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Proton-Assisted Activation of Dihydrogen: Mechanistic Aspects of Proton-Catalyzed Addition of H_2 to Ru and Ir Amido Complexes

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Abstract: This study examines the acid-catalyzed hydrogenation of ketones by amido-amine chelates of Ru and Ir, focusing on the hydrogen activation step. Addition of H_2 to the catalyst Cp*Ir(TsDPEN-H) (**1**, TsDPEN = racemic $H_2NCHPhCHPhNTs^-$) is more favorable than for corresponding (cymene)Ru derivatives. Depending on the acid, the rate of the proton-catalyzed addition of H_2 to **1** varies over 3 orders of magnitude even for strong acids. Acids protonate the *N*H center in the five-coordinate diamides to give the amido-amine, e.g., $[Cp^*Ir(TsDPEN)]^+$ ($[\mathbf{1}H]^+$). The rate of proton-catalyzed hydrogenation of **1** was found to be first order in both H_2 and in $[\mathbf{1}H]^+$ for $X^- = BF_4^-$, OTf^-, ClO_4^-, NO_3^-. For $X^- = ClO_4^-$ and $BAr^F{}_4^-$ ($BAr^F{}_4^- = B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4^-$), the rate showed an additional dependence on [**1**]. The hydrogenation of **1** is proposed to occur via the dihydrogen complex ($[\mathbf{1}H(H_2)]^+$) followed by proton transfer to **1**, either directly (third-order pathway) or via anion-assisted proton transfer (second-order pathway). The pK_a (H−H bond) of $[\mathbf{1}H(H_2)]^+$ is predicted to be 13.88 ± 0.37 (MeCN solution) whereas the pK_a (N−H bond) of $[\mathbf{1}H]^+$ is about 21.6. The rate of hydrogenation of **1** was fastest for acids about 3 orders of magnitude (p$K_a \approx 10$) more acidic than $[\mathbf{1}H(H_2)]^+$, but slower for stronger acids. Although the affinity of H_2 for $[Cp^*Ir(TsDPEN)]^+$ is orders of magnitude lower than for **1** (298 K), the cationic complex adds H_2 far faster. Similar trends are seen for (cymene)Ru(TsDPEN-H) (**2**) and its derivatives. The affinity of H_2 for **2** was found to be 3× less than for **1**.

Introduction

Proton-induced reactions are fundamental throughout chemistry.[1] Pervasive in transformations of organic substrates, proton transfer also is extremely important in many purely inorganic processes related to conversions of N_2, CO_2, and O_2.[2] We recently reported the influence of protons on the activation of H_2 by transition metals. It is logical that the protonation would enhance the metal center's affinity for H_2 because cationic complexes typically display a higher affinity for H_2 than neutral complexes.[3] This proton-induced Lewis acidity could be implemented by protonation at the metal center or at a ligand (Scheme 1). The present paper describes how this acid-induced Lewis acidity is relevant to hydrogenation catalysis. The concept of proton-enhanced Lewis acidity is relevant to Corey's boranamide catalysts for Diels−Alder reactions.[4]

Once considered mature, catalytic hydrogenation is rapidly evolving because of the proliferation of reagents that activate H_2 heterolytically.[5] Of specific relevance to this paper are the numerous amine-supported hydrogenation catalysts. These catalysts, which bear both hydridic and protic hydrogen centers, traditionally transfer H_2 from donors such as isopropanol and formic acid to polar substrates such as ketones.[6] Such catalysts activate H_2 only slowly,[7,8] but recently it was discovered that direct hydrogenation can be rapid when the catalysts are judiciously treated with certain strong acids.[9−12] This innovation, which presents some process flexibility, is leading to an expanded range of substrates and catalytic strategies. For example, triflic acid (HOTf) converts (cymene)Ru(*S,S*-TsDPEN-H) (TsDPEN = $H_2NCHPhCHPhNTs^-$) from a catalyst for asym-

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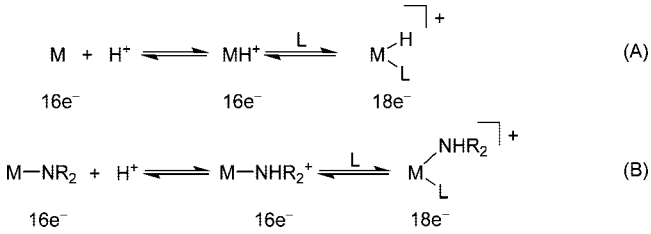
Scheme 1. Possible Protonation Sites for Proton-Induced Lewis Acidity



metric *transfer* hydrogenation to one that effects asymmetric hydrogenation. Still more active catalysts result from the protonation of related Cp*Ir derivatives.[9] These remarkable catalysts activate H_2, as do conventional hydrogenation catalysts, but unlike conventional catalysts, they transfer the two hydrogen atoms to substrates via an outer-sphere mechanism. Hence, these complexes only require a single catalytic site.

Relevant to these advances is the finding that $H(OEt_2)_2BAr^F{}_4$ ($BAr^F{}_4{}^- = B(C_6H_3\text{-}3,5\text{-}(CF_3)_2)_4{}^-$) accelerates the addition of H_2 to the 16e diamido complex Cp*Ir(TsDPEN-H) (**1**) via Lewis-acidic amine derivatives.[13] Noyori and co-workers have proposed that the resulting electrophilic amido-amine complexes bind H_2 to form hydrides (Scheme 2).[11] Hartmann and Chen had previously demonstrated that alkali metal cations activate amido−Ru hydrogenation catalysts toward H_2.[14]

In this paper, we survey the effect of anions on the proton-induced activation of H_2. The coordinating ability of weakly basic anions is known to influence the binding and reactivity of H_2.[15−17] For example, Pfaltz and co-workers showed that Ir−phosphinooxazoline catalysts are optimally active with very weakly coordinating anions $BAr^F{}_4{}^-$ and $Al(OC(CF_3)_3)_4{}^-$.[15] The effects of counteranions on the rate of hydrogenation of alkenes has been recently reviewed by Macchioni.[16] Xiao and co-workers have recently shown that the chirality of counteranion influences the asymmetric hydrogenation of imines.[18]

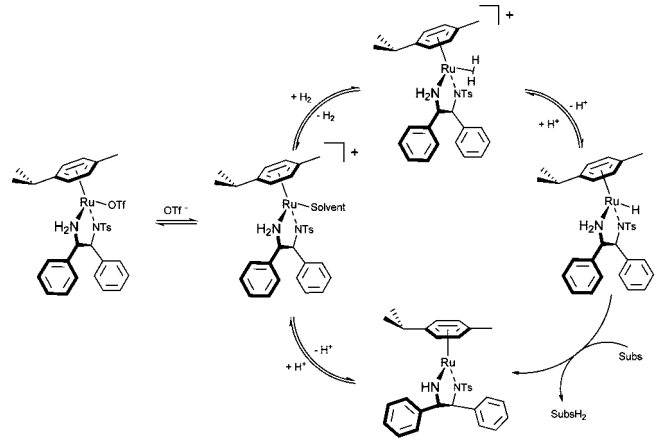
The effects of acids on the reactions of H_2 is also relevant to our recently reported hydrogenation of molecular oxygen by Cp*Ir(TsDPEN)H, **1**H(H). This reaction becomes catalytic in the presence of acid, which is required to regenerate the hydride.[19] A highly efficient system for the dehydrogenation of alcohols using O_2 as a hydrogen acceptor in a related system has been recently reported.[20]

Results and Discussion

Nature of Cp*Ir(TsDPEN)OTf and (cymene)Ru(TsDPEN)OTf. Protonation of Cp*Ir(TsDPEN-H), **1**, and (cymene)Ru(TsDPEN-H), **2**, with triflic acid has been recently reported to give the amines **1**H(OTf) and **2**H(OTf), respectively. In methanolic solution, these species are excellent catalysts for the hydrogenation of arylketones, exhibiting TONs of 720 and <60 and TOFs of 48 and 4 h^{-1}, for **1**H(OTf) and **2**H(OTf), respectively.[9,12] In solvents of high (e.g., CD_3OD, $\varepsilon = 32.66$) and low (CH_2Cl_2, $\varepsilon = 8.93$) dielectric constants,[21] the complex **1**H(OTf)[9] exists as the salt [**1**H]OTf. These solutions are intensely red, characteristic of related unsaturated 16e derivatives.[13] The ^{1}H NMR spectra of [**1**H]OTf in CD_3OD, the most common solvent with this kind of hydrogenation catalysis,[9] indicate axially oriented phenyl groups, as seen for related 16e amido complexes.[22] The downfield shift for the NH_2 signals at δ 4.8 and 6.1 (vs δ 4.1 and 4.3)[13] is indicative of hydrogen-bonding between the counteranion and the amine protons.[16,22] Addition of KOTf to a CD_2Cl_2 solution of [**1**H]BF_4 caused the ^{1}H NMR signals to shift toward those for [**1**H]OTf, confirming the weak electrostatic interactions between the cations and the counteranions. Crystallographic characterization of [**1**H]OTf confirmed that the anion is not coordinated.[13] The triflate anion was found to hydrogen-bond to the axial amine proton, exhibiting an O···H bond of 2.048 Å (Supporting Information).

In contrast to the iridium complex, the ^{1}H NMR spectrum and color indicates that OTf^- is coordinated in **2**H(OTf), even in a MeOH solution.[11,12] The lower catalytic activity of **2**H(OTf) is attributable to competitive binding of OTf^- (Scheme 2).[9]

Scheme 2. Proposed Mechanism for the Hydrogenation of Ketones Catalyzed by (cymene)Ru(OTf)(TsDPEN)[11,12]



Properties of [Cp*Ir(TsDPEN)]X (X^- not OTf^-). A range of salts of the unsaturated, "naked" cation $[\mathbf{1}H]^+$ were prepared by protonation of solutions of the diamide **1** with HX, where $X^- = NO_3{}^-$, $BF_4{}^-$, $ClO_4{}^-$, $PF_6{}^-$, and $BAr^F{}_4{}^-$. These species exist both in solution and in the solid state as salts containing separated $[Cp^*Ir(TsDPEN)]^+$ and anions, as indicated by NMR and IR spectroscopies, as well as X-ray crystallography in the cases of OTf^- and $BAr^F{}_4{}^-$ (see also Supporting Information).[13] Treatment of **1** with HCl merely affords the charge-neutral derivative **1**H(Cl), which is not catalytically active due to the strong coordination of the chloride anion.[23]

For CD_2Cl_2 solutions, the ^{1}H NMR spectra of the amine protons in [**1**H]X were strongly affected by the anions X^-

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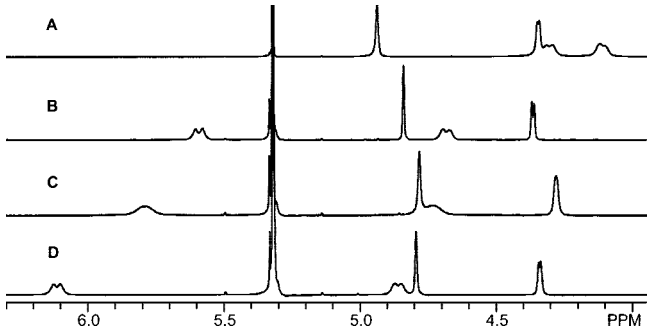

Figure 1. ^{1}H NMR spectra of the amine region of (A) [**1**H]BAr$^F_4$, (B) [**1**H]BF_4, (C) [**1**H]PF_6, and (D) [**1**H]OTf in CD_2Cl_2 solution. The signal at δ 5.32 is for solvent.

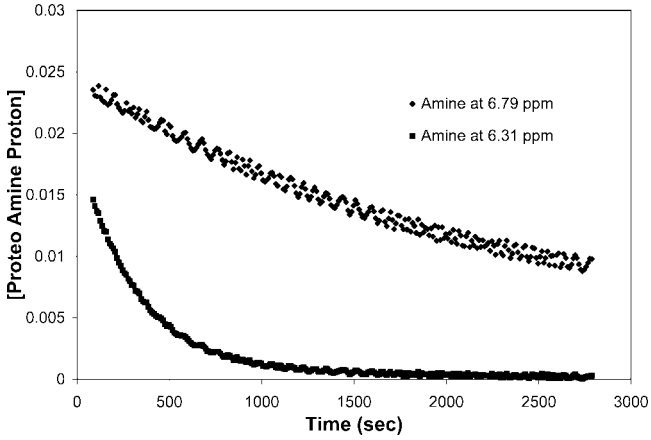

Figure 2. Zeroth order plot of the rate of deuteration of the amine protons of [**1**H]PF_6 in CD_3OD solution.

(Figure 1), but the spectra of CD_3OD solutions were unaffected. In all cases, the backbone (C*H*PhC*H*Ph) signals for [**1**H]BF_4 are diagnostic of diaxial orientation, indicative of a pentacoordinate metal center (viewing Cp* as a tridentate ligand). Only for [**1**H]BAr$^F_4$ and [**1**H]ClO_4 were the chemical shifts for the N*H* signals affected by the addition of small amounts of D_2O to the CD_2Cl_2 solutions of [**1**H]$^+$. This observation is indicative of weak hydrogen-bonding between the counteranion and the amine protons, thus allowing for H/D exchange.

To probe the strength of hydrogen-bonding under catalytically relevant conditions,[9−12] we investigated the relative rates of deuteration of the amine protons in CD_3OD solutions. For the salts [**1**H]ClO_4 and [**1**H]BAr$^F_4$, the NH groups were found to deuterate rapidly, i.e., N*H* signals could not be detected in freshly prepared NMR samples. For the corresponding salts of NO_3^-, BF_4^-, OTf^-, and PF_6^-, deuteration was slower, requiring several minutes. Deuteration of the amines was found to proceed via a process that is first order in the cationic complex (Figures 2 and 3). For these salts, the diastereotopic amine protons were found to deuterate at different rates. Deuteration of the upfield (equatorial) N*H* was faster (Table 1 and Supporting Information). Noyori and co-workers similarly observed that in a CD_2Cl_2/CD_3OD solution, the axial N*H* of (cymene)Ru(OTf)(*S,S*-TsDPEN) deuterated ~4× more slowly than the equatorial N*H* center.[11]

Acid−Base Properties of [Cp*Ir(NCMe)(TsDPEN)]X. In view of the correlation between the rates of H/D exchange and the basicity of the counteranions, we examined the pK_a's of the corresponding adducts [Cp*Ir(NCMe)(TsDPEN)]$^+$ ([**1**H(NCMe)]$^+$). Although [**1**H]$^+$ remains naked in methanol

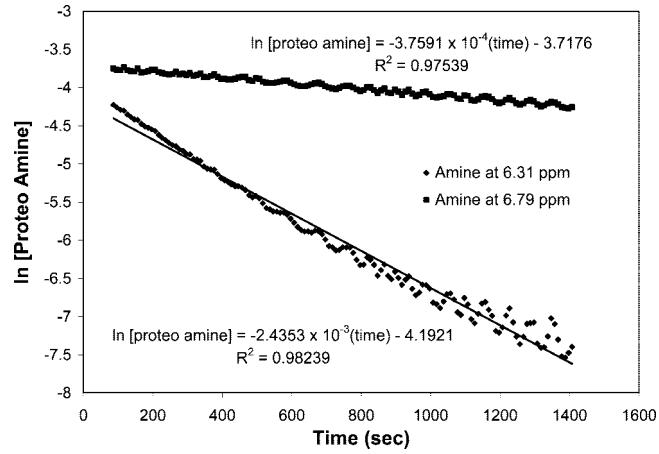

Figure 3. First-order plot of the rate of deuteration of the amine protons of [**1**H]PF_6 in CD_3OD solution.

Table 1. Acidity of Parent Acids and Amines (MeCN), ^{1}H NMR Chemical Shifts, and D^+/H^+ Exchange Rate Constants for [Cp*Ir(rac-TsNCHPhCHPhN*H*$_2$)]$^+X^-$ (CD_3OD Soln)

X^-	pK_a of HX (MeCN soln)	pK_a of [**1**H]X (MeCN soln)	N*H* anti to Ph (δ 6.31)	N*H* syn to Ph (δ 6.79)
ClO_4^-	Complete dissociation	21.09 ± 0.10	$>1.22 \times 10^{-2}$ s^{-1}	$>1.22 \times 10^{-2}$ s^{-1}
BAr$^F_4^-$		21.29 ± 0.11	$>1.22 \times 10^{-2}$ s^{-1}	$>1.22 \times 10^{-2}$ s^{-1}
OTf^-	2.60	21.59 ± 0.17	6.06×10^{-3} s^{-1}	9.85×10^{-4} s^{-1}
BF_4^-	11.45	21.60 ± 0.15	3.11×10^{-3} s^{-1}	6.63×10^{-4} s^{-1}
PF_6^-		−	2.44×10^{-3} s^{-1}	3.76×10^{-4} s^{-1}
NO_3^-	10.65	21.81 ± 0.23	5.01×10^{-4} s^{-1}	1.38×10^{-4} s^{-1}

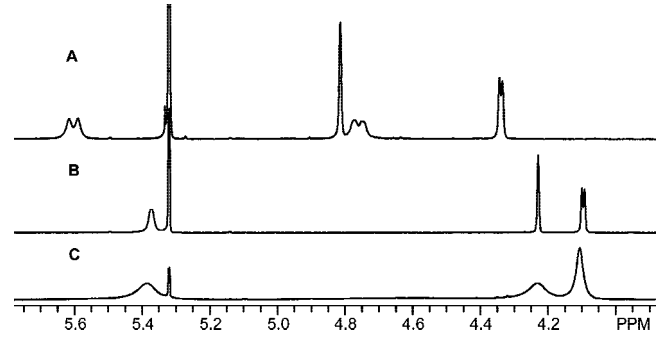

Figure 4. ^{1}H NMR spectra of the amine region of (A) [**1**H]BF_4, (B) **1**, and (C) **1** and 20 mol % [**1**H]BF_4 (CD_2Cl_2 solution). The signal at δ 5.32 is for $CDHCl_2$.

solution, it forms an adduct with MeCN.[13] In MeCN solution, [**1**H(NCMe)]$^+$ and **1** can be readily distinguished by ^{1}H NMR spectroscopy,[25,26] and the pK_a in this solvent is 21.60 (Table 1). Although complicated by the rapid dehydrogenation of the alcohol, the pK_a of [**1**H]$^+$ in MeOH has been estimated to be 11.3.[13] This value can be used to determine the relative binding affinity of MeCN to [**1**H]$^+$ (see below). In CH_2Cl_2 solution, proton exchange between the pentacoordinate complexes **1** and [**1**H]$^+$ is rapid on the NMR time scale (Figure 4).

To estimate the affinity of [**1**H]$^+$ for MeCN, we analyzed the impact of adduct formation on the pK_a value of [**1**H]$^+$. With

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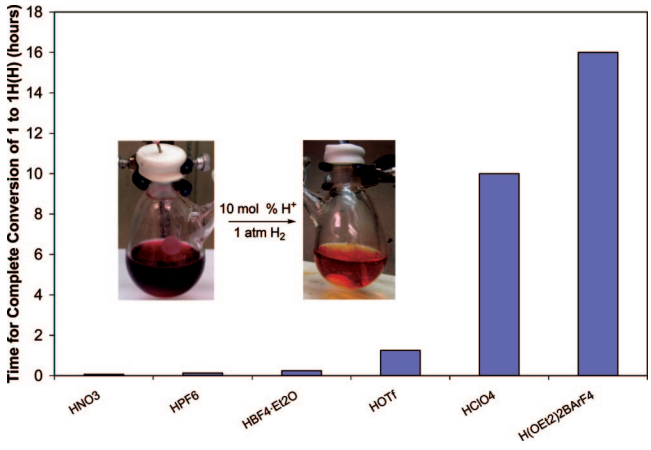


Figure 5. Plot of the time required for the complete conversion of **1** to **1**H(H) as a function of acid. Conditions: CH_2Cl_2 solution, 10 mol % acid, 1 atm H_2.

Table 2. Effect of Counterion, X^-, on the Rates of HX-Catalyzed Hydrogenation of **1** to **1**H(H) (20 °C, THF, 5 mol % HX, 10 equiv $[H_2]$)

counterion, X^-	$t_{1/2}$ (s)	rate constant
no anion	15 600	0.121 M^{-1} s^{-1}
$BAr^F{}_4^-$	2250	5540 M^{-2} s^{-1}
ClO_4^-	753	15 400 M^{-2} s^{-1}
OTf^-	462	1.67 M^{-1} s^{-1}
BF_4^-	288	3.90 M^{-1} s^{-1}
NO_3^-	161	19.27 M^{-1} s^{-1}
PF_6^-	109	23.84 M^{-1} s^{-1}

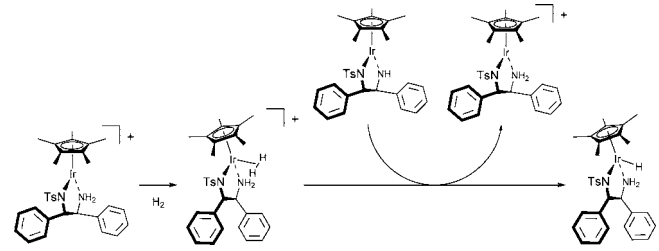
Chmurzynski's correction,[27] the value of 11.3 (MeOH solution)[13] converts to 19.7 (MeCN scale). The pK_a of the MeCN adduct was measured to be 21.60 in MeCN, i.e., about 2 orders of magnitude less acidic relative to the free cation. Using this value, we estimate that $[\mathbf{1}H]^+$ binds MeCN with $K = 85$ M^{-1}, which would give a ΔG_{assoc}(298 K) of −2.63 kcal/mol (see Supporting Information). The weak binding of MeCN in $[\mathbf{1}H(NCMe)]^+$ is consistent with the fact that MeCN can be removed in vacuo and $[\mathbf{1}H(NCMe)]^+$ is moderately reactive toward H_2 (to give $Cp^*{}_2Ir_2H_3^+$).[13,22]

For MeCN solutions of the adduct $[\mathbf{1}H(NCMe)]^+$, the anion−cation interactions are weakened but still anion-dependent. For example, the identity of the anions was still found to affect the pK_a's and N*H* signals in the ^{1}H NMR spectra (see Table 1 and Supporting Information).

Effects of Anions on the Acid-Catalyzed Hydrogenation of 1. With regards to the conversion of **1** + H_2 → **1**H(H), 0.1 equiv of HPF_6 and HNO_3 accelerated the hydrogenation by a factor of about 150 (Figure 5).[28] Confirming the role of the anion, the rate of hydrogenation of a solution of **1** and 10 mol % $[\mathbf{1}H]BAr^F{}_4$ was found to increase 30 fold upon the addition of 3.5 mol % K(18-crown-6)NO_3.

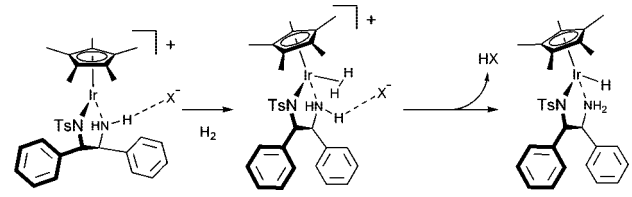
On the basis of their influence on the hydrogenation of **1** to **1**H(H), the acid catalysts fall into two groups. The first group, which includes $H(OEt_2)_2BAr^F{}_4$ and $HClO_4$, accelerate the addition of H_2 by factors of 7× and 20×, respectively (Table 2). To minimize the influence of adventitious water, these measurements employed purified samples of [**1**H]X. For these acids, the rate was found to be first order in [**1**H]X, in **1**, and in H_2 (eq 1, Scheme 3). The dependence on $[H_2]$ was demonstrated: The rate of hydrogenation of **1** was found to decrease by a third upon decreasing the $[H_2]$ by a third (see Supporting Information).

Scheme 3. Proposed Mechanism for the Addition of H_2 to **1** Catalyzed by $HBAr^F{}_4$ and $HClO_4$



The second group of acids, HOTf, HBF_4, HNO_3, and HPF_6, strongly enhanced the rate of hydrogenation of **1**, the most dramatic effects being observed for HPF_6 and HNO_3 (Table 2). The kinetics of hydrogenation for these acids were also first order in cation [**1**H]X and in H_2, *but zeroth order* in **1** (eq 1 and Scheme 4). Although eq 1 contains two rate terms,

Scheme 4. Proposed Mechanism for the Addition of H_2 to **1** Catalyzed by HPF_6, HOTf, HBF_4, and HNO_3



upon varying the concentrations of [**1**H]X between 1 and 15 mol %, only in the case of $[\mathbf{1}H]ClO_4$ did we obtain clear evidence for a shift in reaction order as the concentration of the acid was varied: at $[\mathbf{1}H]ClO_4 \geq 10$ mol %, the rate exhibited no dependence on [**1**] but with <10 mol % of $[\mathbf{1}H]ClO_4$, a first-order dependence on the [**1**] was evident (k_1 is the dominant rate term in eq 1).

$$-\frac{d[H_2]}{dt} = \frac{d[\mathbf{1}H(H)]}{dt} = [H_2][[\mathbf{1}H]X](k_1[\mathbf{1}] + k_2) \quad (1)$$

$$k_1 \gg k_2 \text{ for HX} = HClO_4, HBAr^F_4$$

$$k_2 \gg k_1 \text{ for HX} = \text{HOTf}, HBF_4, HNO_3, \text{and } HPF_6$$

Using *S*,*S*-**1**, we demonstrated that the optical purity of the catalyst had no effect on the rates of hydrogenation of **1** in the presence of either [*S*,*S*-**1**H]BArF$_4$ or [*S*,*S*-**1**H]BF_4, demonstrating that resolved samples gave the same rates as the racemic ones. Hydrogenation experiments using HD in the presence of **1** and $[\mathbf{1}H]BF_4$ resulted in scrambling of the amine protons, showing that both of the amine protons can be relatively acidic (see Supporting Information).

Weak acids were also found to accelerate the hydrogenation of **1**, but only slightly. Thus, the rate of hydrogenation of **1** was found to increase 5× and 1.5×, respectively, upon the addition of 10 mol % $[PhNH_3]BAr^F{}_4$ (pK_a = 10.56 in MeCN)[26] and [pyridinium]$BAr^F{}_4$ (pK_a = 12.33 in MeCN).[26] Carboxylic acids also aid in the hydrogenation of **1** to **1**H(H), despite the

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(28) The rate of hydrogenation of Cp*Ir(TsDPEN-H) was unaffected by the presence of Cp*IrCl(TsDPEN).

fact that they form charge-neutral derivatives **1**H(O_2CR),[29] which are stabilized by intramolecular hydrogen-bonding.[30]

The uncatalyzed hydrogenation of **2** in THF was found to proceed about 20× more slowly than the Ir derivative. Noyori and co-workers have reported that the Ru complex requires 80 atm of H_2 to form the Ru amino-hydride complex, but no reaction time was reported.[8] Addition of 5 mol % of HBF_4 was found to increase the rate 5×. The rate of hydrogenation of the tritylamide Cp*Ir($Ph_2C(NH)C_6H_4$) (**3**)[31] was found to be similar to that for **1**, but the effect of acids on the rate of its hydrogenation was found to be greater than seen in the case of **1** by a factor of 4 with [Cp*Ir($Ph_2C(NH_2)C_6H_4$)]BF_4 ([**3**H]BF_4).

Studies on [Cp*Ir(*N*,*N*-Me$_2$Tsen)]NO_3 Indicate that Dihydrogen is the Proton Donor. Experiments described above support the hypothesis that cationic amido-amine dihydrogen complexes protonate the diamido complexes, either directly or via a more efficient anion-relayed pathway. Since the amido-amino dihydrogen complexes, e.g., [**1**H(H_2)]$^+$, are diprotic, we sought to establish that the proton that is transferred is derived from the dihydrogen ligand. Consistent with this hypothesis, [Cp*Ir(*N*,*N*-Me$_2$Tsen)]NO_3 (*N*,*N*-Me$_2$Tsen = *N*,*N*-Me$_2$NCH$_2$CH$_2$NTs$^-$), which contains no N−H groups, was found to accelerate the addition of H_2 to **1** in CD_2Cl_2 solution at a rate comparable to the effect of [**1**H]NO_3. The coproduct is Cp*IrH(*N*,*N*-Me$_2$Tsen) (eq 2).

$$[\text{Cp*Ir}(N,N\text{-Me}_2\text{Tsen})]^+ + \text{Cp*Ir(TsDPEN-H)} \xrightarrow{H_2}$$

$$[\text{Cp*IrH}(N,N\text{-Me}_2\text{Tsen}) + [\text{Cp*Ir(TsDPEN)}]^+ \quad (2)$$

Acidity of Ir and Ru Dihydrogen Complexes. The relative binding affinity of H_2 toward the cationic complexes could not be determined directly because stable adducts are not observed. Even when an MeCN solution of **1**H(H) was protonated at −30 °C with HBF_4, only [**1**H(NCMe)]$^+$ and H_2 was observed. We therefore assessed the binding of H_2 indirectly using a thermodynamic cycle, which in turn required the determination of the pK_a's of the respective dihydrogen complexes. Protonation of **1**H(H) causes evolution of H_2 by apparent protonation of the hydride.[22,32] We exploited this reactivity to estimate the pK_a's of [**1**H(H_2)]$^+$. Thus, we determined the weakest acid that would convert **1**H(H) into [**1**H]$^+$ (eq 3).[22]

$$\text{Cp*IrH(TsDPEN)} \overset{H^+}{\rightleftharpoons} [\text{Cp*Ir}(H_2)\text{(TsDPEN)}]^+ \overset{H_2}{\rightleftharpoons}$$

$$[\text{Cp*Ir(TsDPEN)}]^+ \quad (3)$$

We employed weaker acids requiring >1 equiv to release H_2 from **1**H(H). We also assumed that the binding of MeCN to [**1**H]$^+$ occurred after equilibrium had been reached between **1**H(H) and the respective acid; thus, the concentration of [**1**H(H_2)]$^+$ is assumed to be equal to [**1**H(NCMe)]$^+$ (see Table 3 and Supporting Information). Through sequential additions of 0.3 equiv of [2,6-lutidinium]BF_4 (pK_a = 14.41 in MeCN)[26,27] to a solution of **1**H(H), we estimated that the pK_a of [**1**H(H_2)]$^+$ is 13.88 ± 0.37 in MeCN.

Table 3. Estimated pK_a Values for Dihydrogen Complexes Examined in This Work

dihydrogen complex	pK_a (MeCN solution)	estimated[27] pK_a (MeOH solution)
[Cp*Ir(H_2)(TsDPEN)]$^+$	13.88 ± 0.37	6.52
[(cymene)Ru(H_2)(TsDPEN)]$^+$	16.15 ± 0.35	8.40
[Cp*Ir(H_2)($Ph_2C(NH_2)C_6H_4$)]$^+$	17.43 ± 0.15	9.45

Using Et_3NHBF_4 (pK_a = 18.46 in MeCN)[25] as the titrating acid, we investigated the protonation of Cp*IrH($Ph_2C(NH_2)C_6H_4$) (**3**H(H)). The pK_a of this metallated tritylamido complex is estimated to be 17.43 ± 0.15. For the ruthenium hydride, we used NH_4BF_4 (pK_a = 16.46 in MeCN),[25] which reacted with **2**H(H) to yield [(cymene)Ru(NH_3)(TsDPEN)]BF_4 (eq 4). Again, assuming that the binding of NH_3 does not affect the protonation of **2**H(H), a pK_a of 16.15 ± 0.35 can be estimated.

$$\text{(cymene)RuH(TsDPEN)} + NH_4BF_4 \rightleftharpoons [(p\text{-cymene})\text{Ru}(NH_3)\text{(TsDPEN)}]BF_4 + H_2 \quad (4)$$

Acidity of [2H]$^+$ and [3H]$^+$. Since the unsaturated species [**2**H]$^+$ complex proved elusive, its acidity was deduced indirectly. We first established the equilibrium constant that relates [**1**H]BF_4 and **2** with [**2**H]BF_4 and **1** in MeCN solution. With this K_{eq}, 468, and with knowledge of the K_a for [**1**H(NCMe)]$^+$, we calculated the K_a of [**2**H(NCMe)]$^+$ using eqs 5, 6, and 7, where the summation of eqs 5 and 6 result in eq 7. The pK_a of [**2**H(NCMe)]$^+$ was estimated to be 24.27 ± 0.15, i.e., the Ru complexes, both [**2**H(NCMe)]$^+$ and [**2**H(H_2)]$^+$, are about 1000× less acidic than the corresponding Cp*Ir derivatives.[33] Titrations of the tritylamine derivative [**3**H(NCMe)]$^+$ with phenyl-1,1,3,3-tetramethylguanidine (pK_a = 20.84 in MeCN) were straightforward.[34] Complex [**3**H(NCMe)]$^+$ was also found to be about 2 orders of magnitude less acidic than [**1**H(NCMe)]$^+$ (pK_a of 23.44 ± 0.23).

$$\mathbf{1} + H^+ + \text{MeCN} \rightleftharpoons [\mathbf{1}\text{H(NCMe)}]^+ \quad {}^1/_{K_a} \quad (5)$$

$$\mathbf{2} + [\mathbf{1}\text{H(NCMe)}]^+ \rightleftharpoons \mathbf{1} + [\mathbf{2}\text{H(NCMe)}]^+ \quad K_{eq1} = 468 \quad (6)$$

$$\mathbf{2} + H^+ + \text{MeCN} \rightleftharpoons [\mathbf{2}\text{H(NCMe)}]^+ \quad {}^1/_{K_{a3}} \quad (7)$$

Analysis of H_2 Affinity. A series of experiments and calculations were conducted in order to estimate the relative affinities of the bis-amide complexes, e.g., **1**, and their conjugate acids. In a sealed NMR tube under 1 atm N_2, an MeCN-d_3 solution of **1**H(H) was found to reach equilibrium with **1** and H_2 after about 48 h at room temperature. From these data, we estimate an upper bound of $K_{1H(H)}$ = 5.43 × 10^4 M^{-1}, eq 8, consistent with the high affinity of the iridium center for H_2 as originally noted by Mashima[35] (see Supporting Information). The relative affinities of a series of related complexes were evaluated by competition experiments (e.g., eq 9).

$$\text{Cp*Ir(TsDPEN-H)} + H_2 \overset{K_{1H(H)}}{\rightleftharpoons} \text{Cp*IrH(TsDPEN)} \quad (8)$$

$$\text{Cp*IrH(TsDPEN)} + (C_5Me_4R)\text{Ir(TsDPEN-H)} \overset{K_{eq}}{\rightleftharpoons} (C_5Me_4R)\text{IrH(TsDPEN)} + \text{Cp*Ir(TsDPEN-H)} \quad (9)$$

(29) Addition of acetic acid to **1** was found to yield an acetate adduct similar to the (cymene)Ru(OAc)(TsDPEN) and (cymene)Ru(OAc)(Tsen) complexes previously reported by Ikariya and coworkers. The complex, Cp*Ir(OAc)(TsDPEN), was found to aid in the catalytic hydrogenation of complex **1**, though it was found to be slow (on the order of [**1**H]ClO_4 in a CD_2Cl_2 solution). ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.72 (s, 15 H, Cp*), 2.02 (s, 3 H, CH_3), 2.23 (s, 3 H, C_6H_4*Me*), 3.55 (d, 11 Hz, 1 H, CH), 4.26 (d, 11 Hz, 1 H, CH), 6.65−7.30 (m, 14 H).

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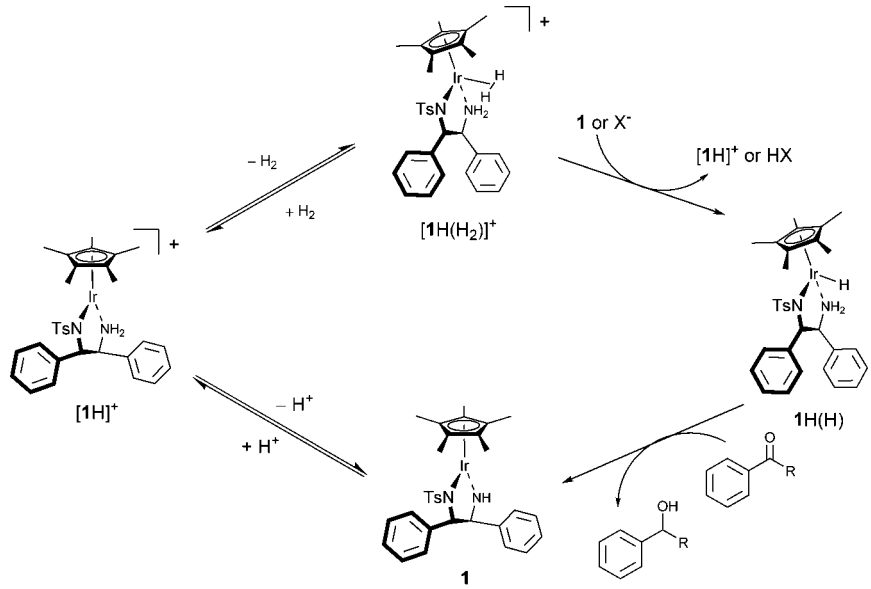
Scheme 5. Proposed Mechanism of Proton Hydrogenation of Ketones Catalyzed by $[\mathbf{1}H]^+$



These experiments demonstrated that **2** binds H_2 about 3× more weakly than does **1**. The cyclometallated tritylamido complex, **3,** exhibited the highest affinity for H_2 in this series (Table 4). From the aforementioned data, the binding constant of H_2 to $[\mathbf{1}H]^+$ can be estimated to be 8.8×10^{-2} M^{-1}. Thus, $[\mathbf{1}H]^+$ binds H_2 far more weakly than does **1**, but the binding process is far more rapid. The relative binding affinities (K_{HH}, eq. 10) for the respective bis-amide complexes are shown in Table 4 and the Supporting Information.

$$\text{(arene)M(bis-amide)} + H_2 \overset{K_{HH}}{\rightleftharpoons} \text{(arene)MH(amido-amine)} \qquad (10)$$

Table 4. Estimated Relative Affinities for Selected Complexes Studied in this Work

complex	relative K_{HH}
Cp*Ir($Ph_2C(NH)C_6H_4$) (**3**)	1.00
Cp*Ir(TsDPEN-H) (**1**)	0.43
(C_5Me_4Et)Ir(TsDPEN-H)	0.40
(C_5Me_4H)Ir(TsDPEN-H)	0.31
Cp*Ir(MsDPEN-H)	0.25
(cymene)Ru(TsDPEN-H) (**2**)	0.15
Cp*Ir(*N*-MeTsDPEN-H)	0.01
$[Cp^*Ir(TsDPEN)]^+$ ($[\mathbf{1}H]^+$)	$>6.9 \times 10^{-7}$
$[Cp^*Ir(TsDPEN)(NCMe)]^+$ ($[\mathbf{1}H(NCMe)]^+$)	$>8.2 \times 10^{-9}$

Summary

The acid-catalyzed addition of hydrogen to diamido complexes of Ru and Ir is the enabling step for an emerging class of hydrogenation catalysts.[11,12] The acid-catalyzed reaction converts 16e amido complexes to 18e amino-hydrides, which are well-known bifunctional catalysts for the reduction of ketones, aldehydes, and imines.[9−12] The acid-catalyzed method, which allows the use of H_2, complements the transfer hydrogenations where the H_2 is extracted from donor solvents.[6] The addition of H_2 to the 16e diamido complexes (e.g., **1**) is strongly favorable but is extremely slow in the absence of acids. Evidence presented in this paper supports the premise that $[\mathbf{1}H]^+$ catalyzes the hydrogenation of **1** via the formation of $[\mathbf{1}H(H_2)]^+$, which forms rapidly but is unstable. Related cationic amine-dihydrogen complexes have been reported.[37] The dihydrogen complex $[\mathbf{1}H(H_2)]^+$ is shown to be sufficiently acidic to protonate the parent diamido **1**, thus propagating the cycle (Scheme 5). Key to the efficiency of $[\mathbf{1}H]^+$ as a hydrogenation catalyst is its tendency to remain unsaturated even in the presence of anions and polar solvents that might otherwise compete with the binding H_2.

Two related pathways were identified for the $[\mathbf{1}H]^+$-catalyzed hydrogenation of **1** in CH_2Cl_2 solution. Both pathways are proposed to involve the rate-determining deprotonation of the dihydrogen complex $[\mathbf{1}H(H_2)]^+$. The faster pathway proceeds via a rate-determining proton transfer from $[\mathbf{1}H(H_2)]^+$ to an anion of moderate basicity, such as nitrate (Schemes 3 and 4). Anions exhibiting the largest accelerating effect are about 1000× less basic than $[\mathbf{1}H(H_2)]^+$. Anions derived from still stronger acids are less effective proton relays and in such cases **1** serves as the base to deprotonate $[\mathbf{1}H(H_2)]^+$. The observed anion effect on the deuteration of amine protons in CD_3OD suggests that the counteranions of $[\mathbf{1}H]^+$ will exhibit similar effects in the rates of hydrogenation of ketones, by aiding in the initial deprotonation of $[\mathbf{1}H(H_2)]^+$ (Scheme 5). Fan and co-workers have recently described the influence of counteranions on the hydrogenation of quinoline by $[\mathbf{1}H]^+$.[38] Anions influence the reactivity of coordinated dihydrogen through hydrogen-bonding interactions.[39] For example, Basallote and co-workers have shown that the rate of deprotonation of *trans*-$[FeH(H_2)(dppe)_2]^+$ by Et_3N is highly sensitive to the anions.[40] Anions capable of

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forming hydrogen bonds, e.g., BF_4^- and PF_6^-, accelerate the deprotonation, whereas BPh_4^- does not.

Experimental Section

CD_2Cl_2 and CD_3CN were dried with CaH_2 and were degassed and placed under vacuum before use. NMR solvents were transferred under vacuum unless otherwise noted. All other reagents were used as received. ^{1}H NMR spectra are referenced to residual solvent signals, and the shifts are reported in ppm downfield from tetramethylsilane. UV/vis spectra were measured on a Cary 50 UV/vis spectrometer. NMR Spectra were measured on a Varian Unity Inova 500NB spectrometer. Cp*Ir(TsDPEN-H), Cp*IrH(TsDPEN), [Cp*Ir(TsDPEN)]BAr^F_4, and [Cp*Ir(TsDPEN)]BF_4 and the C_5Me_4H and C_5Me_4Et derivatives were prepared as previously described.[13,19,22] (cymene)Ru(TsDPEN-H), (cymene)RuH(TsDPEN), and (cymene)Ru(OTf)(TsDPEN) were prepared according to Noyori and co-workers.[8,12] Cp*Ir(HNCPh$_2$C$_6$H$_4$) was prepared according to Ikariya and co-workers.[31] [Cp*Ir(TsDPEN)]OTf and Cp*Ir(MsDPEN-H) were prepared according to Ohkuma and co-workers.[9] All reactions were conducted in air unless otherwise noted.

[1H]X (X = ClO_4^-, PF_6^-, NO_3^-). The cationic complexes were prepared as previously reported for [**1**H]BAr^F_4, where the desired acid was replaced with the acid with the anion of interest.[13] ^{1}H NMR spectra for all of the cationic complexes in CD_3OD and CD_3CN solutions matched the spectra previously reported for [**1**H]PF_6 and [**1**H]$BArF_4$ (except for [**1**H]NO_3 which had a slight shift of the N*H* protons, see Supporting Information).[13] [**1**H]ClO_4: ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.88 (s, 15H, Cp*), 2.30 (s, 3H, C_6H_4-*Me*), 4.36 (s, 1H, H_2NC*H*PhCHPhNTs), 4.81 (s, 1H, H_2NCHPhC*H*PhNTs), 4.85 (br d, 11 Hz, 1H, H*H*NCHPhCHPhNTs), 5.74 (br s, 1H, *H*HNCHPhCHPhNTs), 6.86−7.35 (14H, phenyl protons). Anal. Calcd for $C_{31}H_{36}ClIrN_2O_6S$: C, 46.99; H, 4.58; N, 3.54. Found: C, 46.76; H, 4.58; N, 3.54. For [**1**H]PF_6, ^{1}H NMR (500 MHz, CD_2Cl_2) δ 1.85 (s, 15H, Cp*), 2.29 (s, 3H, C_6H_4-*Me*), 4.28 (s, 1H, H_2NC*H*PhCHPhNTs), 4.74 (br s, 1H, H*H*NCHPhCHPhNTs), 4.78 (s, 1H, H_2NCHPhC*H*PhNTs), 5.79 (br s, 1H, *H*HNCHPhCHPhNTs), 6.86−7.30 (14H, phenyl protons). For [**1**H]NO_3, ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.87 (s, 15H, Cp*), 2.29 (s, 3H, C_6H_4-*Me*), 4.28 (s, 1H, H_2NC*H*PhCHPhNTs), 4.55 (br s, 11 Hz, 1H, H*H*NCHPhCHPhNTs), 4.78 (s, 1H, H_2NCHPhC*H*PhNTs), 6.83−7.32 (14H, phenyl protons), 8.43 (br s, 1H, *H*HNCHPhCHPhNTs).

pK_a Determination for [1H]X. Acetonitrile was chosen as a solvent due to the formation of the NCMe adducts, which would minimize interactions between **1** and its conjugate acid. The concentrations of these two species were measured directly from the spectra in relation to the 1,3,5-trimethoxybenzene internal standard. pK_a values were determined as been previously described.[13,41] The effects of homoconjugation was neglected.[41] The acidity of the cation was observed to vary by about one pK_a unit: salts derived from the more basic anions exhibited less acidic amine ligands (Table 1). We did not determine the pK_a of the PF_6^- salt with high precision; it was readily deprotonated by stoichiometric amounts of 1,1,3,3-tetramethylguanidine (pK_a = 23.3 in MeCN),[42] but not by weaker bases such as proton sponge (pK_a = 18.62 in MeCN)[26] and 2-phenyl-1,1,3,3-tetramethylguanidine (pK_a = 20.84 in MeCN).[26]

pK_a Determination of [1H(H$_2$)]BF_4. Acetonitrile was chosen as a solvent because the initially formed [**1**H]$^+$ immediately is trapped by solvent. Furthermore, spectra of [**1**H(NCMe)]$^+$ and **1**H(H) can be readily resolved by NMR spectra. The pK_a analysis requires that **1**H(H) and [**1**H(H$_2$)]$^+$ equilibrate prior to H_2 dissociation, and it was assumed that the binding of MeCN to [**1**H]$^+$ does not affect the equilibrium between **1**H(H) and [**1**H(H$_2$)]$^+$. A solution of 7 mg (10 μmol) Cp*IrH(TsDPEN) and 5 mg (0.06 mmol) $C_6H_3(OMe)_3$ (internal standard) in 0.75 mL of CD_3CN was treated with 5 μL aliquots of a 0.63 M (3 μmol) [2,6-lutidinium]BF_4 also in CD_3CN solution. Seven aliquots of [2,6-lutidinium]BF_4 were added, and after each addition, spectra were recorded and integrated. Partial conversion to [**1**H(NCMe)]$^+$ was observed with each addition. Prolonged sitting of the resulting solutions (1−2 h) resulted in no further protonation of **1**H(H), indicating that equilibrium had been reached. The concentrations of [**1**H(NCMe)]$^+$, H_2, and **1**H(H) were determined by integration with respect to the $C_6H_3(OMe)_3$ internal standard. The concentration of formed [**1**H(H$_2$)]$^+$ is assumed to be equal to the measured [**1**H(NCMe)]$^+$ concentration (see Supporting Information). This experiment was repeated three times. The same procedure was used in the determination of the pK_a's of **2**H(H) and **3**H(H). Attempted protonation of **2**H(H) with substoichiometric amounts of [2,6-lutidinium]BF_4 appeared to give paramagnetic species; these experiments were not pursued.

[Cp*Ir(H$_2$NCPh$_2$C$_6$H$_4$)]BF_4. Three milliliters of a 0.07 M (210 μmol) $HBF_4 \cdot Et_2O$ (Et_2O solution) was added to a solution of 0.11 g (184 μmol) of Cp*Ir(HNCPh$_2$C$_6$H$_4$) in 0.5 mL of CH_2Cl_2 and 5 mL of Et_2O and 30 mL *n*-hexane resulting in an immediate color change from dark purple to a light yellow color, followed by immediate precipitation. The resulting yellow precipitate was collected and washed with *n*-hexane. Yield: 73 mg (59%). ^{1}H NMR (500 MHz, CD_3CN): δ 1.51 (s, 15H, Cp*), 5.26−5.55 (br m, 2H, H_2NCPh$_2$C$_6$H$_4$), 6.26−7.70 (14H, phenyl protons). Anal. Calcd for $C_{29}H_{31}BF_4IrN \cdot CH_2Cl_2$: C, 47.56; H, 4.39; N, 1.85. Found: C, 47.70; H, 4.64; N, 1.92.

[Cp*Ir(N,N-Me$_2$Tsen)]NO_3. A solution of 0.25 g (414 mmol) of Cp*IrCl(*N*,*N*-Me$_2$Tsen) and 73 mg (430 μmol) of $AgNO_3$ was stirred in 10 mL of CH_3CN for 30 s. A color change from light yellow to a light orange accompanied by the precipitation of a white solid. The slurry was filtered through Celite, and the resulting pale orange solution was evaporated to give a red-colored oil. Trituration of this oil in 20 mL of Et_2O for 12 h gave a solid that was recrystallized from dissolution in CH_2Cl_2 followed by addition of pentane. Yield: 0.17 g (67%). ^{1}H NMR (500 MHz, CD_3CN): δ 1.65 (s, 15H, Cp*), 2.39 (s, 3H, C_6H_4-*Me*), 2.58 (t, 4 Hz, 2H, Me$_2$NCH_2CH$_2$NTs), 2.83 (t, 4 Hz, 2H, Me$_2$NCH$_2$CH_2NTs), 2.94 (s, 6H, *Me*$_2$NCH$_2$CH$_2$NTs), 7.31 (d, 8 Hz, 2H, Ts), 7.70 (d, 8 Hz 2H, Ts). Anal. Calcd for $C_{21}H_{32}IrN_3O_5S \cdot 0.5\ CH_2Cl_2$: C, 38.36; H, 4.94; N, 6.24. Found: C, 38.70; H, 4.83; N, 6.29.

Cp*Ir(N-MeTsDPEN-H). A solution of 400 mg (578 μmol) of Cp*Ir(TsDPEN-H) in 40 mL of CH_2Cl_2 was treated with 250 μL (2.28 mmol) of MeOTf under a N_2 atmosphere. A reddish colored solution resulted after 30 min of stirring. The solution was then transferred into a flask containing 1.0 g of K_2CO_3, and the slurry was allowed to stir for 16 h. The solution was filtered through Celite, resulting in a reddish-purple colored solution. The solvent was removed under reduced pressure, and the reddish-purple residue was triturated with 50 mL of hexane for 16 h. Yield: 300 mg (74% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.82 (s, 15H, Cp*), 2.25 (s, 3H, C_6H_4-*Me*), 2.96 (s, 3H, *Me*NCHPhCHPhNTs), 3.65 (s, 1H, MeNC*H*PhCHPhNTs), 4.23 (s, 1H, MeNCHPhC*H*PhNTs), 6.86−7.62

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(14H, phenyl protons). Anal. Calcd for $C_{32}H_{37}IrN_2O_2S$: C, 54.44; H, 5.28; N, 3.97. Found: C, 54.08; H, 5.26; N, 3.96.

Hydrogenation Experiments. Five milliliters of 1.0×10^{-3} M Cp*Ir(TsDPEN-H) (20 mg, 29.0 μmol, in 25 mL THF) in a THF solution and 0.5 mL of a 1.0×10^{-3} M [Cp*Ir(TsDPEN)]X in a THF solution was added to 15 mL THF under N_2 in a 1-cm UV/vis reaction cell (see Supporting Information, Figure S1). An initial UV/vis spectrum was obtained before addition of hydrogen. Hydrogen ($\sim$1 atm) was transferred to an evacuated sample frozen with liquid N_2. The pressure of the apparatus was measured using a manometer. A hydrogen concentration of 1.0×10^{-3} M was estimated using the Ostwald coefficient for THF (0.0828).[43] The sample was carefully thawed over the course of 120−150 s and shaken vigorously for 10 s before insertion into the spectrometer. The start of thawing of the sample was taken as $t = 0$. The sample was a pink color upon insertion into the spectrometer. About 135 s elapsed before the start of data collection. Data were collected in a scanning kinetics data format for 120 min, where a spectrum was recorded every 15 s at a temperature of 298 K (Figure S2). The sample was not stirred for the duration of the experiment. A yellow-colored solution, characteristic of the presence of **1**H(H), was observed upon reaction completion. Rates were determined by following the disappearance of the absorbance at 540 nm. Every five data points were used in the kinetic analysis, where the first 50 of the 150 data points (accounting for three half-lives) were used in the kinetic analysis. CH_2Cl_2 and THF were selected as solvents for hydrogenation reactions due to convenient hydrogenation rates.

H_2 Transfer between 1H(H) and 1 and Related Exchange Reactions. A solution of 10 mg (14 μmol) of Cp*IrH(TsDPEN), 15 mg ($\sim$25 μmol) of the respective diamide, and 2 mg (12 μmol) of 1,3,5-timethoxybenzene (internal standard) in 0.8 mL of CD_3CN, under an atmosphere of N_2, resulted in a reddish-purple to dark purple solution. Equilibrium between the two complexes was found to require about 24 h. Concentrations of the species were determined by the Cp* signals (Ts signals in the case of Ru complexes) vs the signal for $C_6H_3(OMe_3)$ (δ 6.09).

Deuteration of [Cp*Ir(TsDPEN)]X in CD_3OD. A solution of 20 mg ($\sim$25 μmol) of [**1**H]X in 0.75 mL of CD_3OD was monitored by ^{1}H NMR spectroscopy. Addition of CD_3OD to the sample was taken as $t = 0$. The sample was a reddish color. About 135 s elapsed before the start of data collection. Data were collected in a preacquisition delay array for 60 min: a spectrum was recorded every 15 s with a preacquisition delay of 10 s and an acquisition time of 5 s (293.0 K). The sample was spun at a rate of 20 rpm for the duration of the experiment. The rate of deuteration was calculated from the rate of decrease in the integration values of the amine peaks vs the Cp* peak.

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Supporting Information Available: Further experimental details, IR (KBr) spectra of [**1**H]X, kinetic data on the rate of deuteration of [**1**H]X, proton-catalyzed hydrogenation of **1** in the presence of HD, sample thermodynamic calculations, sample pK_a determinations, molecular structure of [**1**H]OTf, sample calculation of H_2 solubility, and crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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