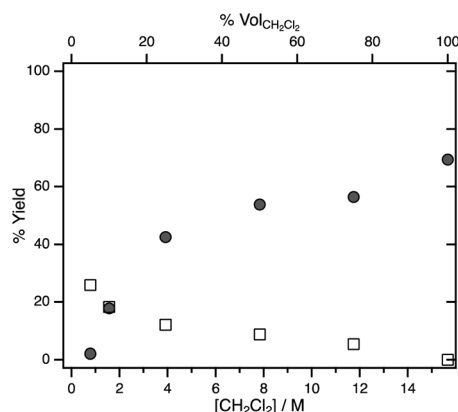
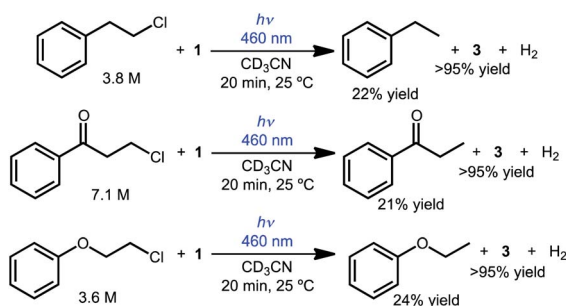


Fig. 1 Yield of dissolved CH₃Cl (filled circles) and H₂ (empty squares) measured by ¹H NMR spectroscopy after 10 min photolysis of **1** in CH₂Cl₂/CD₃CN mixtures of varying solvent ratios (where % vol_{CH₂Cl₂} is the volume percent of CH₂Cl₂ and [CH₂Cl₂] is the concentration of CH₂Cl₂).

Hydride **2** exhibits similar reactivity, producing chloride complex [Cp*Ir(bpy)Cl]⁺ (**4**; >95% yield) and CHD₂Cl (43% yield relative to **2**) after 10 min of 460 nm illumination in CD₂Cl₂ (Scheme 2). When the same experiment was run in CH₂Cl₂, chloromethane (CH₃Cl) was produced in 50% yield. When protected from light, only 6% conversion of **2** was observed after 1 h.

To probe the effect of substrate concentration on the selectivity between H₂ formation and hydrodechlorination systematically, photolysis was carried out in various dichloromethane/acetonitrile mixtures. Fig. 1 shows the yields of dissolved CH₃Cl and H₂ determined by ¹H NMR spectroscopy after illumination of hydride **1** in CH₂Cl₂/CD₃CN mixtures for 10 min. Even when CD₃CN makes up the majority of the solvent, the yield of dissolved CH₃Cl is higher than that of H₂.

To further probe the competition between H₂ evolution and hydride transfer, reactions were carried out in the presence of acid. Illumination of hydride complex **1** in CD₂Cl₂ solutions containing 1 equiv. acetic acid generated the chloride complex **3**—and not the acetate complex expected upon H₂ release.⁴⁴ Even in the presence of acid, selective hydrodechlorination of dichloromethane is observed.



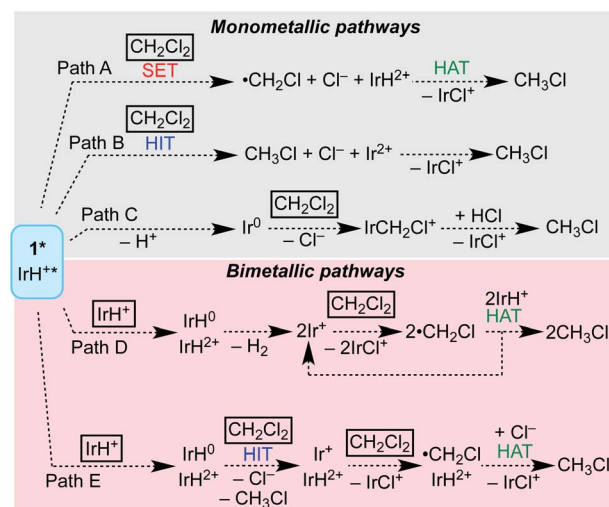
Scheme 3 Photochemical hydrodechlorination of primary alkyl chlorides.

The tolerance of proton donors suggested that an aqueous formate solution could close a catalytic cycle by regenerating the iridium hydride after initial hydride transfer to the substrate. Illumination of biphasic mixtures of chloride complex **3** in CD₂Cl₂ and 1 M formate in H₂O indeed produced chloromethane (TON > 2, see Section III in the ESI† for details).

The reactivity can also be extended to other simple chlorinated organic substrates dissolved in acetonitrile. Three model substrates were selected, 2-chloroethylbenzene, 3-chloropropiophenone, and 2-chloroethoxybenzene. As shown in Scheme 3, illumination of CD₃CN solutions of **1** and the primary alkyl chloride substrate produced the dechlorinated products in approximately 20% yield relative to **1** by ¹H NMR spectroscopy (with the balance presumably producing H₂ gas, detected in solution in up to 66% yield; no other organic products were detected).

The selective hydride transfer reactivity of **1** and **2** in dichloromethane solution draws a sharp contrast to the efficient H₂ evolution reactivity of these same hydride complexes in acetonitrile or water solutions.^{41–44} In pure acetonitrile solutions without any acid present, some H₂ evolution is observed, followed by Ir nucleophilic attack on the solvent to form an iminoacyl complex.⁴⁴ In the presence of acetic acid, triethylammonium, or pyridinium, quantitative H₂ evolution is observed.

In this context, we also examined chlorobenzene as a chlorinated substrate that would be unlikely to undergo reduction *via* hydride transfer.⁴⁷ When chlorobenzene-*d*₅ (C₆D₅Cl) solutions of **1** or **2** were illuminated with a 443 nm lamp, a signal for H₂ was detected by ¹H NMR spectroscopy without evidence for the hydrodechlorination product benzene. Photolysis of a 2 mM solution of **2** in C₆H₅Cl for 35 min produced H₂ in 52% yield (GC). An unidentified iridium-containing yellow precipitate formed in these reactions. The results in chlorobenzene underscore the innate H₂ evolution reactivity of **1** and **2** in the absence of a suitable hydride acceptor, even when no proton donor is added.



Scheme 4 Photochemical hydrodechlorination pathways considered.



To understand the origin of the selective photochemical hydride transfer reactivity, we carried out a series of thermodynamic and kinetic studies to examine the detailed mechanism of photochemical hydrodechlorination by iridium hydride complexes, focusing on the highest yielding substrate, dichloromethane.

Overview of mechanistic pathways considered

Scheme 4 shows several possible reaction pathways for photochemical hydrodechlorination. The pathways can be divided into two categories: in monometallic pathways, the excited state of **1** (**1**^{*}) interacts with CH₂Cl₂ directly; in bimetallic pathways, the excited state undergoes a “self-quenching” process with an equivalent of **1** in the ground state before interacting with CH₂Cl₂.^{31,45,48–50}

Monometallic pathways could proceed *via* Path A, single electron transfer (SET) followed by hydrogen atom transfer (HAT); *via* Path B, hydride ion transfer (HIT); or *via* Path C, photoacid generation of H⁺ and a nucleophilic Ir(i) center.⁵¹ Complex **2** catalyzes thermal hydrodehalogenation of alkyl bromides (but not alkyl chlorides) *via* a HIT mechanism.⁵²

Bimetallic pathways could proceed *via* initial self-quenching electron transfer to form a reactive pair of Ir(II) and Ir(IV) hydrides,⁴⁵ with Path D proceeding by a radical chain reaction; or the PCET Path E proceeding by stoichiometric HIT and HAT steps. Radical chain hydrodehalogenation is observed for reagents such as Bu₃SnH, which requires a radical initiator to generate ·CH₂Cl.⁵³ In the present case, a small amount of Ir hydride could undergo photochemical H₂ release, generating an Ir(II) species that could undergo Cl-atom abstraction from CH₂Cl₂ to generate ·CH₂Cl, which in turn could react with an Ir hydride to furnish CH₃Cl and initiate a new chain (Path D). The alternative bimetallic pathway would involve hydride transfer to CH₂Cl₂ from the neutral hydride complex Cp^{*}Ir(bpy-R)H, followed by Cl[·] abstraction from a second CH₂Cl₂ and finally HAT from the oxidized hydride [Cp^{*}Ir(bpy-R)H]²⁺ (Path E).

Thermochemical analyses of the pathways shown in Scheme 4 were carried out, as detailed in Section V in the ESI.† Each pathway appears to be thermodynamically viable. Some steps are close to ergoneutral, however, and other steps are likely to face significant kinetic challenges. To distinguish between these viable pathways, a kinetic analysis of the photochemical hydrodechlorination reaction was undertaken.

Photoluminescence quenching kinetic studies

The kinetics of excited state quenching, probed by time-resolved photoluminescence measurements, can differentiate amongst the pathways considered in Scheme 4. In monometallic pathways, the luminescence lifetime should shorten with increasing concentration of CH₂Cl₂. In bimetallic pathways, the luminescence lifetime should shorten with increasing concentration of iridium hydride.

The role of CH₂Cl₂ was probed by analyzing the photoluminescence lifetime of **1**^{*} in solutions of CH₃CN with varying concentration of CH₂Cl₂ (and a constant 1 mM concentration of **1**). As shown in Fig. 2, the lifetime of **1**^{*} is essentially invariant

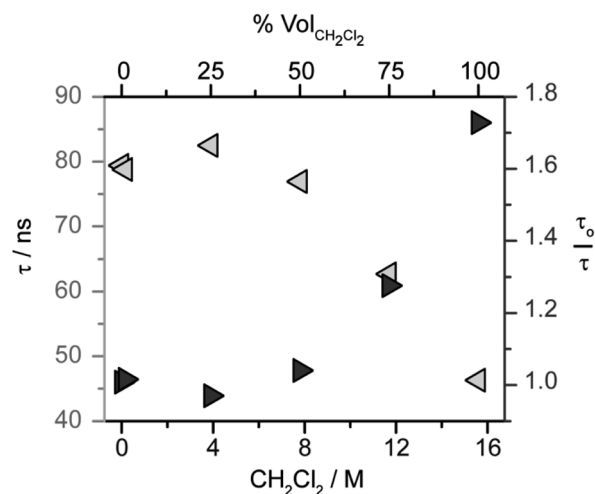
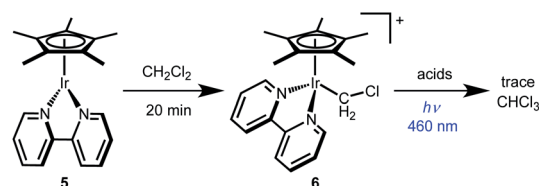


Fig. 2 Evaluation of excited state quenching of [Cp^{*}Ir(bpy-OMe)H][PF₆] (**1**) by CH₂Cl₂ by time-resolved photoluminescence spectroscopy. Observed lifetimes (τ, light gray left arrows) and Stern–Volmer analysis (τ₀ = 80 ns, dark gray right arrows) in CH₂Cl₂/CH₃CN mixtures at a constant 1 mM concentration of **1**. Excitation at 445 nm, luminescence decay monitored at 650 nm. In the axes, % vol_{CH₂Cl₂} is the volume percent of CH₂Cl₂ and [CH₂Cl₂] is the concentration of CH₂Cl₂.

up to 8 M CH₂Cl₂, suggesting that monometallic pathways A and B that involve CH₂Cl₂ quenching are not operative. While the lifetime decreases above 8 M (50 vol%) CH₂Cl₂, the lack of a linear correlation in the Stern–Volmer analysis (Fig. 2) shows that the change in lifetime is not related to a diffusional quenching process. The change in lifetime is instead attributed to solvation effects changing with solvent composition, as has been observed for other charge-transfer-based excited states.^{49,54–57}

The other monometallic pathway, Path C, involves initial photochemical H⁺ release to form Cp^{*}Ir(bpy) (**5**) followed by Ir nucleophilic attack on CH₂Cl₂ to form a chloromethyliridium intermediate [Cp^{*}Ir(bpy)(CH₂Cl)]⁺ (**6**) that could undergo protonolysis to release CH₃Cl. This pathway could not be ruled out by the Stern–Volmer quenching experiment, but was discounted based on independent reactivity of complexes **5** and **6**. Dissolving **5** in CH₂Cl₂ leads to formation of chloromethyliridium complex **6** within 20 min at room temperature (Scheme 5). Chloromethyl complex **6** is quite stable, however. Treatment with various acids does not generate significant amounts of CH₃Cl, even under illumination (Scheme 5). The chloromethyl



Scheme 5 Chloromethyl complex **6** was synthesized and shown to be kinetically incompetent for CH₂Cl₂ reduction.



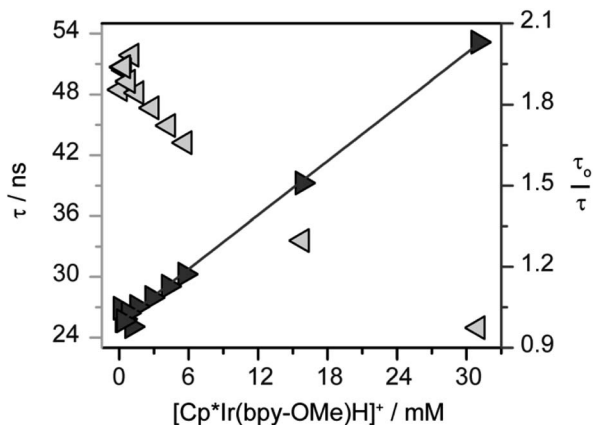


Fig. 3 Evaluation of excited state self-quenching in $[\text{Cp}^*\text{Ir}(\text{bpy-OMe})\text{H}][\text{PF}_6]$ (**1**) by time-resolved photoluminescence spectroscopy. Observed lifetimes (τ , light gray left arrows) and Stern–Volmer analysis ($\tau_0 = 54$ ns, dark gray right arrows) in CH_2Cl_2 . Excitation at 445 nm, luminescence decay monitored at 650 nm. The linear fit corresponds to a $k_q = 6.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

complex **6** is therefore not kinetically competent to carry out the observed reactivity.

To assess the possibility of a bimetallic self-quenching pathway in which excited state **1**^{*} is quenched by hydride **1**, the luminescence lifetime of **1**^{*} in CH_2Cl_2 was evaluated as the concentration of **1** was increased from 0.094 mM to 31 mM (Fig. 3). The luminescence lifetime decreases with increasing concentration of **1**, from which the intrinsic lifetime, $\tau_0 = 50$ ns, can be obtained by extrapolation to infinite dilution (Fig. 3). The intrinsic lifetime of **1** in CH_2Cl_2 is shorter than the intrinsic lifetime of **2** in CH_3CN with 0.1 M $[\text{nBu}_4][\text{PF}_6]$ ($\tau_0 = 98$ ns),⁴⁵ consistent with the radiative decay rates being affected by the solvent composition.

A linear correlation in the Stern–Volmer analysis varying the concentration of **1** (Fig. 3) is consistent with a bimetallic self-quenching pathway, with $k_q = 6.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The rate of self-quenching in CH_2Cl_2 is notably slower than in CH_3CN ($k_q = 3.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$),⁴⁵ perhaps due to the relatively low polarity of CH_2Cl_2 disfavoring the reaction of two cationic metal complexes.

Although the net photochemistry is starkly different in CH_3CN (H_2 evolution) and CH_2Cl_2 (hydrodechlorination), the Ir hydrides undergo the same initial self-quenching reaction in each solvent. The self-quenching step is estimated to be slightly thermodynamically unfavorable (by about 5 kcal mol^{−1} on the basis of excited state redox potentials, Fig. S19†). Other examples of excited state self-quenching are also close to ergoneutral, including a recent nickel example that is substantially endergonic.^{31,45,48–50}

A self-quenching mechanism should give rise to strongly concentration-dependent photochemistry. Fig. 4 presents the quantum yields for consumption of **1** (based on UV-vis spectroscopic monitoring of the initial rate, see ESI† for details) upon photolysis with 443 nm light in CH_2Cl_2 , revealing a dramatic dependence on iridium concentration that reaches

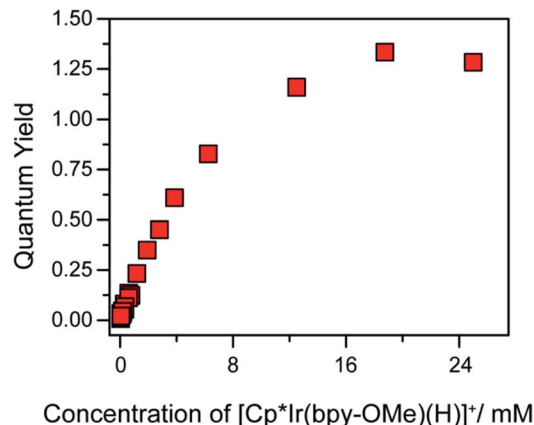


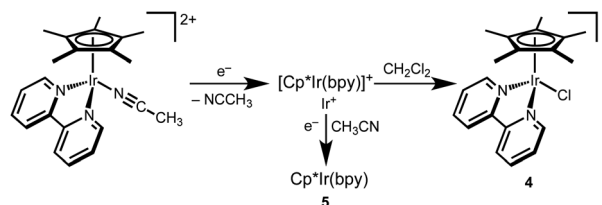
Fig. 4 Quantum yield of photochemical CH_2Cl_2 hydrodechlorination (443 nm illumination) by $[\text{Cp}^*\text{Ir}(\text{bpy-OMe})\text{H}][\text{PF}_6]$ (**1**) as a function of concentration of **1**.

a maximum exceeding unity, $\Phi = 1.3$. The linear increase in quantum yield with increasing iridium concentration up to 8 mM **1** is further evidence of a bimetallic mechanism. The maximum quantum yield exceeding unity suggests either a photochemically triggered radical chain reaction (Path D) or a bimetallic self-quenching pathway that generates two equivalents of chloromethane per photon absorbed (Path E).

Distinguishing between bimetallic pathways

Of the mechanisms considered in Scheme 4, only Paths D and E can explain the bimetallic reactivity with a quantum yield greater than 1. In each pathway, photoexcitation of **1** is followed by self-quenching electron transfer to generate a pair of Ir(IV) and Ir(II) hydrides. In the radical chain mechanism of Path D, photochemical H_2 release would generate an Ir(II) intermediate capable of abstracting a chlorine atom from CH_2Cl_2 , which would initiate radical hydrodehalogenation reminiscent of Bu_3SnH reactivity.^{47,53} The quantum yield for this pathway could be much higher than unity,⁵⁸ depending on the rates of chain propagation and termination. In the stoichiometric mechanism of Path E, the Ir(II) hydride formed after self-quenching would hydrodechlorinate CH_2Cl_2 by hydride transfer. The resulting Ir(II) intermediate would abstract a chlorine atom from CH_2Cl_2 , followed by H atom transfer from the Ir(IV) hydride. This mechanism would have a theoretical quantum yield of 2.

To probe the viability of chlorine atom abstraction from CH_2Cl_2 by an Ir(II) intermediate, cyclic voltammograms of



Scheme 6 Proposed mechanism of electrochemically triggered formation of **4**.

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The second C–H bond-forming pathway involves HAT, rather than hydride transfer.

The present mechanistic study offers insight into future designs. The presence of reactive metal–hydride bonds is a key feature of this system, enabling rapid PCET reactivity immediately after excited state electron transfer. The step that controls the selectivity between H₂ evolution and hydride transfer occurs directly after self-quenching. To maximize hydride transfer reactivity, a high concentration of substrate can be introduced to intercept the reactive hydride pair before H–H coupling can occur. Alternatively, the H–H coupling step could be slowed, for example by changing the structure to provide steric or geometric constraints. Improved understanding of metal hydride photochemical reactivity will open new avenues in photocatalytic synthesis.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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