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Organoiridium Pyridonates and Their Role in the Dehydrogenation of Alcohols

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New derivatives of 2-hydroxypyridine (2-hpH) and Cp*Ir(III) are described. Under conditions for catalytic dehydrogenation of 1-phenylethanol catalyzed by Cp*IrCl(κ^2-2-hp) (**1**), the main species observed are [Cp*$_2$Ir$_2$H$_2$(2-hp)]Cl ([**2**]Cl) and Cp*IrHCl(κ^1-2-hpH) (**3**). Crystallographic analysis confirms that the cation in [**2**]PF_6 consists of a Cp*$_2$Ir$_2$(μ-H)$_x^{2+}$ core complemented by a pyridonate ligand that bridges via O and N centers. Although [**2**]Cl is catalytically highly active, the related salt [**2**]PF_6 is not. Addition of chloride sources reactivates [**2**]PF_6. Collectively, our experiments indicate that [**2**]Cl is a resting state that reverts to a more active species, which we propose is **1** itself. In situ NMR observations and PPh_3 trapping experiments show that under catalytically relevant conditions **1** rapidly converts to **3**, which can be observed spectroscopically. Compound **3** was independently generated by transfer hydrogenation of **1**. In other experiments, **1** was found to ring-open upon treatment with PPh_3 to give Cp*IrCl(κ^1-2-hp)(PPh_3), which in turn was found to react with $AgPF_6$ to give [Cp*Ir(κ^2-2-hp)(PPh_3)]PF_6. Both PPh_3 derivatives proved catalytically inactive for dehydrogenation. Cp*IrCl(κ^2-2-hp-6-Me) was also prepared but could not be converted to κ^1-2-hpH-6-Me derivatives. The complex Cp*IrCl($C_5H_3O_2NH$), nominally derived from the conjugate base of 2,6-dihydroxypyridine, features the novel ligand η^3-$C_3H_3(CO)_2NH$.

Introduction

The coordination chemistry of the tautomeric pair 2-hydroxypyridine/2-pyridone is well established[1,2] and is rich with opportunities for catalytic reactions that would benefit from the these bifunctional ligands in proton-transfer reactions. Ligand-facilitated proton transfer is pervasive in bioinorganic and industrial catalysis, being recently highlighted through studies of the [FeFe]-hydrogenases[3] and alkyne hydration,[4] respectively. A 2-hydroxypyridine-derived cofactor has been discovered at the active site of the hydrogenase enzyme Hmd.[5] Furthermore, the oxygen center of the pyridone/hydroxypyridine projects toward the proposed catalytic coordination site (Figure 1).[6] It is likely that the 2-oxo functionality on the pyridyl ring participates in the hydrogen-transfer reactions catalyzed by this enzyme.[7]

Both the 2-hydroxypyridine and the tautomeric 2-pyridone are known to serve as unidentate ligands, binding metals through N and O, respectively.[2] Complexes with O-bonded pyridones are common with hard metals, for example, [Fe(O-2-$C_5H_4NH)_6$]$^{2+}$,[8] whereas softer metals prefer N-bonded 2-hydroxypyridine (2-hpH).[9] The ligand properties of the pyridonate anion are usefully referenced to the behavior of carboxylates. With a pK_a of 17.0 (DMSO),[10] 2-hydroxypyridine is much less acidic than acetic acid, with a pK_a of 12.3, DMSO.[11] Pyridon*ate* can serve as either an O- or an N-bonded ligand,[12] the latter being more common for soft metals, for example, Ru($NC_5H_4O)_2$(terpy)(H_2O).[13] Most commonly, pyridonates serve as N,O-bridging ligands in polymetallic compounds.[1,14] Monometallic complexes of bidentate pyridonates (κ^2-pyridonates) are rarer.[15,16]

The hydroxyl substituent of 2-pyridinols is known to interact with anionic ligands via hydrogen bonding. For example, hydrogen bonding between 2-pyridinol and hydride ligands

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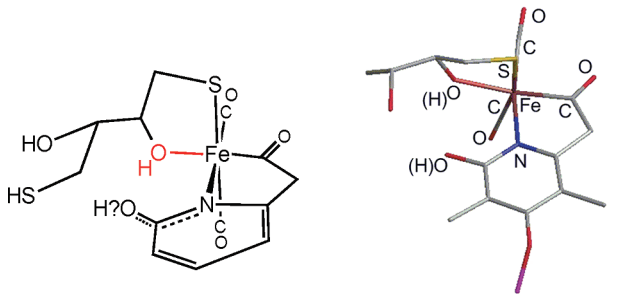
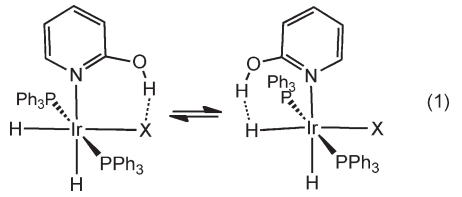


Figure 1. Structure of the dithiothreitol-modified active site of Hmd, showing the binding of the pyridone/pyridinol cofactor.

has been observed by Crabtree and Morris.[17] 2-Hydroxypyridine is also known to form hydrogen bonds to halide and other ligands (eq 1).[18] More complicated ligands that incorporate the 2-pyridone functionality also participate in intramolecular H-bonding.[19]



(1)

Yamaguchi et al. reported that the complex Cp*Ir(2-hp)Cl is a highly active catalyst for the acceptorless dehydrogenation of secondary alcohols.[20] With 1-phenylethanol in refluxing toluene TONs up to 700 were observed. In terms of activity for alcohol dehydrogenation, Cp*Ir(κ^2-2-pyridone)Cl is one of the best (see Supporting Information).[21] Dehydrogenation was proposed to proceed via ring-opening of the Ir(κ^2-2-pyridinoate) center to give a pyridinol-alkoxide complex that undergoes β-hydride elimination.[20] Pursuant to our interests in transfer hydrogenation,[22,23] we sought further insight into the Cp*Ir-2-pyridonate system with the goal of identifying intermediates and improving the efficiency of the catalyst.

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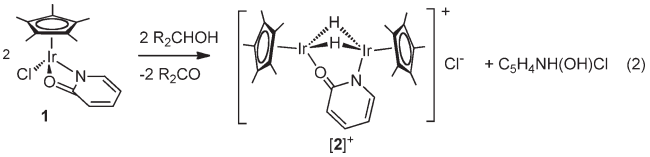
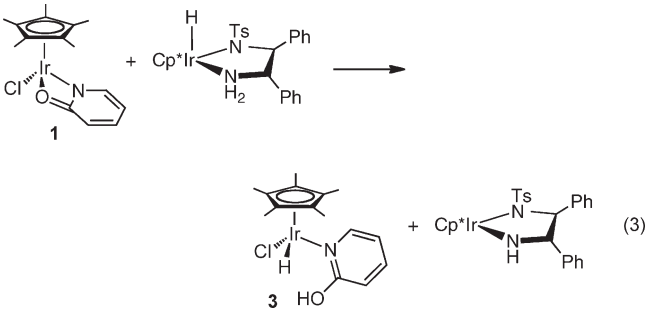
Results

Hydrides Derived from Cp*Ir(κ^2-2-pyridonate)Cl. The relevant catalysts or precatalysts are Cp*Ir(κ^1-2-hydroxypyridine)Cl_2 and Cp*Ir(κ^2-2-pyridonate)Cl (**1**). In the presence of the base (K_2CO_3), the dichloride was found to give the same results as **1**, which was the starting point for our studies. The related pyridonate complex (cymene)Ru(κ^2-2-pyridonate)Cl[16] was also tested but found inactive. Treatment of solutions of **1** with secondary alcohols was found to give hydrides. For example, a CD_2Cl_2 solution of **1** with 5× excess PhCH(OH)Me at 25 °C initially gave a hydride, previously unobserved, which converted cleanly to a more stable hydride over the course of several hours. ESI-MS analysis of reaction mixtures indicated that the stable hydride has the formula $[Cp^*_2Ir_2(\mu\text{-H})_2(\mu\text{-2-hp})]^+$ ($[\mathbf{2}]^+$).



$[Cp^*_2Ir_2(\mu\text{-H})_2(\mu\text{-2-hp})]Cl$ ($[\mathbf{2}]Cl$) was independently generated by treatment of $Cp^*_2Ir_2H_2Cl_2$ with Na2-hp. Its unsymmetrical structure is indicated by two equally intense ^1H NMR signals assigned to the nonequivalent Cp* ligands. Anion exchange with aqueous $NaPF_6$ converted the chloride salt into $[\mathbf{2}]PF_6$, which was obtained in analytical purity. Crystallographic analysis confirmed that the cation in $[\mathbf{2}]PF_6$ is unsymmetrical, with the pyridonate ligand bridging the two Ir centers (Figure 2). The structure is related to the symmetrical compound $[Cp^*_2Rh_2H_2(\mu\text{-OAc})]PF_6$ (r_{Rh-Rh} = 2.60(1) Å),[24] but the dihedral angle (between the Cp* groups) is smaller. In $[Cp^*_2Ir_2H_3]NO_3$ ($[\mathbf{4}]NO_3$) the Cp* groups are perpendicular to the Ir---Ir vector.[25]

A hydride observed in all reactions of **1** with hydrogen donors is proposed to be the 2-hydroxypyridine complex Cp*IrHCl(2-hpH) (**3**). The compound was not isolated in pure form, but the ^1H NMR data are consistent with the proposed stoichiometry. Compound **3** was independently generated by treatment of **1** with the transfer hydrogenation catalyst Cp*IrH(TsDPENH) (TsDPENH = racemic H_2N-CHPhCHPhNTs$^-$).[26] This process occurs rapidly even below 0 °C (eq 3, the enantioselectivity of the intermetallic hydrogen transfer was not investigated).



In the presence of excess MeOH, Cp*IrH(TsDPENH) (as well as (cymene)RuH(TsDPENH)) slowly catalyzes this same

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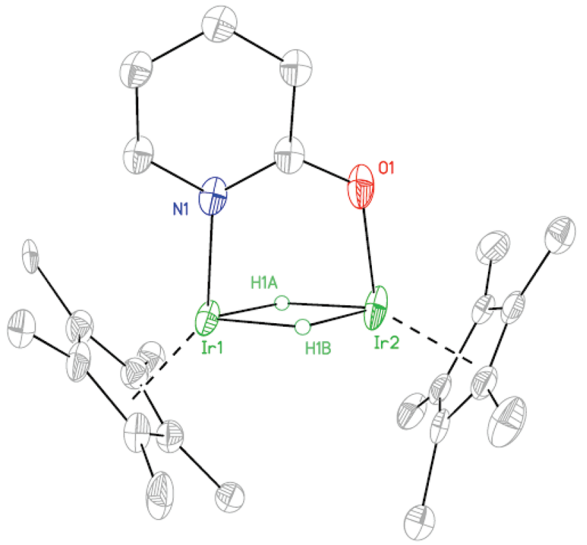

Figure 2. Structure of the cation in [**2**]PF_6. Selected bond lengths (Å) and angles (deg): Ir(1)−N(1), 2.095(9); Ir(1)−N(1B), 2.101(9); Ir(1)−H(1A), 1.59(6); Ir(1)−H(1B), 1.73(7); Ir(2)−O-(1), 2.033(6); Ir(2)−H(1A), 1.74(7); Ir(2)−H(1B), 1.59(6); Ir-(1)−Ir(2), 2.675(3); $Cp_{centroid}$−Ir(1), 1.836; $Cp_{centroid}$(B)−Ir(1), 1.814; $Cp_{centroid}$−Ir(2), 1.807; $Cp_{centroid}$(B)−Ir(1), 1.792; Ir(1)−Ir(2)−H(1A), 35(2); Ir(1)−Ir(2)−H(1B), 38(2).

conversion, the slow step being the regeneration of Cp*IrH-(TsDPENH). Addition of Et_3N to a solution of **3** resulted in the complete and immediate formation of [**2**]$^+$. Solutions of **3** were also found to react with PPh_3 to give Cp*IrClH(PPh_3) (eq 4).

$$\underset{\mathbf{3}}{\text{Cp*IrClH(2-hpH)}} + \text{PPh}_3 \rightarrow \text{Cp*IrClH(PPh}_3\text{)} + \text{2-hpH} \quad (4)$$

The fate of **1** was determined under conditions approximating those used in catalysis,[20] that is, 100 °C with 5 equiv of PhCH(OH)Me vs 110 °C (refluxing toluene) with 1000 equiv of PhCH(OH)Me. We observed the initial formation of a small quantity of **3** followed within minutes by the appearance of [**2**]$^+$ as the predominant species, which persisted for hours at 100 °C. In contrast to its rapid reaction with PhCH(OH)Me, it is interesting neither phenol nor 2,4-dinitrophenol reacts with **1**; thus proton-induced ring-opening is not facile. Similarly, **1** is unreactive toward methanol (25 °C, 24 h).

Solutions of **1** in CD_2Cl_2 were also found to react readily with H_2. Again, **3** was the first detectable hydride, being observed after a few seconds at −30 °C. Conversion of **1** was complete within minutes at room temperature, the main product being [**2**]$^+$ together with a trace of $Cp^*_2Ir_2H_2Cl_2$, as observed by Yamaguchi under similar conditions.[27] Upon prolonged exposure of these solutions to H_2, only [**2**]$^+$ and $[Cp^*_2Ir_2H_3]^+$ ([**4**]$^+$) (δ −15.5) were observed.

Catalytic Role of 2$^+$. We assessed the relative activity of several Cp*Ir-hp complexes for the catalytic dehydrogenation of PhCH(OH)Me (Table 1). Compound **1** was found to be superior to [**2**]Cl, but both were far more active than related compounds. Striking was the finding that [**2**]PF_6 is a very poor catalyst, even though [**2**]$^+$ is the dominant species in solutions of active catalysts (see above). ^{19}F NMR analysis of the mixture after 21 h verified that the majority (~95%) of the PF_6^- remained intact; thus the inactivity of [**2**]PF_6 is not attributable to degradation of the counterion. Addition of PPNCl (PPN$^+$ = N(PPh_3)$_2^+$) to this solution gave activity comparable to that of [**2**]Cl (Figure 3).

Otherwise, further equivalents of PPNCl, which has good solubility under catalytic conditions, had only a modest effect on catalysis by **1**. The addition of a 5 equiv excess of 2-hpH to **1** improves the stability of the catalyst system. Greater excesses of 2-hpH were found to suppress activity, consistent with our finding that the bis(pyridonate) Cp*Ir(κ^2-2-hp)-(κ^1-2-hp) is a modest catalyst.

We also showed that [**2**]Cl converted to **1** in the presence of 2-hpH in refluxing xylene. Thus, treatment of $Cp^*_2Ir_2H_2Cl_2$ with 2-hpH at room temperature initially gave [**2**]$^+$, while heating such solutions gave the monomer **1**.

PPh_3 Derivatives. Phosphine adducts of **1** were examined in order to expand the range of these unusual catalysts and prevent dimerization to species such as [**2**]$^+$. We found that Cp*IrCl_2(2-hpH) reacts with PPh_3 to give Cp*IrCl_2(PPh_3), consistent with the high lability of the κ^1-hpH ligand. Treatment of **1** with PPh_3 cleanly gave Cp*IrCl(κ^1-2-hp)(PPh_3) (**5**). The ^{1}H NMR signals at δ 5.60, 5.87, 6.78, and 8.12 are diagnostic for a N-bonded pyridonate.[28] Treatment of **5** with $AgPF_6$ gave a new single product, [**6**]PF_6, which we propose

Table 1. Turnover Numbers (TON) for Various Catalysts for Conversion of PhCH(OH)Me into PhC(O)Me[a]

catalyst	TON 5 h	TON 21 h
Cp*IrCl(2-hp) (**1**)	237	571
Cp*IrCl(2-hp) (**1**) + 5 equiv 2-hpH	253	640
[$Cp^*_2Ir_2(\mu$-H)$_2$(2-hp)]Cl ([**2**]Cl)	167	408
[$Cp^*_2Ir_2(\mu$-H)$_2$(2-hp)]PF_6 ([**2**]PF_6)	7	107
[$Cp^*_2Ir_2(\mu$-H)$_2$(OAc)]PF_6	38	83
[$Cp^*_2Ir_2(\mu$-H)$_3$]PF_6 ([**4**]PF_6)	57	130
$Cp^*_2Ir_2H_2Cl_2$	44	114
$Cp^*Ir(2\text{-hp})_2$	23	167

[a] Conditions: 6 mL of refluxing toluene, 2.4 mL of 1-phenylethanol, 0.1 mol % Ir complex.

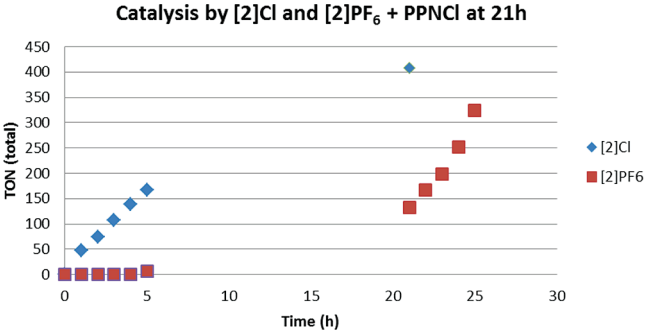

Figure 3. TON (cumulative) vs time for the dehydrogenation of PhCH(OH)Me (0.1 mol % Ir, refluxing toluene) by [**2**]Cl and [**2**]PF_6. The squares mark the results for the PF_6^- salt before and after addition of 2 equiv of PPNCl (at 21 h).

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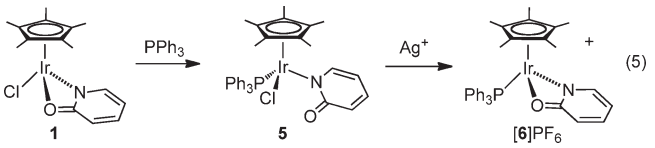
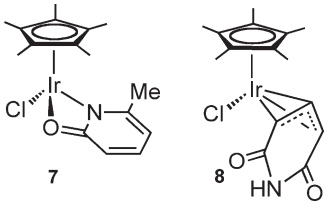
is [Cp*Ir(κ^2-2-hp)(PPh_3)]PF_6 (eq 5). Neither **5** nor [**6**]PF_6 showed any reactivity toward H_2 or toward PhCH(OH)Me.



The above experiments showed that PPh_3 efficiently (i) replaces 2-hydroxypyridine in **3** and (ii) opens the Ir(κ^2-2-hp) chelate ring to produce stable adducts. In view of these results, we repeated the experiments involving hydrogenation of **1** (−25 °C, 1 atm H_2) followed by quenching the mixtures with PPh_3. ^{31}P NMR analysis of these PPh_3-treated mixtures revealed the presence of significant amounts of Cp*IrHCl(PPh_3). This hydrido chloride is proposed to be derived from displacement of κ^1-hydroxypyridine in the transiently formed **3**; under these conditions, $Cp^*_2Ir_2H_2Cl_2$ and PPh_3 react relatively slowly.[29] We also observed Cp*IrCl_2(PPh_3) as well as Cp*IrCl(2-hp)(PPh_3) (**5**), the latter arising from **1**. These same species were generated by the addition of PPh_3 to a cooled catalytic reaction mixture. In this case, a large amount of unreacted PPh_3 was detected, reflecting the low reactivity of [**2**]$^+$ toward PPh_3.

Complexes of Other Pyridones. Given the high catalytic activities seen for **1**, we examined related complexes using 6-methyl-2-hydroxypyridine (6-Me-2-hpH). The new complexes were prepared by combining $Cp^*_2Ir_2Cl_4$ with the sodium salts of these pyridonates. Spectroscopically, the complexes **1** and Cp*Ir(κ^2-6-Me-2-hp)Cl (**7**) are similar. We were unable, however, to prepare Cp*Ir(κ^1-6-Me-2-hpH)Cl_2, the analogue of Cp*Ir(κ^1-2-hpH)Cl_2, via cleavage of $Cp^*_2Ir_2Cl_4$ by 6-MehpH. We propose that the increased steric bulk of this ligand inhibits κ^1-coordination. Furthermore, **7** proved to be a poor catalyst for dehydrogenation of PhCH(OH)Me.



From the reaction of $Cp^*_2Ir_2Cl_4$ with the monodeprotonated derivative of 2,6-dihydroxypyridine, we prepared a species with the nominal formula Cp*Ir($C_5H_4NO_2$)Cl (**8**). ^{1}H NMR measurements, even at −60 °C, indicated that **8** adopts a symmetrical structure. The low-field signal was found to rapidly exchange with D_2O. Crystallographic analysis of the (C_5Me_4Et)Ir analogue of **8** established the presence of an allyl-like ligand, that is, Cp*Ir(η^3-2,6-pyridionate)Cl (Figure 4). The Ir1−C13 and Ir1−C16 distances of 2.219 and 2.227 Å are within the normal distances for an Ir(III)-allyl complex. The Ir1−C12 distance of 2.081 Å is the shortest Ir(III)−C bond among these structures, the closest example

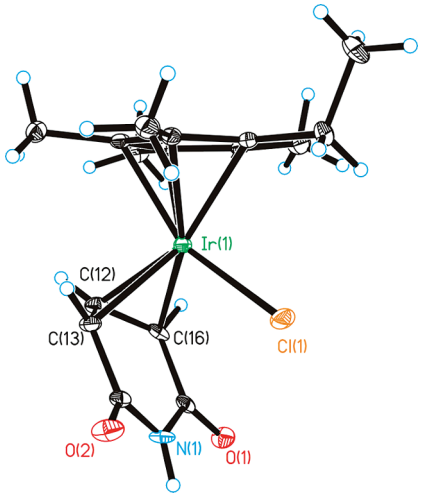


Figure 4. Crystallographically determined structure of (C_5Me_4-Et)IrCl(η^3-2,6-pyridionate). Selected bond distances (Å): Ir1−Cl1, 2.3919(12); Ir1−C12, 2.081(42); Ir1−C13, 2.219(4); Ir1−C16, 2.227(4); C12−C13, 1.436(5); C12−C16 1.417(5); C13−C14 1.464(5); N1−C14 1.387(5); N1−C15 1.391(4); C15−C16 1.463(5); C14−O2, 1.228 (4); C15−O1, 1.229 (4); Cp centroid − Ir1, 1.833.

being Ir(η^3-C_3H_5)I[$N(SiMe_2CH_2PPh_2)_2$] with a C2−Ir of 2.113 Å.[30]

With a TON of 230 (standard conditions, 21 h), complex **8** is an effective catalyst (or precatalyst) for the dehydrogenation of PhCH(OH)Me, but it is inferior to **1**.

Conclusions

Our results confirm that Cp*IrCl(κ^2-2-hp) is highly reactive toward hydrogen donors. Under catalytic conditions, the dominant species in solution is the μ-pyridonato salt [$Cp^*_2Ir_2H_2$(2-hp)]Cl. Our results indicate that this diiridium dihydride arises from the hydroxypyridine hydride complex (eq 6).

$$\underset{\mathbf{3}}{2Cp^*IrHCl(\kappa^1\text{-}2\text{-}hpH)} \rightarrow \underset{[\mathbf{2}]Cl}{[Cp^*2Ir_2H_2(2\text{-}hp)]Cl} + [2\text{-}hpH_2]Cl \quad (6)$$

Required for this conversion is the high substitutional lability of the 2-hpH ligand in Cp*IrHCl(κ^1-2-hpH), which was confirmed by a variety of experiments. Although [$Cp^*_2Ir_2H_2$(2-hp)]$^+$ is the dominant complex in solution during catalysis, it is catalytically inactive. Instead, in the presence of chloride, this diiridium cation converts to a highly active monometallic catalyst system that consists of Cp*IrHCl(κ^1-2-hpH) and its dehydro precuror Cp*IrCl(κ^2-2-hp).

Experimental Section

General Considerations. Unless otherwise indicated, reactions were conducted using standard Schlenk techniques (N_2) at room temperature with stirring. Solvents were dried and degassed prior to use. The following were prepared according to literature methods: Cp*Ir(κ^2-2-hp)Cl,[20] [$Cp^*_2Ir_2H_3$]PF_6,[31] $Cp^*_2Ir_2H_2Cl_2$,[29] [$Cp^*_2Ir_2H_2$(μ-OAc)]PF_6,[29] Cp*IrCl_2(PPh_3),[32] $Cp^*_2Ir_2Cl_4$,[33] and Cp*IrH(TsDPENH).[23] The reaction of $Cp^*_2Ir_2H_2Cl_2$ with

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PPh_3 to produce Cp*IrClH(PPh_3) is much slower than originally described,[29] requiring about 24 h for completion. 2-Hydroxypyridine, 6-methyl-2-hydroxypyridine, 2,6-dihydroxypyridine hydrochloride, NaOMe, Et_3N, and $AgPF_6$ were purchased from Aldrich. Racemic 1-phenylethanol was obtained from Alfa-Aesar.

Electrospray ionization-mass spectra (ESI-MS) were acquired using a Micromass Quattro QHQ quadrupole-hexapole-quadrupole instrument. ^1H, ^{19}F, and ^{31}P NMR spectra were acquired on Varian UNITY INOVA TM 500NB and UNITY 500 NB instruments. Elemental analyses were performed by the School of Chemical Sciences Microanalysis Laboratory utilizing a model CE 440 CHN analyzer.

[Cp*$_2$Ir$_2$H$_2$(μ-2-hp)]X ([2]Cl and [2]PF$_6$). A solution of 400 mg (7.4 mmol) of NaOMe in 5 mL of MeOH was transferred to a solution of 704 mg (7.4 mmol) of 2-hpH in 5 mL of MeOH to give a colorless homogeneous solution. Solvent was removed under vacuum at 60 °C overnight to give an air-stable hygroscopic white powder, assumed to be Na2-hp, which was stored in a desiccator. Yield: 774 mg (6.6 mmol, 89%). ^1H NMR (500 MHz, CD_3OD): δ 6.33 (t, 1H, 6.2 Hz, aryl-C*H*), 6.40 (d, 1H, 8.5 Hz, aryl-C*H*), 7.35 (m, 1H, aryl-C*H*), 7.67 (d, 1H, 5.4 Hz, aryl-C*H*). A solution of 24 mg (0.205 mmol) of Na2-hp in 2 mL of MeOH was transferred to a blue solution of 150 mg (0.205 mmol) of Cp*$_2$Ir$_2$H$_2$Cl$_2$ in 10 mL of CH_2Cl_2 to immediately give a red solution. After stirring 5 min, the solvent was removed under vacuum. The residue was extracted into 10 mL of CH_2Cl_2, and the slurry was cannula-filtered to remove NaCl. The filtrate was concentrated to ~3 mL and diluted with hexanes to produce a brown powder. Yield: 138 mg (0.176 mmol, 86%). ^1H NMR (500 MHz, CD_2Cl_2): δ −14.10 (s, 2H, Ir-*H*-Ir) 1.92 (s, 15 H, Cp*), 1.99 (s, 15 H, Cp*'), 6.57 (d of d of d, 1H, 5.0 Hz, 8.2 Hz, 13.7 Hz aryl-C*H*), 7.28 (m, 2H, aryl-C*H*, aryl-C*H*′), 8.33 (d, 1H, 6.1 Hz, aryl-C*H*). ESI-MS: m/z = 750.2 ([Cp*$_2$Ir$_2$H$_2$(2-hp)]$^+$). Red crystals of [Cp*$_2$Ir$_2$H$_2$(μ-2-hp)]PF_6 precipitated upon the addition of 0.5 mL of a saturated aqueous solution of $NaPF_6$ to an acetone solution of [**2**]Cl. The solid was filtered off, washed with water, and dried under vacuum overnight. Yield: 350 mg (0.39 mmol, 68%). ^1H NMR (500 MHz, CD_2Cl_2): δ −14.10 (s, 2H, Ir-*H*-Ir), 1.92 (s, 15 H, Cp*), 1.99 (s, 15 H, Cp*′), 6.57 (d of d, 1H, 5.3 Hz, 8.9 Hz aryl-C*H*), 7.28 (m, 2H, aryl-C*H*, aryl-C*H*′), 8.33 (d, 1H, 6.3 Hz, aryl-C*H*). ESI-MS: m/z = 750.2 ([Cp*$_2$Ir$_2$H$_2$(2-hp)]$^+$). Anal. Calcd for $C_{25}H_{36}F_6Ir_2NOP$ (found): C, 33.51 (33.37); H, 4.05 (3.97); N, 1.56 (1.63). Crystals suitable for X-ray diffraction were obtained by layering a solution of 60 mg of [**3**]PF_6 in 2 mL of CH_2Cl_2 with 30 mL of Et_2O. Crystals grew over the course of 2 h at room temperature.

Cp*IrH(Cl)(2-hpH) (3) via Transfer Hydrogenation. A solution of 7.9 mg (0.017 mmol) of **1** in 0.8 mL of CD_2Cl_2 was treated with 12.0 mg (0.017 mmol) of Cp*IrH(TsDPENH) at −27 °C. After the addition, the mixture was immediately allowed to warm to room temperature. ^1H NMR analysis of the dark red solution verified that the reaction was complete. ^1H NMR (Figure S5) (500 MHz, CD_2Cl_2): δ −15.8 (s, 1H, Ir-H), 1.54 (s, 15H, Cp*), 6.29 (t, 1H, 6.3 Hz, aryl-C*H*), 6.54 (d, 1H, 7.8 Hz, aryl-C*H*), 7.24 (m, 1H, aryl-C*H*), 8.03 (d of d, 1H, 1.8 Hz, 6.3 Hz, aryl-C*H*). For catalytic hydrogenation see the Supporting Information.

Cp*Ir(2-hp)$_2$. A colorless solution of 88.2 mg (0.753 mmol) of Na2-hp in 6 mL of MeOH was transferred to an orange solution of 150 mg (0.188 mmol) of Cp*$_2$Ir$_2$Cl$_4$ in 5 mL of CH_2Cl_2. After stirring 1 h the solvent was removed by vacuum. The product was extracted into 5 mL of CH_2Cl_2 and filtered to remove NaCl. The filtrate was diluted with 25 mL of hexanes, and this mixture was concentrated under vacuum to 10 mL, producing a yellow powder. The product was collected by filtration and washed with 5 mL of hexanes. Yield: 142 mg (0.274 mmol, 73%). In the room-temperature ^1H NMR spectrum, signals for the κ^2-2-hp and κ^1-2-hp groups appear as an average in the spectrum, as seen previously for a related complex.[17] ^1H NMR (500 MHz, $CDCl_3$ 25 °C): δ 1.68 (s, 15H, Cp*), 5.97 (d, 2H, 8.7 Hz, aryl-C*H*), 6.15 (d of d of d, 2H, 3.1 Hz, 10.4 Hz, 12.7 Hz aryl-C*H*), 7.13 (d of d of d, 2H, 2.0 Hz, 6.8 Hz, 8.7 Hz, aryl-C*H*), 7.75 (d of d, 2H, 1.7 Hz, 5.9 Hz, aryl-C*H*).

Cp*Ir(2-hp)Cl(PPh$_3$) (5). A solution of 329 mg (1.26 mmol) of PPh_3 in 5 mL of CH_2Cl_2 was transferred to a orange solution of 574 mg (1.26 mmol) of **1**. After stirring for 10 min, the reaction solution was concentrated under vacuum and diluted with hexanes to precipitate yellow crystals, which were dried under vacuum. Yield: 721 mg (1.01 mmol, 81%). Alternatively, the product could be obtained by reaction of Cp*IrCl$_2$(PPh_3) with Na2-hp in similar yield. ^1H NMR (500 MHz, CD_2Cl_2): δ 1.35 (d, 15H, 2.1 Hz, Cp*), 5.60 (d of d, 1H, 1.5 Hz, 8.7 Hz, pyr-aryl-C*H*), 5.87 (t of d, 1H, 1.5 Hz, 6.5 Hz, pyr-aryl-C*H*), 6.78 (t of d, 1H, 2.2 Hz, 7.5 Hz, pyr-aryl-C*H*), 7.00 (m, 2H, Ph-C*H*), 7.14 (m, 3H, Ph-C*H*), 7.33 (m, 4H, Ph-C*H*), 7.45 (m, 4H, Ph-C*H*), 7.97 (m, 2H, Ph-C*H*), 8.12 (d of d, 1H, 2.2 Hz, 5.5 Hz, pyr-aryl-C*H*). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 6.53 (s, Ir-*P*Ph_3). Anal. Calcd for $C_{33}H_{34}ClIrNOP$ (found): C, 55.10 (54.96); H, 4.76 (4.71); N, 1.95 (2.10).

[Cp*Ir(κ^2-2-hp)(PPh$_3$)]PF$_6$ ([6]PF$_6$). A solution of 40 mg (0.158 mmol) of $AgPF_6$ in 3 mL of CH_2Cl_2 was transferred to an orange solution of 114 mg (0.158 mmol) of **5** in 4 mL of CH_2Cl_2 to give an immediate colorless precipitate. The solution mixture was filtered to give a pale orange solution. Addition of hexanes to the filtrate gave yellow crystals, which were dried under vacuum. Yield: 103 mg (0.125 mmol, 79%). ^1H NMR (500 MHz, CD_2Cl_2): δ 1.45 (d, 15H, 2.1 Hz, Cp*), 5.46 (d, 1H, 8.7 Hz, pyr-aryl-C*H*), 6.52 (d of d of d, 1H, 1.0 Hz, 5.8 Hz, 6.9 Hz, pyr-aryl-C*H*), 7.11 (t of d, 1H, 1.3 Hz, 7.9 Hz, pyr-aryl-C*H*), 7.41 (m, 12H, Ph-C*H*), 7.49 (m, 3H, Ph-C*H*), 7.77 (d of d, 1H, 0.8 Hz, 5.8 Hz, pyr-aryl-C*H*). ^{31}P NMR (202 MHz, CD_2Cl_2): δ 15.72 (s, Ir-*P*Ph_3), −145.2 (p, 710 Hz, *P*F_6). ESI-MS: m/z = 684.4 ([Cp*Ir(2-hp)(PPh_3)]$^+$), 625.3 ([Cp*Ir-Cl(PPh_3)]$^+$), 589.3 ([Cp*Ir(PPh_3)]$^+$).

Cp*IrCl(6-Me-2-hp) (7). The salt "Na6-Me-2-hp" was synthesized analogously for Na2-hp. ^1H NMR (500 MHz, CD_3OD): δ 2.24 (s, 3H, CH_3), 6.18 (d, 1H, 6.9 Hz, aryl-C*H*), 6.24 (d, 1H, 8.7 Hz, aryl-C*H*), 7.30 (m, 1H, aryl-C*H*). A colorless solution of 110 mg (0.656 mmol) of Na6-Me-2-hp in 5 mL of MeOH was transferred to an orange solution of 261 mg (0.328 mmol) of Cp*$_2$Ir$_2$Cl$_4$ in 10 mL of CH_2Cl_2. After the solution was stirred for 1 h, the solvent was removed by vacuum. The product was extracted into 5 mL of CH_2Cl_2, and this extract was filtered to remove NaCl. The filtrate was concentrated to ~2 mL and then diluted with 10 mL of hexanes to produce a yellow precipitate. Yield: 101 mg (0.213 mmol, 65%). ^1H NMR (500 MHz, CD_2Cl_2): δ 1.72 (s, 15H, Cp*), 2.28 (s, 3H, 6-CH_3), 5.87 (d, 1H, 8.5 Hz, aryl-C*H*), 6.34 (d, 1H, 7.2 Hz, aryl-C*H*), 7.29 (d of d, 1H, 7.3 Hz, 8.4 Hz, 4-C*H*). Anal. Calcd for $C_{16}H_{21}ClIrNO$ (found): C, 40.81 (40.58); H, 4.49 (4.43); N, 2.97 (3.02). A CH_2Cl_2 solution of **7** was treated with 1 atm of H_2 at room temperature over 24 h; ^1H NMR analysis revealed ~95% unreacted **7** as well as a small amount of free 6-Me-hpH.

(C$_5$Me$_4$R)IrCl(η^3-C$_3$H$_3$-2,6-(CO)$_2$NH) (R = Me (8) and R = Et). A solution of 562 mg (10.41 mmol) of NaOMe in 5 mL of MeOH was transferred to a solution of 768 mg (5.2 mmol) of 2,6-dihydroxypyridine·HCl in 5 mL of MeOH to give a homogeneous colorless solution. Solvent was removed under vacuum at 60 °C overnight to give an air-sensitve hygroscopic white powder. Yield of "$NaC_5H_4NO_2$·NaCl": 945 mg (4.94 mmol, 95%). ^1H NMR (500 MHz, CD_3OD): δ 5.40 (d, 2H, 8.2 Hz, aryl-C*H*), 7.23 (t, 1H, 8.2 Hz, aryl-4-C*H*). A solution of 151 mg (0.791 mmol) of $NaC_5H_4NO_2$·NaCl in 3 mL of MeOH was added to a solution of 300 mg (0.377 mmol) of Cp*$_2$Ir$_2$Cl$_4$ in 3 mL of CH_2Cl_2. After stirring for 1 h, the solution was concentrated under vacuum. The residue was extracted into 5 mL of CH_2Cl_2, and this extract was filtered to remove NaCl.

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The filtrate was concentrated to a small volume and diluted with hexanes to produce a yellow powder, which was dried under vacuum. Yield: 280 mg (0.592 mmol, 79%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.84 (s, 15H, Cp*), 4.36 (d of d, 2H, 1.6 Hz 5.4 Hz, aryl-C*H*; exchange in D_2O), 5.61 (t, 1H, 5.4 Hz, 4-aryl-C*H*), 6.69 (s, 1H, N*H*; exchange in D_2O). Anal. Calcd for $C_{15}H_{19}ClIrNO_2$ (found): C, 38.09 (38.30); H, 4.05 (4.47); N, 2.96 (2.56). The (C_5Me_4Et)Ir derivative was obtained similarly. Yield: 128 mg (0.263 mmol, 79%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.14 (t, 3H, 7.6 Hz, CH_2CH_3),1.86 (s, 6H, CH_3), 1.90 (s, 6H, CH_3), 2.17 (q, 2H, 7.6 Hz, CH_2CH_3), 4.44 (d of d, 2H, 1.6 Hz, 5.4 Hz, aryl-C*H* exchanged in D_2O), 5.62 (t, 1H, 5.4 Hz, 4-aryl-C*H*), 6.69 (s, 1H, N*H*; exchange in the presence of D_2O). Single crystals suitable for X-ray diffraction were obtained by diffusion of Et_2O into a concentrated CH_2Cl_2 solution of $(C_5Me_4Et)IrCl(C_3H_3$-2,6-$(CO)_2NH)$.

Catalytic Dehydrogenation of 1-Phenylethanol (see Table 1). In a 100 mL three-necked flask equipped with a nitrogen inlet and reflux condenser was mixed 6 mL of toluene, 2.4 mL of 1-phenylethanol, 0.5 mL of CH_2Ph_2, and 0.1 mol % (Ir) catalyst. The mixture was heated at a vigorous reflux in a 130 °C oil bath. Samples of 100 μL were withdrawn at hourly intervals via syringe-septum techniques for the first 5 h, and a final sample was removed after 21 h. Conversions were analyzed by ^{1}H NMR spectroscopy versus CH_2Ph_2 as an internal integration standard.

Conversion of $Cp^*_2Ir_2H_2Cl_2$ to 1 in the Presence of 2-hpH. Low-Temperature Reaction. A solution of 7.5 mg (0.01 mmol) of $Cp^*_2Ir_2H_2Cl_2$ and 2 mg (0.02 mmol) of 2-hpH in 0.75 mL of CD_2Cl_2 was prepared in a J. Young tube. After 4 h, the characteristic purple color of the $Cp^*_2Ir_2H_2Cl_2$ had faded. ^{1}H NMR analysis of this solution confirmed that $[\mathbf{2}]^+$ was the major product and remained such for 7 days.

High-Temperature Reaction. A solution of 204 mg (0.28 mmol) of $Cp^*_2Ir_2H_2Cl_2$ and 58.6 mg (0.62 mmol) of 2-hpH in 10 mL of *p*-xylenes was heated at reflux for 40 min. An orange precipitate appeared. After cooling to room temperature, the mixture was filtered to give 112 mg of brownish-yellow **1** containing traces of $[\mathbf{2}]^+$.

Chloride Rescue of Catalysis by $[\mathbf{2}]PF_6$. Reaction Conditions. A mixture of 6 mL of toluene, 2.4 mL of PhCH(OH)Me, 0.1 mol % Ir catalyst, and 0.5 mL of CH_2Ph_2 was refluxed in a 130 °C oil bath. After 21 h, 0.7 mL of the reaction mixture was analyzed by ^{19}F NMR spectroscopy, which showed minimal, ~5% decomposition of the PF_6^-. Solid PPNCl (11.4 mg, 0.020 mmol) was added to the mixture. Over the next 4 h, 0.1 mL samples were withdrawn from the reaction mixture, diluted with $CDCl_3$, and assayed by ^{1}H NMR spectroscopy in the usual manner.

PPh_3-Trapping Experiments. Low-Temperature H_2 Reaction. A yellow solution of 81 mg (0.18 mmol) of **1** in 5 mL of CH_2Cl_2 at −25 °C was flushed with 1 atm of H_2. After 40 min, the solution becomes a deep red color and was treated with 46 mg (0.18 mmol) of PPh_3. The flask was flushed with N_2. After stirring the solution for 20 min at −25 °C, 0.8 mL of sample was removed and analyzed by ^{31}P NMR spectroscopy: Cp*IrHCl(PPh_3) (δ 12.9, 9.4%), Cp*IrCl$_2$(PPh_3) (δ 2.4, 19%), PPh_3 (δ −4.96, 12%), as well as Cp*IrCl(2-hp)(PPh_3) (δ 6.5, 47%). A signal at δ 16.3 (14%) could not be assigned.

High-Temperature PhCH(OH)Me Reaction. A solution of 53 mg (0.12 mmol) of **1** in 2 mL of toluene in a three-necked flask fitted with a condenser was heated in a 130 °C oil bath, then treated with 0.7 mL (5.8 mmol) of PhCH(OH)Me. After 30 min, the red solution was cooled in an ice bath and treated with 33.5 mg (0.128 mmol) of PPh_3. After 20 min stirring, 0.7 mL of solution was removed and analyzed by ^{31}P NMR spectroscopy. The following species were observed (% relative amounts based on ^{31}P NMR analysis): Cp*IrHCl(PPh_3) (δ 12.5, 4.2%), Cp*IrCl$_2$(PPh_3) (δ 2.1, 18%), PPh_3 (δ −4.8, 70%), Cp*IrCl(2-hp)(PPh_3) (δ 6.3, 4.9%). A signal at δ 19.0 (2.8%) could not be assigned.

X-ray Cystallography of Compounds $[\mathbf{2}]PF_6$ and $(CpMe_4Et)IrCl(\eta^3$-C_5H_3-2,6-$(CO)_2NH)$. The crystallographic analysis of $[\mathbf{2}]PF_6$ and $(C_5Me_4Et)IrCl(\eta^3$-C_5H_3-2,6-$(CO)_2NH)$ were conducted in the usual way (Supporting Information), but the cation $\mathbf{2}^+$ suffered from severe disorder of the ligands and PF_6 anion. Our model converged with $wR_2 = 0.0914$ and $R_1 = 0.0548$ for 631 parameters with 1198 restraints against all 6133 data. The main residue had both Cp* ligands positionally disordered. The Ir−C distances between an individual Ir-Cp* ligand were constrained to be similar (esd 0.01). The pyridonate ligand was also positionally disordered. Like C−O and Ir−N, distances on the pyrdinate ligand were restrained to be similar (esd 0.01). Rigid-bond restraints (esd 0.01) were imposed on displacement parameters for all disordered sites, and similar displacement amplitudes (esd 0.01) were imposed on disordered sites overlapping by less than the sum of van der Waals radii. Methyl H-atom positions, R-CH_3, were optimized by rotation about R−C bonds with idealized C−H, R−C, and H···H distances. Both hydride, H−Ir, atoms were located in the difference map in asymmetric positions. Full positional refinement of the hydride atoms was not possible because of the heavy Ir atoms and the sever disorder in the structure, so restraints had to be applied. The short Ir1−H1a and Ir2−H1b distances were restrained to be similar (esd 0.01) as well as the longer Ir1−H1b and Ir2−H1a distances (esd 0.01). The remaining H atoms were included as riding idealized contributors. Methyl H atom *U*'s were assigned as 1.5 times U_{eq} of the carrier atom, hydride H atom *U*'s were assigned as 1.5 times U_{eq} of the carrier Ir atom (the carrier atom being the Ir atom that H shared the shortest bond distance with), and remaining H atom *U*'s were assigned as 1.2 times carrier U_{eq}.

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Supporting Information Available: Experimental details and spectra. Crystallographic data for $[\mathbf{2}]PF_6$ and $(C_5Me_4Et)IrCl(\eta^3$-2,6-dhpH) are provided. This material is available free of charge via the Internet at http://pubs.acs.org.