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## Controlling Hydricity of Adsorbed Catalysts with Applied Electric **Fields**

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**ABSTRACT**: We investigate the effects of applied electric fields on the reactivity of two iridium(III) half-sandwich complexes bonded to gold electrodes. Our theoretical results show that applied electric fields precisely and linearly control the aqueous effective hydricities of these catalysts. The field-dependent shifts in the hydricities of Cp\*Ir-bipyridine ([Ir-bpy- $H^{+}$ ) and Cp\*Ir-phenylpyridine (Ir-ppy-H) are compared directly to those induced by chemical substitution, and they are found to be equivalent to a drastic change in substituent Hammett parameter without any chemical modification. Furthermore, we find that the Stark tuning rates of Ir-H vibrational modes are directly correlated with hydricity changes induced by the applied electric field, providing valuable spectroscopic probes of the actual electric field strength at the catalytic site and potential reactivity of the hydride. We anticipate that the reported findings should be particularly valuable for studies of non-Faradaic electrochemical control of catalytic reactivity at interfaces by applied external fields.



Article

### INTRODUCTION

The design of electric fields for non-Faradaic control of chemical reactions is an outstanding challenge of great interest in catalysis and energy research.<sup>1,2</sup> Fundamental understanding of electric field effects could enable the selective control of the reactivity of chemical bonds and modulate the functionality of catalytic compounds. The tumbling of molecular catalysts in solution limits control over orientation-dependent interactions, so control by applied external fields should be most effective in nanoscale environments that constrain the molecular tumbling motion, as occurs with attachment to electrode surfaces. Fields experienced by molecular catalysts at interfaces could behave analogously to those produced by the electrostatic environment at enzyme active sites, which accelerate reaction rates beyond those achievable by molecular systems.<sup>3-5</sup> With suitable control over orientation, applied external fields could enable reactivity beyond the native functionality of molecular catalysts by stabilizing polar transition states with respect to reactants to achieve higher catalytic turnover frequencies, and/ or by stabilizing products versus reactants to favor the reaction thermodynamics. However, very few studies have focused on the characterization of the orientation of heterogenized transition metal catalysts at interfaces or the possibility of controlling their properties and reactivity at the molecular level with applied electric fields.

The concept of controlling heterogeneous catalysis with electric fields can be traced back at least to the work of Lee et al.,<sup>6</sup> showing that an alternating field applied normal to a NiO surface enhances the rate of CO oxidation by 6-fold. In a biological system, Shaik et al.<sup>7,8</sup> theoretically predicted that external electric fields can control the selectivity of the C-H hydroxylation versus C=C epoxidation reactions in cytochrome P450. Similarly, it was theoretically predicted that oriented external electric fields could accelerate Diels-Alder reactions,9 which was subsequently confirmed experimentally.<sup>10</sup> Theoretical studies showed that fields can enhance oxidative addition of alkyl and aryl electrophiles to palladium catalysts, with mechanistic crossover occurring at sufficiently high field strengths.<sup>11</sup> Work by Kanan et al. has shown that external electric fields can alter reaction selectivity in both the context of ion pairing<sup>12,13</sup> and electrochemical interfaces,<sup>14,15</sup> showing evidence of control over selectivity from 10:1 to 1:2 (a 20-fold change simply by adjusting the applied potential) for an organic cyclization reaction when a Rh porphyrin catalyst was immobilized on the surface of a parallel plate capacitor insulated with metal oxides.<sup>15</sup> Conversely, Baik et al. attached reactant molecules to gold electrodes and modified the properties of the reactants to control a Suzuki-Miyaura cross-coupling reaction catalyzed by Pd, comparing the effect of the electrode to that of a tunable functional group.<sup>16</sup> These experiments clearly demonstrated that applied electric fields can dramatically influence the reactivity of heterogenized

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systems and induce vast modulation of the product yield under catalytic conditions. However, the actual fields that modulate catalytic reactivity remain poorly understood at the molecular level, including their influence on the molecular properties and orientation of catalysts on the electrode interface and the resulting impact on the reactivity of the catalyst. Surprisingly, there have not yet been studies that directly characterize surface-attached catalysts at the molecular level as their reactivity is non-Faradaically controlled under bias, motivating theoretical studies that describe the changes in their molecular properties and reactivity.

Here, we analyze the modulation of the aqueous hydricity and molecular properties of catalytic iridium half-sandwich adsorbates induced by applied external electric fields, as characterized by density functional theory (DFT). The reported study builds upon earlier efforts, including previous work showing that the local electric field at the active site of a surface-attached complex can be measured and characterized using a combination of computational modeling and surfacespecific spectroelectrochemistry<sup>17,18</sup> and studies of interfacial field effects on the  $pK_a$  of surface-attached benzoic acids.<sup>19–21</sup> In our previous work with a Re(bpy)(CO)<sub>3</sub>Cl catalyst bound to Au(111), the local electric field was estimated to be on the order of  $10^9$  V m<sup>-1</sup>.<sup>17</sup> Such fields are comparable to the electric fields found at the active sites of enzymes and thus are sufficiently large to significantly alter the reactivity of embedded catalytic cofactors.<sup>22,23</sup> Transition metal complexes with multiple vibrational probes were also used as "molecular rulers," with each vibrational mode reporting on the field at a different location in the double layer.<sup>18</sup> This vibrational Stark shift induced by interfacial fields may reflect changes in the electron density on the metal center and has been compared to an effective ligand Hammett parameter by Dawlaty.<sup>24</sup> Thus, we make a direct comparison between the effects of external fields and chemical substitution on the reactivity and molecular properties of the surface-attached complexes. We anticipate that the current theoretical study should be particularly valuable for guiding the design of field controllable catalysts at interfaces.

We theoretically investigate the effects of applied electric fields on the reactivity of two iridium(III) half-sandwich complexes, Cp\*Ir-bipyridine ([Ir-bpy-H]<sup>+</sup>) and Cp\*Ir-phenyl-pyridine (Ir-ppy-H), covalently attached to a gold electrode with a thiolate linker (Figure 1), and correlate these reactivity changes to Stark tuning rates that can be probed by sum frequency generation spectroscopic methods.<sup>25</sup> Iridium half-sandwich complexes are valuable catalysts for transfer hydrogenation reactions of a wide variety of substrates.<sup>26–31</sup>



**Figure 1.** Surface-attached Ir half-sandwich complexes,  $[Ir-bpy-H]^+$  (X = N) and Ir-ppy-H (X = C), influenced by an applied electric field.

Additionally, they are especially suitable for the analysis of non-Faradaic effects because they afford a wide window of approximately 2 V under which no redox chemistry occurs. This extended voltage range should allow for observation and utilization of electric field effects that would otherwise be masked by the interference processes of electrochemical oxidation/reduction reactions.

We focus on the *effective hydricity*,  $\Delta G^{\circ}_{H^{-}}(Cl^{-})$ , of the Ir–H catalysts, including computations as a function of the applied electric field strength. As shown in Figure 2A, this effective



**Figure 2.** (A) Reaction diagram for the effective hydricity,  $\Delta G^{\circ}_{H^{-}}(Cl^{-})$ , of the unsubstituted Ir bipyridyl complex. (B) Scheme showing that the difference between the hydricities of a donor, D, and an acceptor, A, gives the free energy of a hydride transfer reaction,  $\Delta G^{\circ}_{HT}$ .

hydricity is the free energy change associated with the exchange of a hydride anion for a chloride to form an Ir-Cl complex. Hydricities are highly solvent dependent, so we focus on aqueous hydricities as electrochemical experiments are typically performed in aqueous conditions. Chloride is chosen as the binding counterion so that our theoretical results can be directly compared to previous experimental measurements of substituted Ir-bpy complexes that were performed in the presence of chloride.<sup>32</sup> For a stable metal hydride,  $\Delta G^{\circ}_{H^-}(Cl^-)$ always has a positive value, as the complex does not spontaneously exchange H<sup>-</sup> for Cl<sup>-</sup> in solution. However, the free energy change associated with this standard reaction can be compared with the hydricities of other molecules under the same conditions. These absolute hydricities can be used to determine the thermodynamic favorability of hydride transfer between a particular donor (D) and acceptor (A): the difference between the absolute hydricities of D and A gives the free energy of the hydride transfer from D to A (Figure 2B). Smaller hydricity values indicate that a molecule is "more hydridic" (i.e., a better hydride donor).

It is important to distinguish the effective hydricity, which is the focus of this work, from the *thermodynamic hydricity*  $(\Delta G^{\circ}_{H^{-}})$ , which corresponds to the removal of a hydride anion without replacement by another ligand.<sup>33</sup> Both of these quantities are also closely related to the bond dissociation free energy and acidity  $(pK_a)$ , which correspond to M–H dissociation to form a H atom and proton, respectively (Figure S1). Here, we focus on the effective hydricity,  $\Delta G^{\circ}_{H^{-}}(Cl^{-})$ , as the hydride should be replaced by a counterion under electrochemical conditions and the reaction involving chloride has already been experimentally studied for a series of substituted Ir-bpy half-sandwich complexes in water.<sup>32</sup> In this work, the "hydricity" of the Ir–H complexes always refers to the aqueous effective hydricity where hydride is exchanged for a chloride (Figure 2A).

As described in the Results and Discussion, we demonstrate that electric fields at an electrode interface can linearly modulate the hydricity of transition metal complexes by  $\sim 3$ kcal mol<sup>-1</sup> without chemical modification. We compare these hydricity shifts to those that result from chemical substitution of the bpy and ppy ligands at the 4 and 4' positions, and we find that they are slightly larger than those produced by changing from electron donating OH substituents to strongly electron withdrawing NO<sub>2</sub> substituents. Further, we show that even a small change in the ligand from a bipyridine to a phenylpyridine results in a significantly different influence of the electric field on molecular properties while maintaining a similar level of reactivity control. The field effect is shown to be primarily through-space, with no significant dependence on the Au electrode surface. In addition, we find that the vibrational frequency of the hydride provides a probe of the local electric field at the M-H bond and a quantitative measure of the complex hydricity. However, the M-H vibrational mode most suitable for Stark effect measurements differs for the two complexes. These theoretical results are widely applicable since hydride transfer plays a central role in many important chemical reactions, including transfer hydrogenation,<sup>33,34</sup> CO<sub>2</sub> reduction,<sup>35</sup> formate oxidation,<sup>36</sup> and hydrogen evolution,<sup>3</sup> where the distinct hydricity of reaction intermediates often dictates the efficiency of the reaction. Therefore, controlling hydricity with external fields can enhance the native reactivity of reaction intermediates and open new reaction pathways for the wide variety of important processes containing a hydride transfer step.

#### METHODS

Our characterization of the effect of an external field on surface-attached [Ir-bpy-H]<sup>+</sup> and Ir-ppy-H is based on density functional theory (DFT) calculations. The molecular configurations were determined by geometry optimization of the complexes on a model slab surface of Au(111) consisting of 35 gold atoms. Electric fields were applied normal to the Au(111)surface in the range of  $\pm 1$  V nm<sup>-1</sup>, comparable to the ranges measured for other attached catalysts on gold.<sup>17,18</sup> Geometry optimizations and frequency calculations were performed using the PBE functional<sup>38</sup> with Grimme's D3 dispersion correc-tion,<sup>39,40</sup> as recommended by previous benchmarking studies of organic molecules attached to Au.<sup>41</sup> Nonmetal atoms were treated with the 6-31G(d,p) basis set,<sup>42,43</sup> while Au and Ir atoms were treated with the LANL2DZ basis set and pseudopotential.<sup>44</sup> Frequencies were scaled by 0.986 as recommended by the NIST CCCBDB for PBE with a 6-31G(d,p) basis set (the most similar method with a standard scaling factor).<sup>45</sup> It is not possible to accurately calculate the energy of a solvated hydride anion using DFT, so we used a thermodynamic cycle involving the experimentally measured effective hydricity of the unsubstituted bpy complex (27.0 kcal/mol). The free energy of hydride transfer ( $\Delta G^{\circ}_{HT}$  in Figure 2B) was computed with each complex acting as the hydride donor (D) and the unsubstituted bpy complex acting as the reference acceptor (A). Combining the experimentally measured hydricity of the acceptor with the DFT-computed  $\Delta G^{\circ}_{HT}$  gave the absolute hydricity  $\Delta G^{\circ}_{H}(Cl)$  for each molecule (see example in Figure S4). To ensure that these calculations of hydricities were accurate, we performed benchmark calculations for the experimentally reported aqueous hydricities of substituted Ir half-sandwich analogues (Tables S1-S4).<sup>32</sup> Ultimately, the  $\omega$ B97-XD functional<sup>46</sup> was

selected for single point calculations with the 6-31+G(d,p) basis set<sup>47</sup> on nonmetal atoms and the Def2SVP basis set and pseudopotential<sup>48</sup> for Ir and Au. Solvent effects were included using the solvation model based on density (SMD) continuum model for water.<sup>49</sup> All calculations were performed in Gaussian 16, rev. A.03.<sup>50</sup> Note that all electric fields are reported with the standard physics convention of field vectors pointing away from positive charges (i.e., positively charged surface generates a positive field), which is the inverse of the convention used by the Gaussian 16 software. Additional computational details and discussion are available in the Supporting Information (section S2).

#### RESULTS AND DISCUSSION

Figure 3A,C shows the configurations of the complexes [Ir-bpy-H]<sup>+</sup> and Ir-ppy-H adsorbed on Au(111) model surfaces.



**Figure 3.** Minimum energy configurations of Ir complexes on Au, including (A) [Ir-bpy-H]<sup>+</sup>, (B) [Ir-bpy-Cl]<sup>+</sup>, (C) Ir-ppy-H, and (D) Ir-ppy-Cl. The vectors indicate the magnitude and direction of the *z*-component of the molecular dipole moment (blue), which is aligned with the applied electric field (black). The radii of Au atoms are enlarged for visualization purposes.

The two complexes interact strongly with the Au surface through the thiolate linker and dispersion interactions with the aromatic ligand and exhibit similar binding orientations, with both the bpy and ppy ligand planes at approximately 20° relative to the surface. Figure 3B,D shows the configurations of the two complexes after exchanging the hydride anion for a chloride. The [Ir-bpy-Cl]<sup>+</sup> and Ir-ppy-Cl products also have similar orientations and approach the surface more closely, with bpy/ppy tilt angles of  $\sim 15^{\circ}$  from the surface. The Au surface has no significant effect on the computed zero-fieldhydricity value for [Ir-bpy-H]<sup>+</sup>, which has the same hydricity of 25.8 kcal/mol regardless of whether it is attached to the surface or in solution. However, the Au surface has a larger effect on Ir-ppy-H, lowering the zero-field hydricity from 26.0 to 22.7 kcal/mol. The z-components of the dipole moments of the reactants and products are also shown in Figure 3 using the Gaussian software's convention of pointing the dipole moment toward positive charge such that the total energy decreases when the dipole and field are aligned. For both complexes, exchange of a hydride for a more electronegative chloride alters the dipole moments so that they point more toward the surface (i.e., more negative charge on Cl than on H).

Figure 4A shows the calculated hydricities,  $\Delta G^{\circ}_{H^{-}}(Cl^{-})$ , of complexes [Ir-bpy-H]<sup>+</sup> and Ir-ppy-H as a function of the



**Figure 4.** (A) Hydricities of complexes  $[Ir-bpy-H]^+$  and Ir-ppy-H as a function of the applied electric field with best-fit lines of +1.4 and +1.7 kcal mol<sup>-1</sup>/V nm<sup>-1</sup>, respectively ( $R^2 > 0.98$  for both fits). (B) Measured hydricities as a function of substituent Hammett parameter for chemically modified ligands on  $[Ir-bpy-H]^{+,32}$  (C) Relative free energy shift of the iridium hydride complexes as a function of field strength. (D) Relative free energy shift of the iridium chloride products as a function of field strength. The differences between individual free energy shifts in (D) and (C) correspond to the shift in hydricity.

strength of the electric field applied normal to the Au(111)surface (reaction scheme in Figure S7). Electric field strengths in the range of  $\pm 1$  V nm<sup>-1</sup> are typical in electrochemical measurements of self-assembled monolayers.<sup>17,25</sup> Smaller hydricity values correspond to a more favorable hydride transfer reaction (Figure 2). Here, we define the sign of the field as positive for a positively charged electrode, indicating that an increasingly negative bias promotes hydride transfer, while a more positive bias inhibits it. The hydricities of the each complex change linearly by  $\sim$ 3 kcal/mol as the electric field changes within the range of  $\pm 1$  V nm<sup>-1</sup> (Figure 4A), which is slightly larger than the hydricity range previously accessed by chemical substitution of the bpy complex (Figure 4B).<sup>32</sup> These hydricity changes as a function of field strength correspond to a strong modulation of the hydride transfer reactivity of the complexes without any kind of chemical modification. At all field strengths, Ir-ppy-H is more hydridic than [Ir-bpy-H]<sup>+</sup>, but the magnitude of the hydricity shifts are very similar. The possibility of strong electric fields stabilizing higher triplet spin states was also considered, but the singlet state was much more favorable in all cases (Table S6).

The hydricity shifts for the two complexes (Figure 4A) might suggest that the individual bpy and ppy molecules interact with the field in a similar fashion. However, Figure 4C,D shows that the individual molecules respond quite differently to the perturbational influence of the external electric field. In fact, the comparison of the relative free energies of the bpy and ppy molecules shows that the individual hydride species exhibit nearly opposite energetic shifts as a function of applied field strength (Figure 4C). While [Ir-bpy-H]<sup>+</sup> is stabilized by a positive field, Ir-ppy-H is destabilized by the same field. The energetic shifts of [Ir-bpy-Cl]<sup>+</sup> and Ir-ppy-Cl are also distinct, with the bpy complex again being stabilized by the same field (Figure 4D). Despite these differences in the energetic response of the individual species,

the shift in the free energy difference between the hydrides and chlorides (i.e., hydricity) remains consistent between the bpy and ppy complexes. This underscores the importance of always considering electric field effects in terms of their relative impact on both the reactant and product molecules rather than only considering the stabilization of a particular molecule.

The different responses of the two hydrides to the same applied electric field are consistent with their distinct charge distributions and dipole orientations relative to the applied field that is normal to the surface (Table 1, Figure 3). The bpy

Table 1. Projection of Dipole Moment along the Field Axis  $(\mu_z)$  for Complexes on Au Surface<sup>*a*</sup>

species	$\mu_z$ [D]
[Ir-bpy-H]+	10.9
[Ir-bpy-Cl] <sup>+</sup>	7.3
Ir-ppy-H	-4.2
Ir-ppy-Cl	-10.3
$^{a}\Delta\mu_{z}$ is –3.6 D for the bpy complex a	nd –6.1 D for the ppy complex.

complexes have molecular dipole moments that point away from the surface (positive value of  $\mu_z$ ); thus, they exhibit a response opposite that of the ppy species with dipoles pointing toward the surface. However, the loss of a hydride results in a similar change in  $\mu_z$ , the dipole projection along the field axis, for both complexes (-3.6 D for [Ir-bpy-H]<sup>+</sup>, -6.1 D for Ir-ppy-H, Table 1) which results in a similar field effect on the reaction free energy (i.e., hydricity). The negative  $\Delta \mu_z$  values result from the greater electron density on the electronegative chloride ligand of the product in comparison to the hydride ligand of the reactant, and they suggest that positive fields should stabilize the Ir-H complexes relative to the corresponding Ir-Cl complex (increase hydricity). The similar change in  $\mu_z$  can be understood intuitively from the fact that the two complexes have very similar orientations, so exchange



Figure 5. (A) Reaction scheme for the example hydride transfer reaction between the surface-attached [Ir-bpy-H]<sup>+</sup> and a methoxy-substituted Irbpy complex in solution. (B)  $\Delta G^{\circ}_{HT}$  and (C) equilibrium constant ( $K_{eq}$ ) for the reaction as a function of electric field strength. Note that  $\Delta G^{\circ}_{HT}$  has the same slope of +1.4 kcal mol<sup>-1</sup>/V nm<sup>-1</sup> as  $\Delta G^{\circ}_{HT}$  (Cl<sup>-</sup>) in Figure 4A; the free energy values are just shifted by the hydricity of the acceptor.

of the same type of ligand (hydride to chloride) should result in a similar dipole change even though the individual molecular dipoles are quite different.

The values of  $-\Delta \mu_z$  can be used to approximate the hydricity shifts caused by an electric field. In this case,  $-\Delta \mu_z$ corresponds to energy shifts of +1.8 and +3.0 kcal mol<sup>-1</sup>/V  $nm^{-1}$  for  $[Ir-bpy-H]^+$  and Ir-ppy-H, which are slightly larger than the actual hydricity slopes of +1.4 and +1.7 kcal mol<sup>-1</sup>/V nm<sup>-1</sup> (a detailed discussion of using  $-\Delta\mu_z$  to predict reaction thermodynamics is included in the Supporting Information, section S7). In brief,  $-\Delta \mu_z$  corresponds to the linear component of the field-induced shift of the total electronic energy of the reaction without structural or conformational changes. Thus, it is useful for providing qualitative insights into the effect of the field on the hydride transfer reaction, but it does not precisely predict the hydricity shifts. Future efforts to computationally design field controllable catalysts could initially focus on maximizing the magnitude of  $\Delta \mu_z$ . These values can be obtained for molecules optimized on surfaces without the need for field-dependent calculations, enabling large numbers of calculations varying each component of the system (complex, electrode surface, surface attachment method). Once promising candidates have been identified through this screening process, calculations with an applied field would be performed to make quantitative predictions about the effect of electric fields on the reaction thermodynamics.

It is important to note that the linear shifts in the hydricities of  $[Ir-bpy-H]^+$  and Ir-ppy-H also result from the fact that the orientations of these molecules do not change dramatically as the field is applied. Changes in the orientation of molecules can alter the alignment between the molecular dipole and the field, which would result in nonlinear hydricity (free energy) shifts. Such changes in orientation would complicate the analysis and prediction of field effects but could also be exploited to control chemical reactivity. The design of systems with field-controlled orientations on electrode surfaces is an interesting topic for further study, but no such behavior is observed in the current system.

The computed hydricity shifts within a  $\pm 1$  V nm<sup>-1</sup> field range represent a significant change in the hydride transfer reactivity of the surface-attached complexes. As discussed in the Introduction, absolute hydricity values are primarily useful for computing the free energy change for hydride transfer between a particular donor and acceptor (Figure 2B). As an example,  $\Delta G^{\circ}_{HT}$  was computed with the surface-attached [Irbpy-H]<sup>+</sup> complex as a hydride donor and a methoxysubstituted Ir-bpy molecule as an example hydride acceptor in solution (Figure 5). Note that this type of graph can be made for any arbitrary hydride acceptor with a known hydricity value by simply subtracting the hydricity of the acceptor (in this case 26.2 kcal/mol) from that of the donor. At zero field, the reaction is very near equilibrium with an equilibrium constant  $(K_{eq})$  of 1.8 due to the slightly lower hydricity of [Irbpy-H]<sup>+</sup>. As a negative field is applied, [Ir-bpy-H]<sup>+</sup> becomes more hydridic and hydride transfer is favored such that at -1V/nm  $K_{eq}$  is 30.3 and [Ir-bpy-Cl]<sup>+</sup> is highly favored over [Irbpy-H]<sup>+</sup>. Conversely, applying a positive field makes [Ir-bpy-H]<sup>+</sup> less hydridic and decreases the thermodynamic favorability of hydride transfer such that at +1 V/nm  $K_{eq}$  is 0.2 and [Ir-bpy-H]<sup>+</sup> is dominant on the surface. These dramatic shifts in the equilibrium constant could be readily measured experimentally via vibrational spectroscopy. Note that this example calculation assumes that the acceptor molecule is in solution and unaffected by the applied field. In a practical experiment, such a similar complex might not be the best choice for a hydride acceptor since it might coadsorb on the surface rather than stay in solution. However, this same principle could be used to predict field control of hydride transfer to a more suitable acceptor molecule for which the aqueous hydricity has been determined. For example, the reported hydricity of formate in water is 24.1 kcal/mol.<sup>51</sup> The thermodynamic favorability of transferring a hydride to  $CO_2$  to produce formate can be predicted for the surface-attached complexes by comparing their hydricities (Figure 4A) to that of formate; if the complex has a hydricity under 24.1 kcal/mol, hydride transfer to CO<sub>2</sub> is favorable (see reaction scheme in Figure S8). The zero-field hydricity of [Ir-bpy-H]<sup>+</sup> is 25.8 kcal/ mol (unfavorable hydride transfer), and applying a negative field causes the hydricity to approach that of formate promoting hydride transfer. Conversely, the zero-field hydricity of Ir-ppy-H is 22.7 kcal/mol (favorable hydride transfer), and applying a positive field causes the hydricity to increase toward that of formate reducing the favorability of hydride transfer.

Coincidentally, the hydricity of  $[Ir-bpy-H]^+$  with a -1 V/nm external field (24.2 kcal/mol) and that of Ir-ppy-H with a +1 V/nm external field (24.6 kcal/mol) are both very near the aqueous hydricity of formate (24.1 kcal/mol), showing how the effects of the ligand and interfacial field combine to determine the hydricity. Similar predictions of significant field modulated hydride transfer could be made for any other molecule with an aqueous hydricity in the range of ~21-27 kcal/mol obtained for the two surface-attached complexes in the  $\pm 1$  V nm<sup>-1</sup> field range.

The effect of electric fields on catalytic adsorbates can be dependent on the type of electrode surface used. Thus, the field-dependent hydricity was analyzed in the absence of gold (Figure 6). For comparison to the corresponding results in the



**Figure 6.** Hydricity values of complexes [Ir-bpy-H]<sup>+</sup> and Ir-ppy-H as a function of the strength of an applied electric field in absence of the Au surface with best fit lines of +1.8 and +2.1 kcal mol<sup>-1</sup>/V nm<sup>-1</sup>, respectively ( $R^2 > 0.99$  for both fits).

presence of the Au slab, shown in Figure 4A, we maintained the orientation of the complexes relative to the field while removing the electrode surface (details provided in the Supporting Information, section S2). This comparison allows analysis of whether the perturbative effect of the field on

hydricity is similar and determined by through-space interactions, or if the response is strongly affected by through-bond interactions, including specific Au-thiolate interactions as has been suggested for gold-thiolate linkers under sufficiently large electric fields.<sup>52</sup> Similar trends with only slightly different slopes, shown in Figures 4A and 6, suggest that the influence of the field on hydricity is mostly through-space, with no evidence for any significant fielddependent Au-thiolate interaction at the electrode surface. Notably, only small changes (~10%) are observed in the  $\Delta \mu_z$ values when the surface is removed (Table S7). The most noticeable effect of removing the surface is that the hydricity values for Ir-ppy-H are systematically lower on the Au surface. This suggests that the surface plays a role in stabilizing the Irppy-Cl product relative to Ir-ppy-H, but this interaction is not dependent on the applied field. Thus, we conclude that the only major effects of gold on the computed hydricities are those on the binding orientations of the complexes and the zero-field hydricity of Ir-ppy-H, rather than any surface-specific field-dependent effect.

The characterization of the electric field strength at specific sites of an electrode surface is rather challenging, although it can be achieved by combining theory and spectroelectrochemical measurements of Stark tuning rates of vibrational probes.<sup>17,18,25</sup> In an electrochemical experiment, the applied potential is controlled and the vibrational frequency is measured. In this theoretical study, the applied electric field is controlled and the vibrational frequency is computed. The theoretical results reported in this paper could be combined with Stark effect measurements from a future experiment to determine the field strength as a function of the applied potential. We first investigated whether the Ir-H stretching mode can be used as a Stark tuning probe of the electric field that controls the hydricity of the complex. This mode would be a particularly valuable probe because it is isolated from all other vibrational peaks (there are no other peaks between 1600



**Figure 7.** Field dependence of the Ir–H stretching frequencies of (A)  $[Ir-bpy-H]^+$  and (D) Ir-ppy-H and the Ir–H wagging frequencies of (B)  $[Ir-bpy-H]^+$  and (E) Ir-ppy-H. All plots have the Stark slopes indicated. Two extreme points were omitted from the  $[Ir-bpy-H]^+$  Ir–H stretch linear fit ( $R^2$  of 0.98 in the chosen region). All other fits have  $R^2 > 0.99$ . The spectral region around the Ir–H wagging mode is shown for (C)  $[Ir-bpy-H]^+$  and (D) Ir-ppy-H with the relevant peak labeled with a black arrow.



**Figure 8.** (A) Effective hydricity values of 4,4'-substituted Ir-bpy and Ir-ppy complexes as a function of Hammett parameter ( $\sigma_p^-$ ). The chemical structures of the complexes are shown, with substituents added to the X positions. (B) Ir–H stretching frequency and (C) NBO partial charge on H for the substituted complexes versus  $\sigma_p^-$ . (D) NBO charges as a function of applied field for the surface-attached [Ir-bpy-H]<sup>+</sup> and Ir-ppy-H complexes. The CO<sub>2</sub><sup>-</sup>-substituted complexes were outliers due to their negative total charge and were excluded from the analysis in (B)–(D).

and 2900 cm<sup>-1</sup> for either complex; see Figure S10). Figure 7D shows that indeed Ir-ppy-H displays a significant Stark tuning rate for the Ir-H stretching mode, with a frequency shift of >22 cm<sup>-1</sup> over the  $\pm 1$  V nm<sup>-1</sup> range of interfacial electric fields of typical electrochemical measurements. In fact, the Ir-ppy-H Stark tuning rate of 10.9 cm<sup>-1</sup>/V·nm<sup>-1</sup> is larger than those previously reported for catalytic centers (~7.5  $\text{cm}^{-1}/\text{V}$ ·  $nm^{-1}$ ),<sup>17</sup> suggesting that it is an ideal candidate for experimental investigation. In contrast, the Ir-H stretch of [Ir-bpy-H]<sup>+</sup> exhibits only a negligible shift with applied field (Figure 7A). It is interesting to note that the z-components of the dipole derivatives associated with the Ir-H stretching modes are quite comparable (-0.695 D Å<sup>-1</sup> u<sup>-1/2</sup> for [Ir-bpy-H]<sup>+</sup>, -0.607 D Å<sup>-1</sup> u<sup>-1/2</sup> for Ir-ppy-H), so this does not appear to play a major role in the Stark slopes. The Ir-H bond length of [Ir-bpy-H]<sup>+</sup> shows negligible changes under the applied fields when compared to Ir-ppy-H, which is likely connected to its much smaller Stark slope (Figure S11).

In contrast to the Ir–H stretching mode, the Ir–H wagging mode (Figure S12) of  $[Ir-bpy-H]^+$  with zero-field frequency 595 cm<sup>-1</sup> has a large Stark slope of -15.1 cm<sup>-1</sup>/V·nm<sup>-1</sup>, which could be used to measure the electric field strength (Figure 7B). The mode is well separated from other stretching modes (Figure 7C), making it a suitable candidate for Stark measurements. The same mode in Ir-ppy-H has a significant but smaller Stark slope of -6.2 cm<sup>-1</sup>/V·nm<sup>-1</sup> (Figure 7E). However, this vibration is not separated from other modes (Figure 7F), so the Ir–H stretch would be a better choice for a Stark probe. The distinct vibrational Stark effect results further demonstrate that the effect of the electric field on the molecular properties of the individual hydride complexes is

quite different, and they underscore the importance of computing vibrational Stark slopes even for similar molecules. While the hydricities of both complexes can be similarly controlled by an applied electric field, the different spectroscopic responses of the two complexes necessitate a different choice of vibrational mode to experimentally quantify the field strength. The underlying cause of these ligand-induced changes in the Stark response of M–H bonds, particularly M–H stretching vibrations, will be the subject of future work. In general, differences in Stark effect measurements between similar complexes could be minimized by adding a nonreactive vibrational probe, such as a nitrile group, as a ligand substituent which might act as a more predictable local Stark probe.

As discussed in the Introduction, the effect of an applied electric field has previously been compared to that of a ligand substituent.<sup>16,17,24</sup> Thus, we directly compared the effects of fields and substituents on the hydricities,  $\Delta G^{\circ}_{H^-}(Cl^-)$ , and molecular properties of the Ir complexes to better understand their relationships at the molecular level. The previously studied series of five Ir-bpy complexes substituted at the 4 and 4' positions was expanded to include 10 total complexes with substituents across a larger range of Hammett parameters  $(\sigma_{\rm p}^{-})$  ranging from -0.37 for the most electron donating OH substituent to 1.27 for the most electron withdrawing NO2 substituent.53 Additionally, the hydricities of the equivalent 10 substituted versions of the Ir-ppy complex were computed (hydricity values for each substituted complex are reported in Tables S9 and S10). The ranges of the hydricities were 2.7 kcal/mol for the substituted Ir-bpy complexes and 3.0 kcal/ mol for the substituted Ir-ppy complexes (Figure 8A); these



**Figure 9.** Contour maps of the difference in ESP after applying fields of (A) +1 and (C) -1 V/nm to  $[Ir-bpy-H]^+$ . Lines are spaced by units of 0.002 au = 0.054 V, with black lines for positive values and blue lines for negative values. Potential difference values mapped onto an electron density surface (isovalue = 0.005 au) for fields of (B) +1 and (D) -1 V/nm. A bar is included to show the color scaling in units of  $10^{-2}$  au.

were slightly smaller than the ranges of 2.9 and 3.3 kcal/mol obtained for  $[\text{Ir-bpy-H}]^+$  and Ir-ppy-H with  $\pm 1~\text{V}~\text{nm}^{-1}$ applied fields. The relationships between  $\Delta G^{\circ}_{H^{-}}(Cl^{-})$  and  $\sigma_{\rm p}^{-}$  were approximately linear; the slopes were +1.6 kcal/mol  $(\hat{R}^2 = 0.96)$  for the bpy complexes and +1.9 kcal/mol ( $R^2 =$ 0.94) for the ppy complexes (Figure 8A). In combination with the field-dependent slopes from Figure 4A, it was determined that the studied  $\pm 1$  V/nm field range results in hydricity shifts that are roughly equivalent to those induced by substituents with Hammett parameter ranges of 1.68 for the bpy complexes and 1.78 for the ppy complexes. This is a substantial modulation of the hydride transfer reactivity of these complexes without any chemical modification. The directionality of the hydricity shifts is the same for the substituents and electric fields. As is the case for the substituents, more "electron donating" (negative) fields decrease the hydricity of the complexes promoting hydride transfer.

Ir-H stretching vibrational frequencies were computed for the substituted complexes for comparison with the fielddependent values (Figure 8B). It was found that the relationship between  $\sigma_{\rm p}^{-}$  and Ir–H frequency is linear but otherwise bears no resemblance to the field dependence. For the substituted complexes, the Ir-H stretching frequency increases substantially as the complex becomes more hydridic (substituents are more electron donating). The magnitude of this shift is much larger than the computed Stark shift of [Irbpy-H]<sup>+</sup> and is in the complete opposite direction of the shift for Ir-ppy-H. These results show that using Stark shifts to relate electric fields to substituents must be done with great caution, particularly if one wants to make conclusions about chemical reactivity. The shifts in hydricity as a function of field (Figure 4A) and substituent (Figure 8A) are similar in magnitude and direction, but the shifts in the Ir-H stretching frequencies (Figures 7A,D and 8B) are entirely different.

A more useful comparison between the field and substituents was revealed using natural bond orbital analysis. Calculations were performed using NBO 3.1 as implemented in Gaussian 16.<sup>54,55</sup> This analysis was used to monitor the partial charge on the hydridic H; an increase in the electron density on H should correlate with decreased hydricity (more

favorable hydride transfer). Indeed, both electron donating substituents (Figure 8C) and negative electric fields (Figure 8D) cause the partial charge of H to become more negative, favoring hydride transfer. In fact, the slope of  $\Delta G^{\circ}_{H^{-}}(Cl^{-})$ versus the NBO charge on H is similar for all complexes regardless of whether the values are shifted by an external field or by a chemical substituent (Figure S13), suggesting that modulating the character of the H atom plays a key role in the hydricity shifts. Overall, the comparison between substituents and electric fields shows that they are similar in their effects on hydricity and charge distribution, but their spectroscopic impacts are quite distinct. An interesting area for future study is the combination of substituent and field effects to achieve even more precise control of hydricity. The thiolate substituent of [Ir-bpy-H]<sup>+</sup> and Ir-ppy-H is strongly electron donating, resulting in comparatively low hydricity values for the surfaceattached complex. Alternative functional groups such as the electron withdrawing cyano group might allow for higher hydricity values while still strongly attaching the complex to the Au surface to enable field control.<sup>56</sup>

Recent studies have emphasized the inhomogeneity of the local electric fields at electrochemical interfaces.<sup>57</sup> Our theoretical model, which consists of a constant external field perpendicular to the Au surface, contains a substantial amount of this inhomogeneity via the polarization of the surfaceattached molecules to generate nonuniform local fields. In other words, while there is a constant applied external field, the field is not uniform across the molecule. This is exemplified by the plot of the local changes in the electrostatic potential (ESP) near  $[Ir-bpy-H]^+$  due to the applied field (Figure 9). The greatest change in ESP occurs near the hydridic H atom as shown through the convergence of the contour lines around that point (Figure 9A,C) and the dark blue/red regions near the H on the mapped potential difference surfaces (Figure 9B,D). The shape of the ESP response reported by the contour lines is essentially the same regardless of whether the applied field is positive or negative. Similar results were observed for Irppy-H with slightly larger changes in ESP (Figure S14). Note that the molecule was kept fixed at the zero-field geometry to obtain meaningful contour plots and mapped potential

analysis. To further investigate the inhomogeneity of the electrostatic response at different points in the molecule, the ESP at the hydridic H and Ir atoms (Figure S15) were plotted for the two complexes, with the largest change in ESP observed at H. The changes in ESP were linear for both complexes, with the ESP becoming more positive (negative) as electron density decreases (increases) as a positive (negative) field is applied. The local electric field change was also examined, with stronger fields at H than at Ir (Figure S16). For both H and Ir, the total change in the local field is larger than the strength of the external field, showing that the field-induced changes in electron density and nuclear positions amplify the local effect of the external field. The interplay of these local electrostatic effects arising from polarization of the surface-attached complexes may be important to the observed changes in reactivity. It is important to note that in an electrochemical experiment there would be other conformational and local field effects due to specific interactions with solvent and counterion molecules that are not accounted for in our model. These atomic level effects can be highly dependent on the specific choice of electrolyte, but for a sufficiently thick double layer a continuum electric field model should describe their influence on the system.<sup>58</sup> These local effects would vary significantly over time and space, and they would be sensitive to the experimental conditions. Thus, we present the current model for a general understanding of electrostatic effects on hydricity, but we anticipate the importance of future atomistic studies of the interfacial dynamics of a working experimental system with field-controlled hydricity.

#### CONCLUSIONS

We have found that the hydricities of Ir half-sandwich complexes, including [Ir-bpy-H]<sup>+</sup> and Ir-ppy-H, can be precisely controlled with applied electric fields and probed by Stark tuning rates of the Ir-H vibrational stretching and wagging modes. These linear changes in hydricity enable predictions of the hydride transfer reactivity of the surfaceattached complexes. The field-controlled hydricities are compared to those obtained for chemically modified complexes, and they are shown to be equivalent to a large change in the electronic character of the ligand. These results demonstrate that external electric fields can extend the reactivity of molecular catalysts into new regimes and produce catalytic devices with an unprecedented level of control. Therefore, we anticipate the reported findings will be particularly valuable for the development of non-Faradaic electrochemical control of catalytic systems.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.3c00829.

Supplementary reaction schemes, additional computational details, benchmarking of hydricity calculations, table of field-dependent hydricity values, evaluation of higher spin states, analysis of dipole moments, additional vibrational analysis, table of hydricities of substituted complexes, additional local electrostatic analysis, control calculations with neutral systems (PDF)

DFT-optimized coordinates (ZIP)

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#### Notes

The authors declare no competing financial interest.

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