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Iridium Dihydroxybipyridine Complexes are Effective Catalysts for Hydrodeoxygenation of Vanillyl Alcohol in Water

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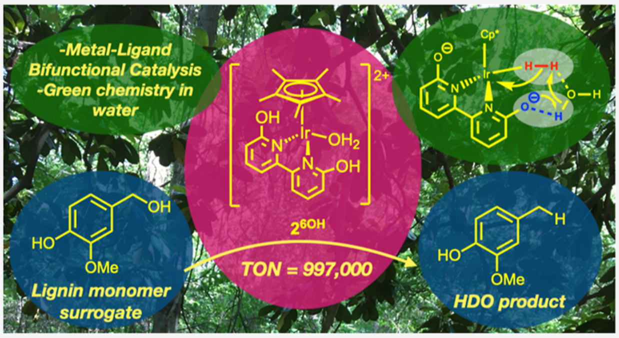
ABSTRACT: The selective reduction and deoxygenation of lignin-derived organic compounds are of interest for modeling a key reaction in the utilization of biomass. Toward this goal, vanillyl alcohol is used as a lignin monomer surrogate herein, and we study its reduction to form creosol in an aqueous solution. Four water-soluble iridium catalysts of the type $[Cp^*Ir(OH_2)(bpy^{R2})](OTf)_2$ ($\mathbf{2^R}$, where Cp* = η^5-pentamethylcyclopentadienyl anion and bpy^{R2} = n,n'-R_2-2,2′-bipyridine with n = 4 or 6) with different R substituents (R = H, OH, Me) in different positions on the bipyridine ligands were studied for this hydrodeoxygenation (HDO) reaction on vanillyl alcohol. Modification of the bipyridine ligands demonstrated that a more electron-rich bpy-derived ligand (R = OH) gives a more efficient HDO reaction. The addition of base serves to further enhance the HDO reaction by deprotonating the protic OH groups (OH groups on n,n'-dihydroxybipyridine where n = 4 in $\mathbf{2^{4OH}}$ or 6 in $\mathbf{2^{6OH}}$) resulting in a more electron-rich catalyst. Proximal OH groups in $\mathbf{2^{6OH}}$ produce our most active catalyst, and we can suggest that a metal−ligand bifunctional mechanism of H_2 activation and/or transfer to the substrate may be responsible for the greater efficiency of $\mathbf{2^{6OH}}$ vs $\mathbf{2^{4OH}}$. The catalyst loading could be reduced to 5×10^{-5} mol % of $\mathbf{2^{6OH}}$ with 0.5 mol % Na_2CO_3 and 997,000 turnovers (TON) could be achieved in 20 h at 100 °C. Furthermore, the same catalyst at 1×10^{-4} mol % produces 836,000 TON under similar but base-free conditions. Such catalytic efficiency in a dilute aqueous solution is noteworthy for potential applications.



INTRODUCTION

With increasing worldwide energy demand, renewable fuels are predicted to be the fastest growing energy source.[1] Lignin is the second most abundant biopolymer on the earth,[2] and around 50 million tons of lignin is produced every year.[3] For such a large quantity available, 98−99% industrial lignin is used to generate steam and energy.[3] Due to its high oxygen content, lignin has low heating values.[4] There have been advances in isolating lignin from biomass and performing depolymerization to monomer and dimer units such as vanillyl alcohol.[5−10] Hydrodeoxygenation (HDO) methods (e.g., Scheme 1) can be then applied to the small molecules to increase their energy density[11] and generate important aromatic chemicals.[12] HDO is a specific example of a hydrogenolysis process. Heterogeneous hydrogenolysis of benzylic alcohols is well established and often uses Pd on C catalysts.[13,14] For example, heterogeneous Pd nanoparticle catalysts can achieve >99% conversion of vanillyl alcohol to creosol, but often these reactions require high catalyst loadings and higher temperatures.[15−17] Molecular catalysts can address these issues, and over-reduction products are typically avoided due to the lack of a metallic surface that can lead to aromatic ring hydrogenation products.[18] Molecular palladium catalysts in homogeneous solution[19] and attached to a surface[20] have demonstrated the exclusive formation of the HDO product without ring hydrogenation on benzylic alcohol substrates.

Vanillyl alcohol, which can be derived from lignin depolymerization, was previously converted to creosol via HDO with several Ru catalysts shown in Scheme 1.[21] Based on the results, the electron donor strength of the ligands has a strong influence on the catalytic activity. In the absence of the base, the catalysts of type $\mathbf{1^R}$ (Chart 1) can produce the desired HDO product creosol (Schemes 1 and 2) with an order of increasing yield with R = H < Me < NMe_2 < OMe < OH. The trend revealed that a strong π-donor group on the pyridine ring is necessary to produce the HDO product in good yield. The evidence for partial π bonding (C═N or C═O) with NMe_2 and OMe/OH substituents included IR data, ^{1}H NMR data and single crystal X-ray crystallography.[21] With OH as a substituent, this π bonding interaction was enhanced by deprotonation with base. However, in the absence of a base

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Scheme 1. HDO of Vanillyl Alcohol by Ruthenium (1^{R}) and Iridium (2^{R}) Catalysts in Previous and Current Work, Respectively

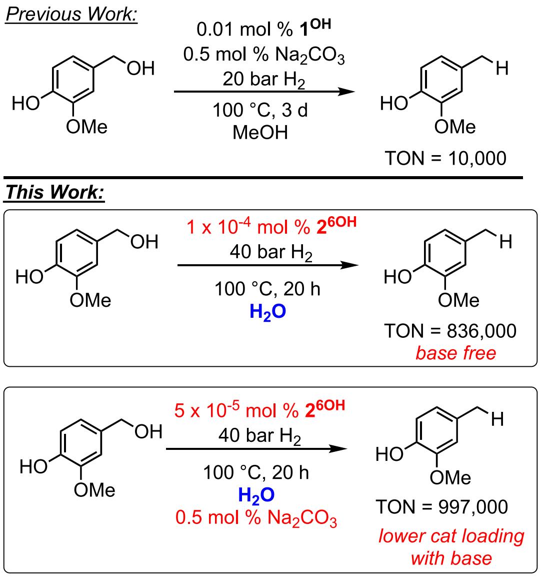
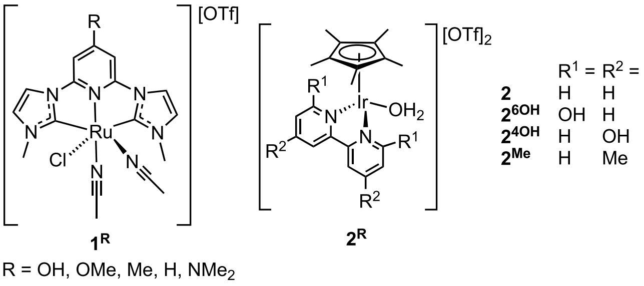
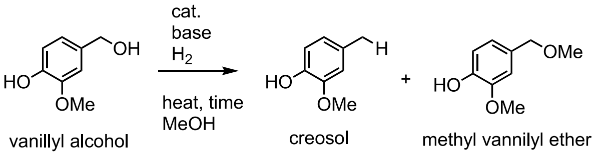


Chart 1. Ruthenium (1^{R}) and iridium (2^{R}) catalysts used herein and previously.



Scheme 2. Possible Products from Vanillyl Alcohol HDO in Methanol

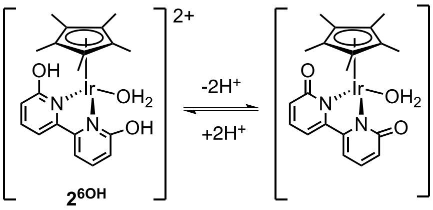


with catalysts 1^{R}, a competing methylation reaction at the benzylic OH group yields methyl vanillyl ether as a side product (Scheme 2). Using Na_2CO_3 as a base, the selectivity for the desired hydro-deoxygenation product improved significantly. Our most active catalyst (1^{OH} at 0.01 mol %) in the presence of Na_2CO_3 yielded a 10,000 turnover number (TON) over 3 days (Scheme 1) with >99% selectivity for creosol. Three key roles are suggested for the base. (1) It can deprotonate the OH in catalyst 1^{OH} leading to a more electron-rich pyridinolate pincer ligand which should facilitate the generation of a free site on Ru for catalysis. (2) The base can accelerate hydrogen activation by deprotonating the Ru(η^2−H_2) complex formed in situ. (3) Base can improve the selectivity for creosol even with aprotic catalysts 1^{R} (R = OMe etc.) by removing H^+ which is involved in the methylation pathway to form the methyl vanillyl ether side product.

Given the role of OH groups on the catalyst for the acceleration of the HDO reaction, it was logical to explore other OH-bearing protic ligands (e.g., dihydroxybipyridine) and metal complexes thereof. We have also replaced ruthenium(II) with iridium(III) and the coligands now include Cp* and aqua in this study (Chart 1). Iridium(III) complexes including 2^{6OH} were superior to Ru(II) complexes of 6,6′-dhbp for CO_2 hydrogenation and the reverse reaction, formic acid dehydrogenation.[22] Furthermore, iridium(III) complexes have been used frequently for (de) hydrogenation reactions involving alcohol substrates in aqueous solution.[23,24] Therefore, it seemed logical for us to start with Ir(III) complexes of type 2^{R} in this study.

Catalysts with OH groups near the metal center (e.g., in 6,6′-dihydroxy-2,2′-bipyridine = 6,6′-dhbp in 2^{6OH}, Chart 1) can serve as metal−ligand bifunctional catalysts in substrate hydrogenation reactions by hydride transfer from the metal combined with H^+ transfer from the ligand.[22,25−29] Examples of metal−ligand bifunctional catalysts bearing protic OH/NH groups proximate to the metal center have included work by Noyori,[30,31] Shvo,[32−34] and Himeda[35−38] and others.[39−44] Furthermore, metal complexes of 6,6′-dhbp undergo changes in electronic properties as a function of pH (Scheme 3).[22,25−29] For example, $[Cp^*IrOH_2(6,6'\text{-dhbp})](OTf)_2$ (2^{6OH}) undergoes double deprotonation with an apparent pK_a value of 4.1.[37] Deprotonation of the 6,6′-dhbp ligand results in a more electron rich metal center that can serve to accelerate hydrogenation reactions yielding more a more active metal catalyst.[22] With this information in hand, catalyst 2^{6OH} was tested and found to have a high catalytic activity for HDO of a lignin monomer surrogate in aqueous solvent.

Scheme 3. Deprotonation of the 6,6′-dhbp Ligand in 26^{OH} Produces a More Electron Rich Amide Type Ligand and a Neutral Product



RESULTS

Using vanillyl alcohol (Scheme 2) as a surrogate for a monomer that can be derived from lignin depolymerization,[45−51] we began a systematic study of the HDO reaction using iridium catalysts, 2^{R}. Several catalysts of type 2^{R} were used, including 2^{6OH} with proximate OH groups, 2^{4OH} with distal OH groups, 2^{Me} with distal methyl groups, and **2** lacking bpy substituents (Chart 1). The use of proximate and distal OH groups can distinguish between rate acceleration due to ligand deprotonation with base resulting in a more electronically rich ligand vs rate acceleration due to a cooperative metal−ligand bifunctional mechanism. Furthermore, methyl groups provide a more electron-rich ligand without protonation/deprotonation events.

The HDO reactions were studied in aqueous solution in a Parr reactor pressurized with H_2 gas and containing catalyst 2^{R}

(1.3×10^{-5} M) and vanillyl alcohol (0.52 M). These conditions were chosen based on our prior work and some initial optimization.[21] Following reaction completion, the reaction mixture was diluted with methanol and analyzed by gas chromatography (GC) to obtain TON (where TON = moles of product/moles of catalyst). Reactions were analyzed after 1 h (for all catalysts) and 20 h (for the more active catalysts) to measure higher TON values.

Optimizing the Base. The amount of base added to the reaction mixture was tested to find the optimal identity and quantity of base for HDO catalysis (Table 1). In our past work with catalyst $\mathbf{1}^{\mathbf{R}}$, a catalyst-to-base ratio of 1:50 was optimal for this series of Ru catalysts,[21] which is the same as in entry 2. However, in this work, the yield of creosol increased (up to 91%) with increasing quantities of base (entries 1−5, Table 1). Several other bases were tested to study the identity of the base at 2.5 mol %. However, comparing Na_2CO_3, $NaHCO_3$, K_2CO_3, and NaOH (entries 3, 6, 7, and 8, respectively) showed that Na_2CO_3 appears to be the optimal base.

Table 1. HDO of Vanillyl Alcohol Using Catalyst $\mathbf{2}^{\mathbf{6OH}}$ with Different Bases and Control Experiments[a]

entry	base	base (mol %)	creosol (% yield)[b]
1	Na_2CO_3	0.0625	69.9 (4)
2	Na_2CO_3	0.125	71.0 (3)
3	Na_2CO_3	2.5	85.2 (2)
4	Na_2CO_3	3.75	86.6 (1)
5	Na_2CO_3	6.25	91.0 (7)
6	$NaHCO_3$	2.5	74.2 (1)
7	K_2CO_3	2.5	72.6 (7)
8	NaOH	2.5	81 (1)
9	none[c]	0	1.7 (1)
10	Na_2CO_3[c]	2.5	5.5 (5)
11	none	0	65 (1)

[a] All experiments were done in triplicate and were analyzed by GC. Conditions: 2.59 mmol vanillyl alcohol in 5 mL H_2O, 0.0025 mol % of catalyst (unless otherwise indicated), 40 bar of H_2, 100 °C for 1 h. See the Supporting Information for further details. [b] Yield is calculated from the GC data. [c] No catalyst was added.

Catalyst and base were both present in substoichiometric amounts relative to the substrate. In order to test the impact of the catalyst and base, several control experiments were performed. Without catalyst and base (entry 9, Table 1), a low yield (1.7%) of creosol is obtained. By the addition of base only (entry 10, Table 1), slightly more product (5.5%) was formed. However, the catalyst alone without base (entry 11, Table 1) produced a 65% yield of creosol. These data also show that a catalyst is necessary for the efficient conversion of vanillyl alcohol to its HDO product, giving a reasonable yield of product which can be further enhanced by the addition of base.

Substituent Effects on the Catalyst. We set out to determine the impact of the catalyst ($\mathbf{2}^{\mathbf{R}}$) identity in terms of bpy substituents and their relative reactivity in the HDO reaction (Chart 1 and Table 2). These catalysts were tested using an intermediate concentration of Na_2CO_3 base (2.5 mol %) and in the absence of base (0 mol %). This quantity of base was chosen because it resulted in good yields while avoiding high concentrations of the base, which may lead to side reactions for base-sensitive substrates. Entries 1 and 2 (Table 2) with $\mathbf{2}^{\mathbf{6OH}}$ are repeated from Table 1 for the purpose of comparison. Catalyst $\mathbf{2}^{\mathbf{6OH}}$ is water soluble and water stable, which allows us to avoid the use of methanol as the solvent, and this also prevents the formation of methylation byproducts as shown in Scheme 2. Thus, creosol is formed as the sole product in this reaction. Entries 3 and 4 show that $\mathbf{2}^{\mathbf{4OH}}$ is also an effective catalyst (61% yield), which is enhanced by the presence of a base (72% yield). It is clear from entries 1−4 that the protic ligands lead to more effective catalysts ($\mathbf{2}^{\mathbf{6OH}}$ and $\mathbf{2}^{\mathbf{4OH}}$) which are enhanced by base vs their aprotic analogs in entries 5−8. The aprotic catalysts **2** and $\mathbf{2}^{\mathbf{Me}}$ show low activity (3−4% yield without base, entries 5 and 7) and there is no enhancement in the presence of base (2−3% yield with base, entries 6 and 8). The activities of these catalysts are similar to the no catalyst control (1.7 and 5.5% yield without and with base, entries 9 and 10, Table 1). Thus, our most active catalyst, which was chosen for further optimization, is $\mathbf{2}^{\mathbf{6OH}}$ in the presence of base (entry 2).

Table 2. Evaluation of $\mathbf{2}^{\mathbf{R}}$ Catalysts for HDO of Vanillyl Alcohol in the Presence and Absence of Base[a] **Entries 1 and 2 are Repeated from Table 1 for Comparison**

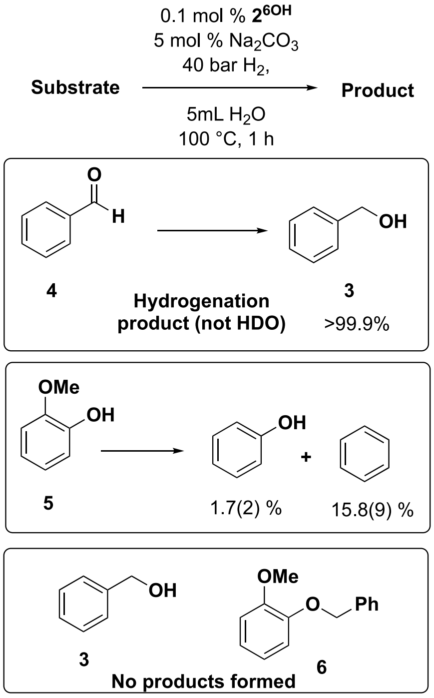
entry	cat	Na_2CO_3 (mol %)	creosol (% yield)[b]
1	$\mathbf{2}^{\mathbf{6OH}}$	0	65 (1)
2	$\mathbf{2}^{\mathbf{6OH}}$	2.5	85.2 (2)
3	$\mathbf{2}^{\mathbf{4OH}}$	0	61 (2)
4	$\mathbf{2}^{\mathbf{4OH}}$	2.5	72 (1)
5	**2**	0	3.1 (2)
6	**2**	2.5	2.1 (2)
7	$\mathbf{2}^{\mathbf{Me}}$	0	3.9 (3)
8	$\mathbf{2}^{\mathbf{Me}}$	2.5	3.1 (2)

[a] All experiments were done in triplicate and were analyzed by GC. Conditions: 2.59 mmol vanillyl alcohol in 5 mL H_2O, 0.0025 mol % of catalyst, 40 bar of H_2, 100 °C for 1 h. See the Supporting Information for further details. [b] Yield is calculated from the GC data.

Low Catalyst Loading Experiments with $\mathbf{2}^{\mathbf{6OH}}$. With the information accumulated from previous experiments, attempts were made to reduce the catalyst loading to achieve higher TONs. Frequently, reduced catalyst concentration leads to higher TON values due to reduced decomposition events involving catalyst−catalyst interactions.[52,53] Reactions were run both with and without base to get the highest TON for the best catalyst, namely $\mathbf{2}^{\mathbf{6OH}}$. With 5×10^{-5} mol % of $\mathbf{2}^{\mathbf{6OH}}$ and 0.5 mol % Na_2CO_3, nearly a 997,000 TON was achieved for the HDO reaction on vanillyl alcohol in 20 h. For certain substrates, base-free conditions are desirable, and this reaction can be run base free with 1×10^{-4} mol % of $\mathbf{2}^{\mathbf{6OH}}$ yielding 836,000 TON in 20 h. Thus, high TON values can be achieved under base-free conditions, but typically, a higher catalyst loading is required.

Alternative Substrates. Lignin depolymerization readily leads to other monomers that would require the HDO reaction prior to being used as fuels. These monomers include benzyl alcohol (**3**), benzaldehyde (**4**), guaiacol (**5**), and 3-methoxyphenyl anisole (**6**) (Scheme 4).[13,54] Given the high efficiency of catalyst $\mathbf{2}^{\mathbf{6OH}}$ in the HDO reaction on vanillyl alcohol, we wanted to broaden our study by testing these additional substrates in the HDO reaction with 40 bar of H_2, 5 mol % Na_2CO_3 base, and 0.1 mol % catalyst as shown in Scheme 4 (see the Supporting Information for further details). Benzyl alcohol (**3**) and 3-methoxyphenyl anisole (**6**) were unreactive, and no products were detected by GC analysis. Benzaldehyde (**4**) underwent hydrogenation to form benzyl

Scheme 4. Further Alternative Substrates 3, 4, 5, and 6 Were Tested for the HDO Reaction with 0.1 mol % of $\mathbf{2^{6OH}}$ Catalyst



alcohol (**3**) in quantitative yield, which is a well-known transformation for iridium catalysts,[55] but no HDO products involving oxygen loss were observed. Only substrate **5** produced HDO products with phenol [1.7 (2)%] and benzene [15.8 (9)%] being produced and detected by GC. Although the yields here are low, this reaction is not yet optimized and shows the potential for catalyst $\mathbf{2^{6OH}}$ to fully deoxygenate guaiacol in water to form benzene. Overall, we note that the differences in reactivity between vanillyl alcohol and the substrates used here suggest that reactivity is enhanced by the additional OH and OMe groups present in vanillyl alcohol relative to benzyl alcohol, which likely includes electronic effects and improved water solubility.

■ DISCUSSION

As previously observed for iridium complexes with dihydroxybipyridine ligands, the hydroxy groups can be deprotonated under basic conditions as shown in Scheme 3.[26,37,56] The quantities of base (2.5 mol % Na_2CO_3 relative to vanillyl alcohol) typically used lead to a pH of 9.3[57] for which $\mathbf{2^{6OH}}$ will be doubly deprotonated (pK_a value of 4.1 for both OH groups).[37] Thus, the increased TON values with base (for $\mathbf{2^{6OH}}$ and $\mathbf{2^{4OH}}$, Tables 1 and 2) likely relate to increasing quantities of the deprotonated catalyst and the multiple roles that base can play in this reaction, as shown in Scheme 5. Carbonate base can potentially deprotonate the vanillyl alcohol substrate or assist in key steps in Scheme 5 (e.g., deprotonation of an iridium η^2−H_2 complex). The deprotonated form of catalyst $\mathbf{2^{6OH}}$ or $\mathbf{2^{4OH}}$ has a more electron-rich iridium center to enhance the HDO reaction as described further below. Even without a base present (pH ∼ 6.8 based upon the acidic nature of the protic catalysts, $\mathbf{2^{6OH}}$ and $\mathbf{2^{4OH}}$), a majority of deprotonated catalysts (e.g., 99.8% doubly deprotonated for $\mathbf{2^{6OH}}$ at pH 6.8)[58,59] is expected to be present.[55] Thus, our mechanistic proposal drawn in Scheme 5 is proposed to go through this doubly deprotonated species which is expected to be both more active and more prevalent vs the OH-bearing catalysts.[22]

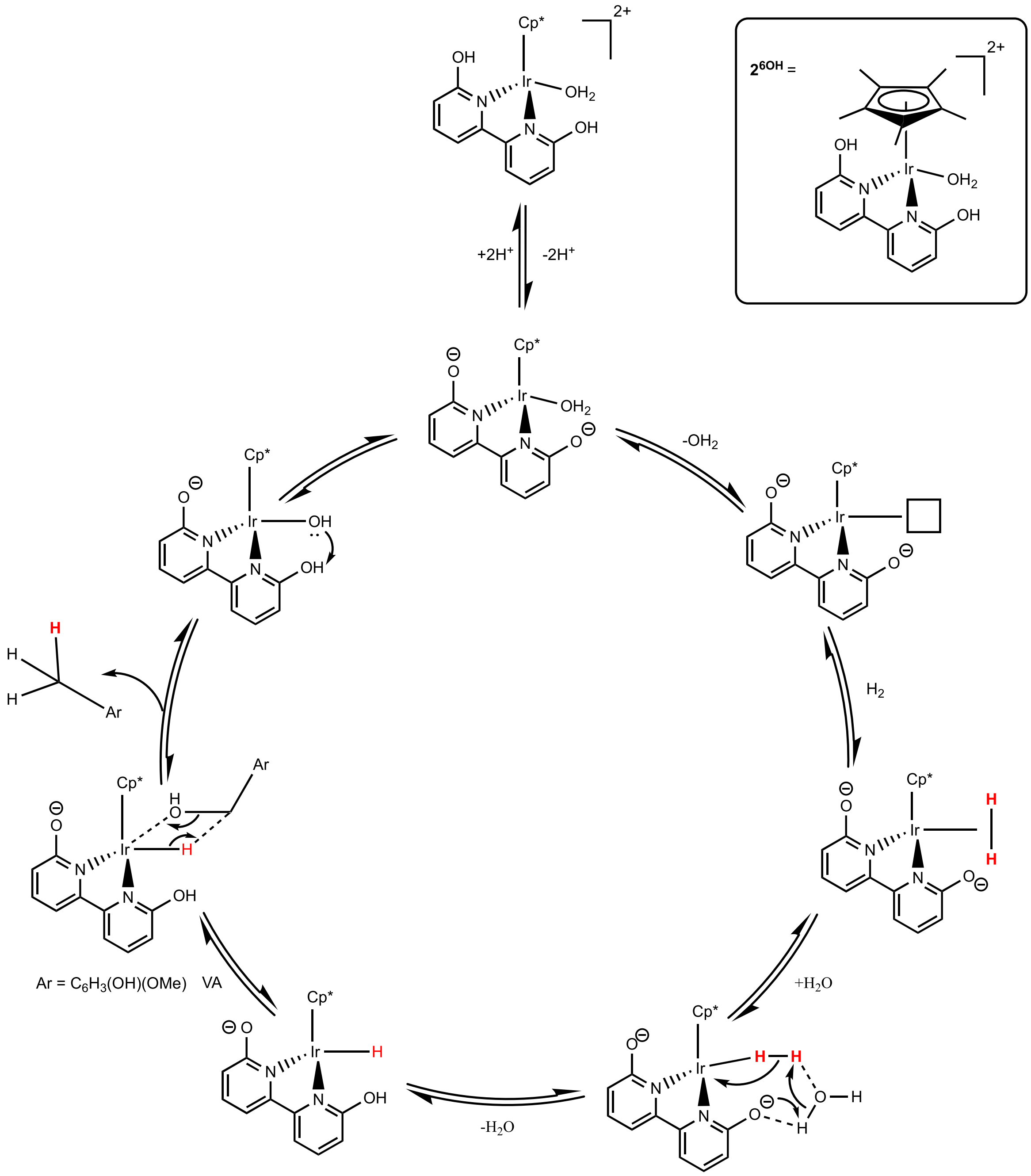
Following catalyst deprotonation in Scheme 5, the loss of the water ligand on Ir can generate a free site for H_2 binding. H_2 coordination is proposed to generate a transient η^2-H_2 complex (with computational evidence in past studies)[22,60] that can then be heterolytically cleaved to generate an iridium hydride with H^+ added to the oxyanion of the ligand. Water (and base if present) is proposed to assist in the internal proton transfer to the pendant base, as has been demonstrated in other computationally studied mechanisms for CO_2 hydrogenation with $\mathbf{2^{6OH}}$.[38,60] The Ir−H formation step was proposed to be rate limiting for the CO_2 hydrogenation reaction.[37,38] Once the iridium hydride is formed, it is proposed to transfer hydride to vanillyl alcohol, and OH can serve as a leaving group via either an outer sphere mechanism or with a weak interaction between the OH group and iridium. Hydride transfer involving alcohols is well precedented and is a key step in the dehydrogenation of alcohols to form ketones or aldehydes.[41,55,61,62] However, OH serving as a leaving group and OH transfer to the metal are proposed here without extensive precedence. Kinetic studies for Pd/C catalyzed hydrogenolysis of benzyl alcohol derivatives showed an S_N2 mechanism for primary alcohols.[63] In one example, metal hydride attack on benzyl alcohol resulted in an HDO reaction as implied by kinetic studies.[20] We note that this vanillyl alcohol OH group is not acidic enough to protonate the iridium hydride under these conditions to form H_2, as hydrogen evolution from the closely related $[Cp^*IrH(bpy)]^+$ catalyst required light energy, reducing conditions, and strong acids.[64,65] Following this step (hydride attack and OH loss), the creosol product is then released and intramolecular proton transfer can occur to restore the catalyst resting state with an aqua ligand on Ir and a deprotonated 6,6′-dhbp ligand.

This mechanism shows several advantages for protic ligands over their aprotic analogs. The deprotonated dhbp ligands in $\mathbf{2^{nOH}}$ (using n = 4 or 6) are much more electron rich vs **2** and $\mathbf{2^{Me}}$. In fact, $\mathbf{2^{nOH}}$ complexes are neutral once doubly deprotonated, whereas **2** and $\mathbf{2^{Me}}$ are dications. This facilitates several key steps in the mechanism: loss of the aqua ligand and activation of the η^2−H_2 complex by putting the electron density into the σ^* orbital on H_2. Furthermore, a nearby pendant base can help deprotonate bound H_2 as shown in Scheme 5. These factors allow for the metal−ligand bifunctional mechanism[27,35−38] to be operative for $\mathbf{2^{6OH}}$ as shown in Scheme 5 and can explain the improvements in the yield of creosol for $\mathbf{2^{6OH}}$ vs $\mathbf{2^{4OH}}$.

■ CONCLUSIONS

Compared to our previous best catalyst using a central pyridinol ring within the Ru-bound CNC ligand ($\mathbf{1^{OH}}$ with 10,000 TON with base), the iridium catalyst $\mathbf{2^{6OH}}$ led to a greatly increased TONs for the HDO reaction on vanillyl alcohol both without and with base (836,000 and 997,000, respectively) even considering the shortened reaction time (20 h with $\mathbf{2^{6OH}}$ vs 3 days with $\mathbf{1^{OH}}$). The reaction solvent has also changed from MeOH to the more environmentally friendly solvent of H_2O which also serves to avoid the formation of methylation side products.[21] Furthermore, high TONs even without a base can allow for the HDO of base-sensitive substrates. However, further studies are needed to optimize the

Scheme 5. Mechanistic Proposal for HDO of Vanillyl Alcohol with Iridium Catalyst 2^{6OH}



HDO reaction on other lignin monomer surrogates (e.g., **3**−**6**) with $\mathbf{2^{6OH}}$ in aqueous solution.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.3c00273.

Experimental details on synthesis, characterization, and HDO reactions (PDF)

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Notes

The authors declare the following competing financial interest(s): E.T.P. and A.K.V. have filed a patent application related to this chemistry.

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