

Photoswitchable Hydride Transfer from Iridium to 1-Methylnicotinamide Rationalized by Thermochemical Cycles

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S Supporting Information

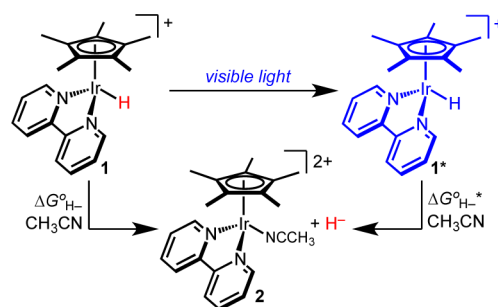
ABSTRACT: Visible light-triggered hydride transfer from $[\text{Cp}^*\text{Ir}(\text{bpy})(\text{H})]^+$ (**1**) to organic acids and 1-methylnicotinamide (MNA^+) is reported (Cp^* = pentamethylcyclopentadienyl; bpy = 2,2'-bipyridine). A new thermochemical cycle for determining excited-state hydride donor ability (hydricity) predicted that **1** would be an incredibly potent photohydride in acetonitrile. Phototriggered H_2 release was indeed observed from **1** in the presence of various organic acids, providing experimental evidence for an increase in hydricity of at least 18 kcal/mol in the excited state. The rate and product selectivity of hydride transfer to MNA^+ are photoswitchable: 1,4-dihydro-1-methylnicotinamide forms slowly in the dark but rapidly under illumination, and photolysis can also produce doubly reduced 1,4,5,6-tetrahydro-1-methylnicotinamide.

Hydride (H^-) transfer between a transition metal and an organic substrate is involved in numerous catalytic transformations, especially hydrogenations and dehydrogenations.¹ To improve catalysis, one can tune the hydride donor ability (hydricity) of the catalyst. This strategy is empowered by thermodynamic measurements of hydricity (the free energy required for heterolytic $\text{M}-\text{H}$ bond cleavage) that have emerged over the past 15 years as a quantitative guide in catalyst design.^{2,3} The hydricity of a catalytic intermediate is typically tuned through synthetic modification, such as installing more strongly donating ligands to generate more hydridic intermediates.

This work pursues an alternative strategy for tuning reactivity while avoiding synthetic modification: harnessing visible light to enhance hydricity. Hydride $[\text{Cp}^*\text{Ir}(\text{bpy})(\text{H})]^+$ (**1**) releases H_2 in the presence of weak acids only under visible light illumination. Thermochemical cycles and experimental studies are both consistent with net H^- transfer being greatly promoted by light. In reactions with the organic acceptor 1-methylnicotinamide (MNA^+), illumination dramatically accelerates H^- transfer and exhibits photoswitchable product selectivity.

Hydride **1** was investigated because it is commonly invoked as a catalytic intermediate in hydrogenation and dehydrogenation reactions, among other transformations.⁴ While most of these reactions proceed without any influence of light, **1** also exhibits photochemical reactivity, including stoichiometric light-promoted proton transfer⁵ and photocatalytic water/gas shift reactivity.⁶ Photochemical H_2 release involving formal H^- donation from a metal hydride to a proton source is rare.⁶⁻⁸ Photohydride transfer from a $\text{M}-\text{H}$ bond to an organic substrate

Scheme 1



is unprecedented, despite the potential utility of light-triggered reductions.

We recently harnessed the proclivity of **1** to release H_2 under illumination to realize a photoelectrocatalytic water reduction cycle.⁹ Hydride **1** is produced in an electrochemical step before undergoing light-triggered H_2 evolution. The action of light is striking: no catalytic activity is observed in the dark, but visible light illumination triggers catalysis. The formal photohydride reactivity of **1** sparked our interest in understanding the difference between ground-state and excited-state hydricity and in expanding such photohydride reactivity to organic substrates.

Thermodynamic calculations were a useful starting point in rationalizing the reactivity of **1** and its excited state, **1***. All thermodynamic values are determined and reported in CH_3CN solvent, in order to facilitate comparisons with values previously established for other hydrides.¹⁰ The ground-state hydricity of **1** ($\Delta G_{\text{H}^-}^\circ$) can be determined by obtaining the $\text{p}K_a$ of **1** and the reduction potential of $[\text{Cp}^*\text{Ir}(\text{bpy})(\text{NCCH}_3)]^{2+}$ (**2**), according to eq 1.¹¹ The constant C_{H^-} (79.6 kcal/mol) is the formal potential (vs $\text{Cp}_2\text{Fe}^{+/0}$) for $2e^-$ reduction of H^+ to H^- .¹¹

$$\Delta G_{\text{H}^-}^\circ = 1.37(\text{p}K_a) - (-46.12)(E_{1/2}) + C_{\text{H}^-} \quad (1)$$

Spectrophotometric titration of hydride **1** in CH_3CN with 1,8-diazabicyclo[5.4.0]undec-7-ene provided a $\text{p}K_a$ value of 23.3.¹² Cyclic voltammetry of CH_3CN complex **2** revealed a quasi-reversible $2e^-$ reduction at -1.07 V vs $\text{Cp}_2\text{Fe}^{+/0}$. These values provide the ground-state hydricity of **1** (eq 1): $\Delta G_{\text{H}^-}^\circ = 62$ kcal/mol. The hydricity of **1** is similar to the ubiquitous biological H^- -transfer reagent NADH.¹³

The relatively weak ground-state hydricity of **1** leads to good stability even in quite acidic environments when protected from light. In the dark, hydride **1** showed no reaction after 1 h when

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mixed with acetic acid (HOAc, $pK_a = 23.5$),¹⁴ triethylammonium ($[\text{HNEt}_3]^+$, $pK_a = 18.8$),¹⁵ or pyridinium ($[\text{Hpy}]^+$, $pK_a = 12.5$).¹⁵ Even after 2 months in the dark, only 35% of **1** had reacted with $[\text{Hpy}]^+$, and heating **1** and $[\text{Hpy}]^+$ to 80 °C for 3 h led to only ~10% consumption of **1**. Only moving to the stronger methanesulfonic acid ($pK_a = 10.0$)¹⁶ was rapid H_2 release observed in the dark (along with complete consumption of **1** and formation of **2**). These observations are consistent with the determined hydricity of **1**, according to DuBois's equations for predicting H_2 release from a hydride and an acid.¹⁷ The relative acid stability of **1** may explain the high activity of Cp^*Ir -based catalysts for hydrogenation of carboxylic acids and disproportionation of formic acid.^{4f,g}

A thermodynamic measure of excited-state hydricity was developed next. Thermodynamic studies of photohydrides (unlike photoacids)¹⁸ are lacking, but an excited-state hydricity, $\Delta G_{\text{H}^-}^{\circ,*}$, can be considered in the context of $\Delta G_{\text{H}^-}^{\circ}$ (Scheme 1). The excited-state hydricity of **1** can be predicted using eq 2:

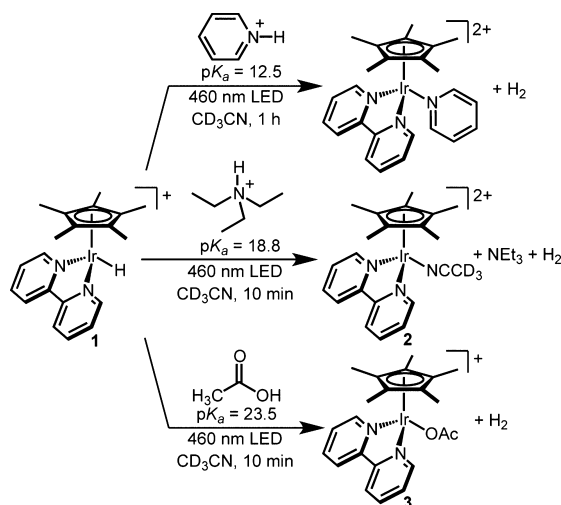
$$\Delta G_{\text{H}^-}^{\circ,*} = -(E_{00}/350) + 1.37(pK_a) - (-46.12)(E_{1/2}) + C_{\text{H}^-} \quad (2)$$

The thermochemical cycle (Supporting Information (SI), Scheme S1 and Eqs S8–S11) assumes that H^- transfer is coupled to ground-state relaxation, in analogy to excited-state electron transfer and some photoacid reactions.^{12,19,20}

The pK_a^* of **1** (eq 2) was estimated on the basis of the energy difference between the lowest vibrational states of **1** and **1*** (E_{00}) and the ground-state pK_a value. Hydride **1** exhibited featureless emission ($\lambda_{\text{em,max}} = 708 \text{ nm} = 14\,100 \text{ cm}^{-1}$) in CH_3CN that did not overlap with the excitation spectrum appreciably, consistent with previously reported triplet emission from a charge-transfer transition.^{5,6} The low-energy edge of the emission spectrum was used to estimate $E_{00} = 16\,900 \text{ cm}^{-1}$, providing $pK_a^* = -12$.¹² The strongly photoacidic excited state is consistent with the reported ability of **1*** to protonate CH_3OH .⁵

The experimental data lead to a predicted value of $\Delta G_{\text{H}^-}^{\circ,*} = 14 \text{ kcal/mol}$, suggesting that **1** is a much stronger H^- donor in its triplet excited state than in its ground state, consistent with observed photocatalysis.⁹ Strikingly, excited state **1*** is predicted to be an incredibly potent H^- donor, thermodynamically stronger than the “super hydride” $[\text{HBEt}_3]^-$ (~26 kcal/mol) used extensively in organic reductions.²¹

Scheme 2



It is noteworthy that the thermochemical cycles predict that **1*** is *both* a stronger acid *and* a stronger H^- donor than **1**. The strongly hydridic excited state, in particular, poses a paradox: the excited state **1*** was previously assigned as originating from a MLCT transition in which transfer of electron density onto the bpy ligand leads to formal oxidation of the Ir center,^{5,22} seemingly indicating an *acidic* (rather than hydridic) excited state. This paradox can be rationalized by noticing that while **1*** is a strong acid, the reduced bpy ligand is simultaneously a strong reductant, rendering the net transfer of a H^- ($\text{H}^+/2e^-$) thermodynamically favorable.

Experimental validation of the thermodynamic predictions was sought through photoreactivity of **1** with organic acids (Scheme 2), with **1** formally donating H^- . H_2 release is favorable if the sum of the hydricity ($\Delta G_{\text{H}^-}^{\circ}$) and the free energy of proton loss ($1.37pK_a$) is $<76 \text{ kcal/mol}$ (the free energy of heterolytic H_2 cleavage).¹² As discussed above, no H_2 release was observed in the dark with $[\text{Hpy}]^+$, $[\text{HNEt}_3]^+$, or HOAc over 1 h at room temperature. If the hydricity of **1** is sufficiently enhanced upon photoexcitation, however, H_2 release should be observed.

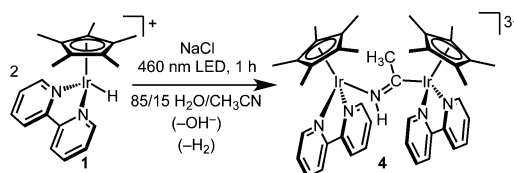
Illuminating solutions of **1** and $[\text{Hpy}]^+$ in CD_3CN with a 460 nm LED lamp led to rapid H_2 release within 1 h at room temperature. Complete conversion to $[\text{Cp}^*\text{Ir}(\text{bpy})(\text{py})]^{2+}$, as judged by ^1H NMR spectroscopy and electrospray ionization–mass spectrometry (ESI–MS), was accompanied by the formation of H_2 gas (^1H NMR δ 4.57).

Photohydride reactivity was also observed with the weaker acid $[\text{HNEt}_3]^+$, with complete consumption of **1** (and formation of **2**) after 10 min of illumination (Scheme 2). The quantum yield (Φ) for this reaction was assessed using the ferrioxalate actinometer.²³ The photon flux passing through an NMR tube was determined to be $2.18 \times 10^{-8} \text{ (mol-photon)/s}$, providing $\Phi = 0.29$.

Even HOAc, a relatively weak acid in CH_3CN , reacted rapidly with **1** to release H_2 after 10 min of photolysis. The Ir-containing product was $[\text{Cp}^*\text{Ir}(\text{bpy})(\text{OAc})]^+$ (**3**) according to ESI–MS, with further confirmation from an independent synthesis of **3**.¹² A 74% yield of H_2 was quantified by headspace gas chromatography.

Photoexcitation clearly enhances the ability of **1** to perform a net H^- transfer. Only a hydride featuring $\Delta G_{\text{H}^-}^{\circ} < 43 \text{ kcal/mol}$ is thermodynamically capable of H_2 release with HOAc. Accordingly, irreversible H_2 photoevolution from **1** and the weak acid HOAc establishes a limiting hydricity value, according to eqs S26–S28 (SI): $\Delta G_{\text{H}^-}^{\circ,*} < 43 \text{ kcal/mol}$. This represents an almost 20 kcal/mol enhancement in experimentally measured hydricity relative to the ground-state hydricity.

Scheme 3



The experimental hydricity value is apparently limited by the acidity of **1** ($pK_a = 23.3$). When acids weaker than HOAc are employed, decomposition to a mixture of species is observed upon illumination, suggesting that **1** may also be acting as a sacrificial proton donor in these reactions.¹² In the presence of a chloride source, however, photolysis of **1** in water/acetonitrile

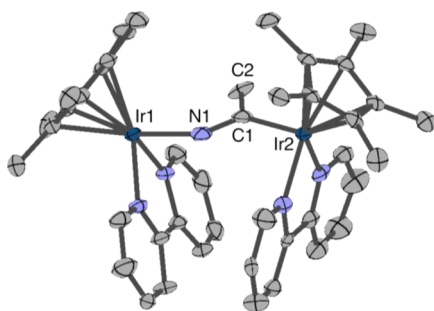


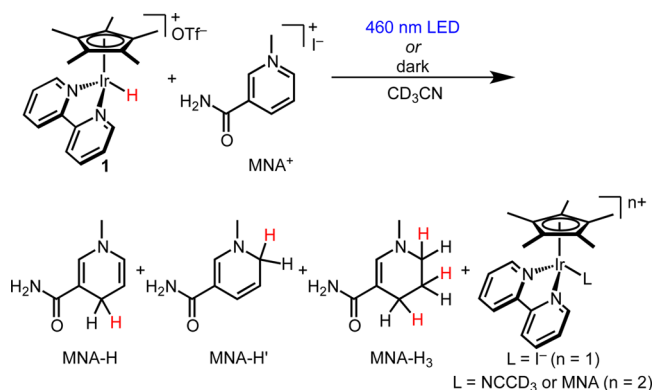
Figure 1. Structural representation of **4** (ellipsoids at 50% probability). Three PF₆ ions, two CH₃CN molecules, and H atoms omitted for clarity. A H-bond between one CH₃CN and the imine NH is observed (N–N 3.201 Å). Selected bond distances (Å) and angles (deg): Ir1–N1 2.149, Ir2–C1 2.126, N1–C1 1.245, C1–C2 1.503, Ir1–N1–C1 131.8, Ir2–C1–N1 119.7, Ir2–C1–C2 129.5.

gave clean conversion to a new product (Scheme 3). No discernible reaction took place in the dark. NMR spectroscopy of the photoproduct revealed two distinct sets of Cp* and bpy resonances in a 1:1 ratio. X-ray diffraction of yellow single crystals of the product revealed an unusual bridging iminoacyl structure [Cp*Ir(bpy)(μ-N(H)C(CH₃))(bpy)IrCp*]³⁺ (**4**, Figure 1).²⁴ The mechanism by which **4** is formed is unclear at this time (as is the role of chloride), but **4** is commonly observed as a side product in reactions that do not undergo clean H[−] transfer.

With a better understanding of the thermodynamics of photohydride transfer in hand, the ability of **1** to reduce organic substrates was assessed using nicotinamide derivatives. The calculated hydricity of 1,4-dihydro-1-methylnicotinamide (MNA-H) is ΔG_{H[−]}^o = 56 kcal/mol,^{10b} similar to other 1,4-dihydro-nicotinamide derivatives (ΔG_{H[−]}^o ≈ 56–64 kcal/mol).^{8a,13} Hydride transfer from **1** to MNA⁺ should thus be unfavorable, while that from **1**^{*} to MNA⁺ should be highly favorable. Mixtures of **1** and [MNA][BF₄] showed no detectable reaction after 1 h in the dark, consistent with the thermodynamic predictions. After 1 h illumination, however, significant conversion to the *doubly reduced* product, 1-methyl-1,4,5,6-tetrahydronicotinamide (MNA-H₃, ~10% yield) was observed. The reduction of a nicotinamide derivative to the tetrahydro product by a homogeneous transition metal hydride is extremely rare.²⁵ Typical conditions for the double reduction of pyridinium salts include strong main group H[−] donors (e.g., NaBH₄)²⁶ or Pd/C under H₂.^{27,28} Transition metal hydride complexes, including strong H[−] donors such as [Cp*Rh(2-phenylpyridine)(H)]⁺ (ΔG_{H[−]}^o = 49 kcal/mol)²⁹ and [Ru(2,2′:6′,2″-terpyridine)(bpy)(H)]⁺ (ΔG_{H[−]}^o = 39 kcal/mol),³⁰ give only 1,4- and 1,6-reduced species.³¹ The double reduction of MNA⁺ in a fashion analogous to borohydride reagents is further evidence of the greatly enhanced excited-state hydricity of **1**^{*}.

Strategies to tune the product selectivity were considered next. To provide more thermodynamic driving force (and avoid possible reversion in the dark), the iodide salt of MNA⁺ was utilized in order to produce a more stable Ir–I product. As shown in Table 1, mixtures of **1** and excess [MNA][I] (1:4.4) produced the normally observed 1,4-reduced product MNA-H in 52% yield (with respect to **1**) after just 10 min of illumination. Only small amounts of 1,6-reduced MNA-H′ (10%) and doubly reduced MNA-H₃ (7%) were observed, even after 20 min. The major Ir-containing product was [Cp*Ir(bpy)(I)]⁺; the adduct of the conjugate base of MNA⁺, [Cp*Ir(bpy)(MNA)]²⁺, was also observed in small quantities.^{31c} The quantum yield for

Table 1. Visible Light-Promoted Hydride Transfer from [Cp*Ir(bpy)(H)]⁺[OTf][−] (**1**) to [MNA][I]⁺^a



[1]:[MNA ⁺]	time (min)	yields (%)					
		MNA-H		MNA-H′		MNA-H ₃	
		dark	light	dark	light	dark	light
1:4.4	10	0	52	0	7	0	3 ^b
	20	0	59	0	10	0	7 ^b
4.0:1	10	8	18	5	3	0	13
	60	21	0	13	0	0	21

^aYields determined by ¹H NMR and calculated relative to limiting reagent. ^bMaximum yield is 50%. See the SI for full details.

production of singly reduced products (sum of MNA-H and MNA-H′) varied between 0.03 < Φ < 0.20, depending on reaction conditions. No reduced products were observed in the dark, even after 1 h.

Upon photolysis of MNA⁺ in the presence of excess **1**, doubly reduced MNA-H₃ was the sole reduced nicotinamide product after 60 min of illumination (21% yield with respect to MNA⁺, Table 1). When the same mixture was allowed to react in the dark for 60 min, only small amounts of singly reduced products were formed, and no MNA-H₃ was observed in reactions carried out in the dark, even with reaction times up to 6 h. Doubly reduced MNA-H₃ is apparently formed by two sequential H[−] transfers, in addition to one proton transfer. MNA-H and MNA-H′ are observed as intermediates at early times (Table 1 and SI, Figure S23). The product MNA-H₃ forms in the absence of water, so MNA⁺ or **1** itself may be acting as an acid. With high concentrations of **1**, H₂ release and formation of bimetallic **4** become competitive.

The photohydride strategy offers powerful tunability of nicotinamide reductions. First, dramatic *rate enhancements* are observed under illumination: in ~1:1 mixtures of **1**:MNA⁺, visible light illumination accelerated the production of 1,4-reduced product (MNA-H) by a factor of ~200 compared to reactions carried out in the dark (SI, Table S1). Second, *selectivity* can be photoswitched from singly reduced to doubly reduced products with complete fidelity (Table 1).

In summary, visible light has been shown to promote hydride-transfer reactions from [Cp*Ir(bpy)(H)]⁺ to several organic acids and to 1-methylnicotinamide. A method for determining excited-state hydricity was presented, revealing an increase in hydride donor ability of at least 18 kcal/mol upon light absorption. In reactions with nicotinamide derivatives, illumination accelerates production of 1,4-reduced species. Under conditions of excess hydride, illumination leads to a complete switch in selectivity, producing an unusual doubly reduced product. The products are consistent with net photohydride

reactivity, but questions remain concerning the detailed mechanism: the reaction could proceed via concerted H^- transfer, separate transfer of H^+ and $2e^-$, or even stepwise H^\bullet and e^- transfer. Deeper mechanistic understanding and the promise of utilizing light to tune catalytic hydrogenations motivate future research.

■ ASSOCIATED CONTENT

📄 Supporting Information

Full synthetic and experimental details, thermochemical cycles, crystallographic data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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