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Kinetics and Thermodynamics of H⁻/H•/H⁺ Transfer from a Rhodium(III) Hydride

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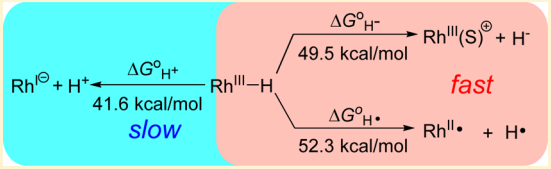
Supporting Information

ABSTRACT: The thermodynamics and kinetics of all three cleavage modes for Rh−H, the transfer of H⁻, H⁺, or H•, have been studied for the Rh(III) hydride complex Cp*Rh(2-(2-pyridyl)phenyl)H (**1a**). The thermodynamic hydricity, $\Delta G^\circ_{H^-}$, for **1a** has been measured (49.5(1) kcal/mol) by heterolytic cleavage of H_2 with Et_3N in CH_3CN. The transfer of H⁻ from **1a** to 1-(1-phenylethylidene)pyrrolidinium is remarkably fast (k_{H^-} = 3.5(1) × 10⁵ M^{-1} s^{-1}), making **1a** a very efficient catalyst for the ionic hydrogenation of iminium cations. The pK_a of **1a** in CH_3CN has been measured as 30.3(2) with (*tert*-butylimino)tris(pyrrolidino)phosphorane (**12**), and the rate constant for H⁺ transfer from **1a** to **12** has been estimated (k_{H^+} = 5(1) × 10⁻⁴ M^{-1} s^{-1}) from the half-life of the equilibration. Thus, **1a** is a poor H⁺ donor both thermodynamically and kinetically. However, **1a** transfers H• to TEMPO smoothly, forming a stable Rh(II) radical Cp*Rh(2-(2-pyridyl)phenyl)• (**14a**) that can activate H_2 at room temperature and 1 atm. The metalloradical **14a** has a *g* value of 2.0704 and undergoes reversible one-electron reduction at −1.85 V vs Fc^+/Fc in benzonitrile, implying a bond-dissociation enthalpy for the Rh−H bond of **1a** of 58.2(3) kcal/mol—among the weakest Rh(III)−H bonds reported. The transfer of H• from **1a** to Ar_3C• (Ar = *p*-^{t}BuC_6H_4) is fast, with $k_{H•}$ = 1.17(3) × 10³ M^{-1} s^{-1}. Thus, **1a** is a good H⁻ and H• donor but a poor H⁺ donor, a combination that reflects the high energy of the Rh(I) anion [Cp*Rh(2-(2-pyridyl)phenyl)]⁻.



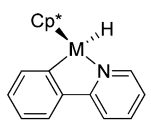
INTRODUCTION

Transition-metal hydride (and dihydrogen) complexes can serve as intermediates in the transfer of H⁺, H•, or H⁻ to catalytic substrates from H_2 gas. The hydrogenation of polar double bonds (C═N, C═O) often requires H⁺ transfer from an H_2 complex and then H⁻ transfer from the metal,[1] while certain hydroformylation and cyclization reactions begin with H• transfer.[2] Proton-coupled electron transfer (PCET) to and from an M−H bond is an important step in H_2 production and oxidation.[3] The transfer of H⁺ from transition-metal hydride complexes is important in many catalytic[4] and biological[5] processes, particularly photochemical water splitting[6] and fuel cell electrocatalysis.[4c] Measurement of the thermodynamics of removing a proton from a hydride complex (its pK_a) is important in determining the strength of its M−H bond and its other thermodynamic properties.[7]

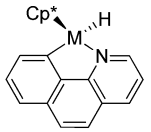
The ability of Ru(II) hydride complexes to transfer hydride ligands to C═N bonds (iminium cations, pyridinium cations, etc.) is well established,[1e,8] and similar behavior can be expected on the part of electronically similar (also d^6) Rh(III) and Ir(III) hydrides. Indeed, several rhodium(I) hydrides are known to have high thermodynamic hydricities, i.e., they have relatively small positive values of $\Delta G^\circ_{H^-}$ for eq 1. For $HRh(dppbz)_2$ (dppbz =1,2-bis(diphenylphosphino) benzene) $\Delta G^\circ_{H^-}$ for the formation of the acetonitrile cation is 34 kcal/mol, while for $HRh(dmpe)_2$ (dmpe =1,2- bis(dimethylphosphino) ethane) it is only 26 kcal/mol — comparable to that of $Li[HBEt_3]$.[9]

$$M{-}H \xrightarrow[S]{\Delta G^\circ_{H^-}} M(S)^+ + H^- \qquad (1)$$

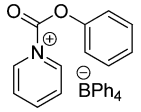
The Rh and Ir hydrides we recently reported (**1** and **2**) proved very reactive at hydride transfer to the pyridinium cation **3**,[10] so it seemed worthwhile to compare their reactivity with that of Ru(II) hydrides toward a common electrophile. We therefore examined the reactions of **1** and **2** with the iminium cation **4**, for which rate constants from several Ru(II) hydrides had been reported.



1a. M = Rh
1b. M = Ir



2a. M = Rh
2b. M = Ir



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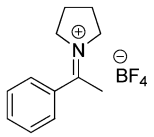

4

All of the complexes **1** and **2** transferred their hydride ligands to **4**, but the rate at which **1a** did so was extraordinary: the reaction of dilute **1a** (3.6 × 10⁻³ M) with dilute **4** (7.2 × 10⁻³ M) in CD_2Cl_2 was too fast to monitor by NMR even at −80 °C. However, we have been successful at measuring the rate of that H⁻ transfer by stopped-flow methods. We have also determined

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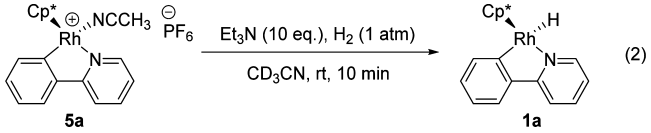
the thermodynamics of H^- removal from **1a**, along with the kinetics and thermodynamics of H• and H^+ removal. We believe that **1a** is the first hydride complex for which both the kinetics (with appropriate substrates) and the thermodynamics of all three transfers (H^+, H•, and H^-) have been determined. (The kinetics and thermodynamics of e^-, H^+, and H• transfers among Mo complexes have, however, been reported by Protasiewicz and Theopold in 1993.[11]) We have thus been able to explore the relationships among these parameters.

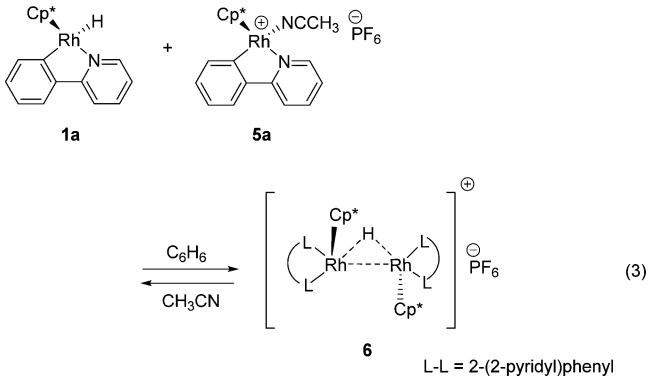
RESULTS

Improved Synthesis of the Rhodium Hydride 1a. Nucleophilicity of its Rh–H Bond. We knew that the coordination of CH_3CN in the Rh cation **5a** was very weak,[10] which suggested that we might be able to displace it by H_2; removal of H^+ would then give us the hydride **1a**. (We had used a similar method for our earlier synthesis of [Cp*Ru(dppc)H]-PF_6.)[12] Indeed, 1 atm of H_2 converted [Cp*Rh(2-(2-pyridyl)-phenyl)(CH_3CN)]$^+$ (**5a**) to the hydride **1a** at room temperature in 10 min and in the presence of a 10-fold excess of Et_3N (eq 2).



(2)

We saw, however, the formation of an intermediate **6**, with a triplet (J = 24 Hz) resonance in the hydride region (δ = −19.87) of the ^{1}H NMR. The J value is close to that reported (23 Hz) for a hydride bridging two Rh(III)'s[13] and suggests a (μ_2-H)Rh_2 structure; probably the result of nucleophilic attack by the Rh–H bond of **1a** on the vacant coordination site created by the dissociation of CH_3CN from **5a**.[14] The intermediate can be obtained as a red solid by adding solid **5a** to a benzene solution of 1 equiv of **1a** (eq 3). If this red solid is dissolved in CD_2Cl_2 or

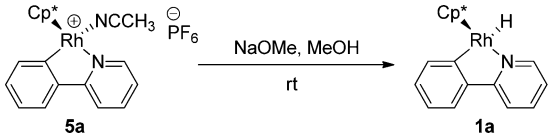


(3)

THF-d_8, three triplets of different intensities can be seen in the hydride regions of the ^{1}H NMR (Figure 1, δ = −13.33 (only 3% of the total intensity), −19.82, and −19.96), all with the same coupling constant (J = 24 Hz). The ratio of the two most intense triplets, the upfield ones, remains constant at 10:1, as does the ratio of a corresponding pair of Cp* peaks.[15] These two sets of signals probably belong to conformational isomers, which we will call **6** and **6′**; possibilities are shown in Chart 1. (The Cp* ligands are surely trans.) When dissolved in CD_3CN the red **6**/**6′** mixture reverts to **1a** and **5a**-d_3 (the reverse of eq 3).

The IR spectrum of the **6**/**6′** mixture shows a broad band at 1689 cm^{-1}, which shifts (as expected for a hydride ligand) to 1224 cm^{-1} upon deuteration. A range of frequencies has been reported for (μ_2-H)Rh_2 structures,[16] down to 1151 cm^{-1} for a neutral (μ_2-H)(μ_2-Cl) dimer,[13] but 1689 cm^{-1} is consistent with other cationic cases, e.g., the 1665 cm^{-1} reported for [(triphos)-Rh(μ_2-H)$_3$Rh(triphos)]$^+$.[17]

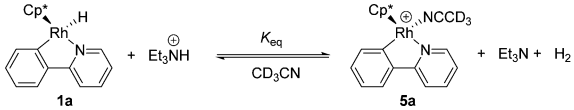
The hydride **1a** can also be made by stirring the cation **5a** overnight with NaOMe in MeOH at room temperature (**1a** precipitates from the solution, so isolation is easy) (eq 4).



(4)

The corresponding deuteride is easily made and purified by this method. (Scrambling results when $NaBD_4$ is used in the higher-temperature procedure we published earlier,[10] and the isolation of **1a**-d_1 from eq 2 with D_2 is difficult because of the excess Et_3N and the formation of the intermediate **6**.)

Thermodynamic Hydricity of 1a. Equilibrium studies of the heterolytic cleavage of H_2 by **5a** and appropriate bases have been used to determine the thermodynamic hydricity (defined by eq 1) of the hydride complex **1a**. The addition of eq 7, and a



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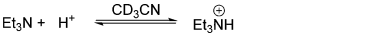
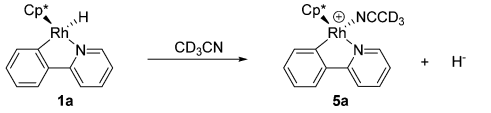


(6)

(7)

protonation reaction eq 6, to a cleavage reaction eq 5 results in eq 8, so ΔG for eq 8 can be determined (eq 9) from K_{eq} for eq 5.



(8)

(This method for the determination of the hydricity of transition-metal complexes was first reported by DuBois and co-workers.)[18]

These studies were complicated by the displacement of CD_3CN from **5a** by many common bases (e.g., triazabicyclodecene (TBD), 1,8-diazabicycloundec-7-ene (DBU), 1,3,3-tetramethylguanidine (TMG)) and the unidentified byproducts that they gave with **5a**. With the tertiary amine Et_3N the displacement reaction is much slower, but there is still decomposition, while the more hindered Hünig's base $Et_2{}^iPrN$ is blocked from coordination. However, a solution of $Et_2{}^iPrN$ with **5a** under H_2 gave unidentified byproducts immediately. It proved best to estimate the equilibrium constant for eq 5 by treating a low concentration of **1a** with Et_3NH^+ in the presence of a large excess of Et_3N, which suppressed the formation of **5a** and kept the formation of **6** and other byproducts negligible. Equilibrium was typically achieved within 7 h (SI-1), while decomposition was not appreciable until 24 h. The ratio of **5a**/**1a** at equilibrium was determined by intergrating the Cp* signals in the ^{1}H NMR. The activity of hydrogen at 1.0 atm was taken as unity. An equilibrium constant of 3.6 (6) atm was measured for eq 5 from three independent experiments in which the equilibrium was approached from the left. Substitution of this value for K_{eq} and

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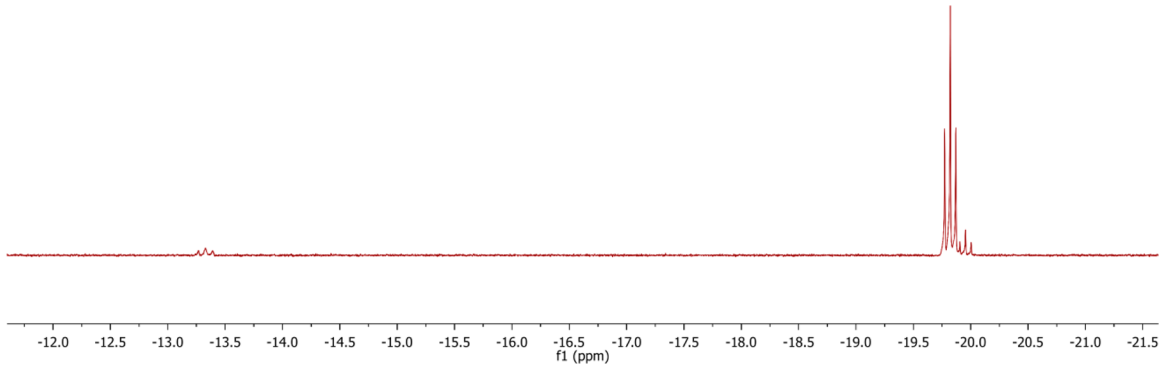
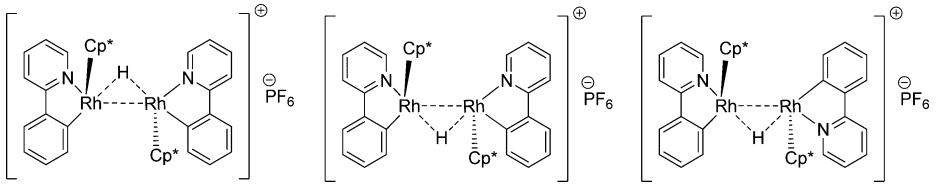


Figure 1. Hydride region of the ^{1}H NMR spectrum of the red solid resulting from the reaction of **1a** with **5a**.

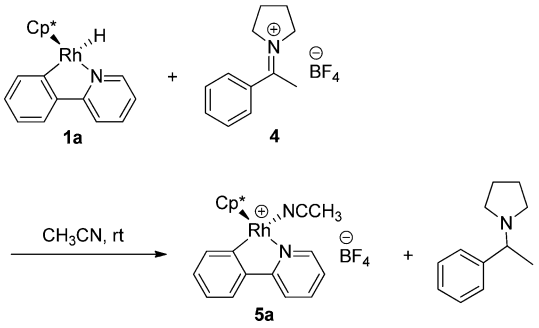
Chart 1. Possible Structures of 6 and 6′



the pK_a (CH_3CN) of Et_3NH^+ into eq 9 gave 49.5 (1) kcal/mol as the $\Delta G^\circ_{H^-}$ for eq 8.

$$\Delta G^\circ_{H^-}(\text{kcal/mol}) = -1.364\log K_{eq} - 1.364\text{p}K_a(Et_3NH^+) + 76.0 \quad (9)$$

Hydride Transfer Rate from the Rhodium Hydride 1a to the Iminium Cation 4. Stoichiometric hydride transfers like the one in eq 10 are best performed in the presence of a coordinating solvent like CH_3CN (or CD_3CN), to fill the vacant coordination site that remains after H^- transfer.



(10)

It proved impossible to monitor the reaction (in CD_2Cl_2 with 4 equiv of CD_3CN) by ^{1}H NMR, even at −80 °C with low concentrations of **1a** and **4**. However, stopped-flow methods proved practical even at room temperature (22 °C), allowing the use of CH_3CN as a solvent. With a 10-fold excess of **4** the reaction was finished within the time of mixing, but its progress was observable when **1a** (2.6×10^{-4} M) was treated with only 2 equiv of **4**.

Such a 1:2 ratio (**1a**:**4**) means that a second-order reaction will follow eq 11, where $[\mathbf{1a}]_0$ is the initial concentration of **1a**, $[\mathbf{1a}]_t$ is the concentration of **1a** at time t, and k_{H^-} is the second-order rate constant for H^- transfer.

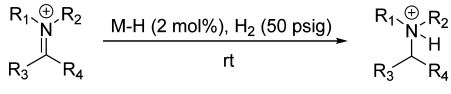
$$\ln\left(1 + \frac{[\mathbf{1a}]_0}{[\mathbf{1a}]_t}\right) = k_{H^-}[\mathbf{1a}]_0 t + \ln 2 \quad (11)$$

The reaction was monitored at 400 nm, an absorbance maximum for the disappearing hydride **1a**. A Beer's law plot of absorbance at that wavelength vs concentration of **1a** in CH_3CN (SI-2) was linear from 0.2 to 1.8 absorbance units, and ε(**1a**) was determined to be 4742.5 $M^{-1}cm^{-1}$ from the data in this linear region. If we rewrite eq 11 in terms of absorbance (at 400 nm) and the uncertainty Δt in the time at which the reaction begins, eq 11 can be rewritten as eq 12.

$$\ln\left(1 + \frac{A_0}{A_t}\right) = k_{H^-}[\mathbf{1a}]_0(t + \Delta t) + \ln 2 \quad (12)$$

The change in absorbance with time during a typical experiment is shown in Figure 2. The initial absorbance A_0 is calculated from the initial concentration of **1a** and ε(**1a**). The signal-to-noise during the first 20 ms improves considerably when multiple experiments (23 in our determination of k_{H^-}) are averaged. The resulting data (Figure 3) confirm a linear relationship between $\ln(1 + A_0/A_t)$ and t. (Because of reaction during mixing the y-intercept is not exactly ln 2, but the uncertainty in the time does not have any appreciable effect on the slope.) From the slope we obtain the second-order rate constant for H^- transfer from **1a** to **4** at room temperature, $k_{H^-} = 3.5(1) \times 10^5$ M^{-1} s^{-1}. This value is 10^6 times that (6.4×10^{-1} M^{-1} s^{-1}) of the Ru complex, CpRu(dppm)H, that transfers H^- most quickly to **4**![19]

Performance of 1a as a Catalyst for the Ionic Hydrogenation of Iminium Cations. As hydride transfer is the slowest step in the operation of Ru hydride catalysts for the ionic hydrogenation of iminium cations (eq 13),[1e] **1a** should be a



(13)

particularly effective catalyst for that reaction. However, finding an effective solvent has been challenging. The hydride **1a** is unstable in most of the solvents that dissolve iminium salts, although it persists long enough in methanol (its ^{1}H NMR can

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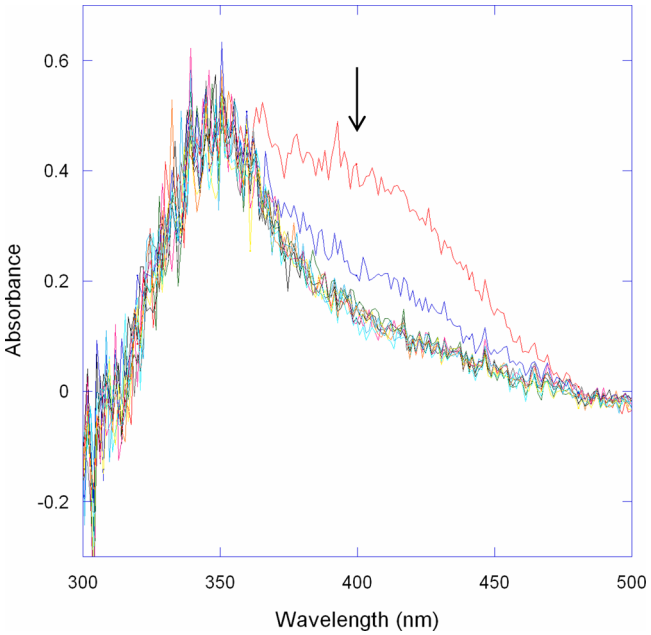


Figure 2. Plot of absorbance vs wavelength as a function of time during a typical stopped-flow experiment for hydride transfer from **1a** to **4** at 22 °C in CH_3CN. The time interval Δt between adjacent spectra is 10 ms.

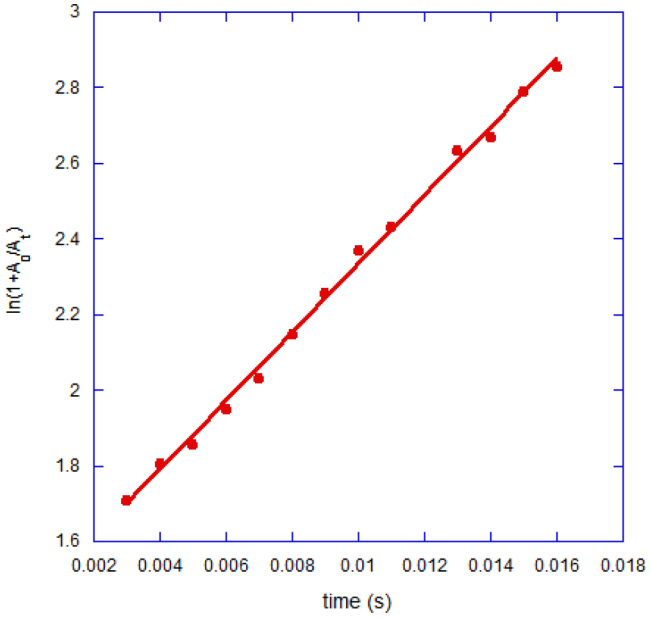


Figure 3. Plot of $\ln(1 + A_0/A_t)$ vs t for hydride transfer from **1a** to **4** at 22 °C in CH_3CN. Initially $[\mathbf{1a}] = 2.6 \times 10^{-4}$ M, $[\mathbf{4}] = 5.2 \times 10^{-4}$ M.

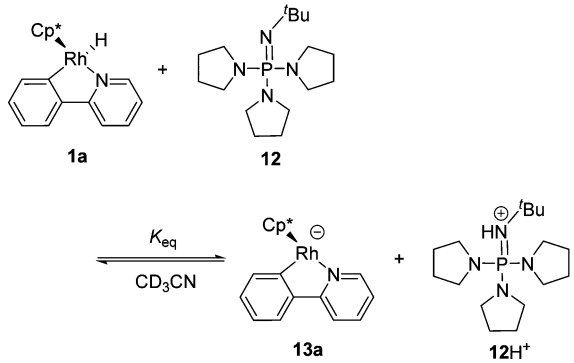
still be detected after an overnight run) to be effective as a catalyst.

Table 1 shows that, in methanol under 50 psig of H_2, **1a** is effective at concentrations as low as 0.4−1% of the substrate. The cations **7** and **9**−**11** are hydrogenated quantitatively within 4 h; the cation **8** gives a lower conversion even after an overnight run (about 18 h). Tetrahydroisoquinoline alkaloids like salsolidine, the hydrogenation product of **11**, are common natural products,[20] having physiological activity relevant to Parkinson's and other neurotic diseases.[21]

CH_3CN can also serve as a solvent, but only for the iminium salt **4** (50% conversion overnight at room temperature, atmospheric pressure H_2, with 2 mol % loading of the catalyst **1a**).

The pK_a of 1a in CH_3CN. Kinetics of Proton Transfer. The rhodium hydride **1a** has proven to be a very weak acid, and the common strong bases, such as TBD and DBU, do not deprotonate it in CH_3CN. It is, however, deprotonated by the phosphazene base (*tert*-butylimino)tris(pyrrolidino)-phosphorane (BTPP) (**12**). The protonated phosphazene salt **12H$^+$MsO$^-$** was prepared separately. Its N−H proton gave a ^{14}N-broadened ^{31}P-split doublet (δ = 3.99, J_{P-H} = 8.7 Hz) in CD_3CN. All the other resonances of **12H$^+$** averaged with those of added **12**, implying fast proton self-exchange between **12** and **12H$^+$**. The second-order rate constant for this self-exchange appeared to be greater than 3×10^4 M^{-1} s^{-1} in CD_3CN at room temperature, from the collapse of the ^{31}P-split doublet of **12H$^+$** as **12** was added (SI-10).

Equilibration of **1a** with a small excess of **12** required around 19 h in CD_3CN, but the slowness of proton self-exchange between **1a** and its conjugate base **13a** made it possible to integrate their ^{1}H NMR signals separately. (The Cp* signals of **1a** and **13a** overlap with the signals of **12** and **12H$^+$**, so the lowest-field signals of the 2-(2-pyridyl)phenyl ligands for **1a** and **13a** were used (SI-5).) The concentrations of **12** and **12H$^+$** were then calculated from those of **1a** and **13a** at equilibrium and used to obtain the equilibrium constant, K_{eq}, for eq 14 (K_{eq} = 0.012(5)). The known pK_a of **12H$^+$** in acetonitrile (28.35)[22] gave a pK_a of 30.3(2) for the hydride **1a**.



(14)

A slight broadening, of unknown origin, was observed for all signals of **1a** and **12** immediately after they were mixed at room temperature, when no **13a** or **12H$^+$** had yet formed (SI-4). (The broadening disappeared if the sample was cooled.) The peaks of the rhodium anion **13a** did not broaden (SI-5), implying that it is not protonated at a significant rate by any acid in the system, **12H$^+$** or **1a**. The approach to equilibrium reaction of eq 14 followed first-order kinetics, with a half-life ($t_{1/2}$) of about 4 h implying a rate constant k_e of about 5×10^{-5} s^{-1}. We can then estimate the second-order rate constants k_f (5×10^{-4} M^{-1} s^{-1}) and k_r (4×10^{-2} M^{-1} s^{-1}) of the forward and reverse proton transfer in eq 14 from eqs 15 and 16, in which $[\mathbf{1a}]_e$, $[\mathbf{12}]_e$, $[\mathbf{13a}]_e$, and $[\mathbf{12H^+}]_e$ are the concentrations of **1a**, **12**, **13a**, and **12H$^+$** at equilibrium.

$$k_e = k_f([\mathbf{1a}]_e + [\mathbf{12}]_e) + k_r([\mathbf{13a}]_e + [\mathbf{12H^+}]_e) \quad (15)$$

$$K_{eq} = \frac{k_f}{k_r} \quad (16)$$

Thermodynamics of the Homolytic Dissociation of the Rh−H Bond in 1a. The pK_a of **1a** enables us to calculate the

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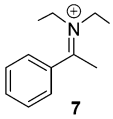
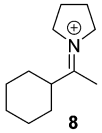
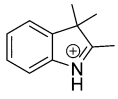
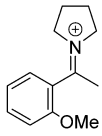
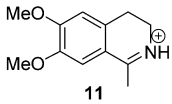
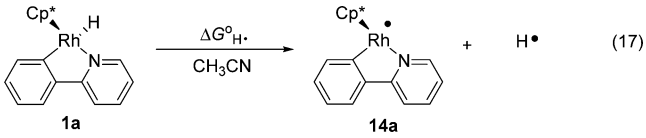
Table 1. Comparison of Ru Hydrides and 1a as Catalysts for the Ionic Hydrogenation of Various Iminium Cations[a]

Iminium	Ru hydrides[b] time	Ru hydrides[b] NMR yield (Isolated yield)	1a[c] time	1a[c] NMR yield (Isolated yield)
	CpRu(dppm)H			
 7	—	—[d]	4h	> 99%(92%)
 8	90h	95%(54%)	18h	78%(-)
	CpRu((*S*,*S*)-Chiraphos)H			
 9	—	—[d]	4h	> 99%(97%)
 10	7d	22%(-)	3.5h	> 99%(94%)
 11	2d	24%(-)[e]	4h	> 99%(99%)

[a]The counteranion is BF_4^- in all cases. [b]Reaction condition: in CH_2Cl_2, [iminium cation] = 0.05−0.1 mol/L, RuHs 1−2 mol %, H_2 50 psig, room temperature. [c]Reaction condition: in CH_3OH, [iminium cation] = 0.06 mol/L, **1a** 0.4−1 mol %, H_2 50 psig, room temperature. [d]No reaction after 2 days. [e]CH_3OH as solvent.

thermodynamics associated with the homolytic cleavage of its Rh−H bond (eq 17). If we combine that pK_a with the potential in



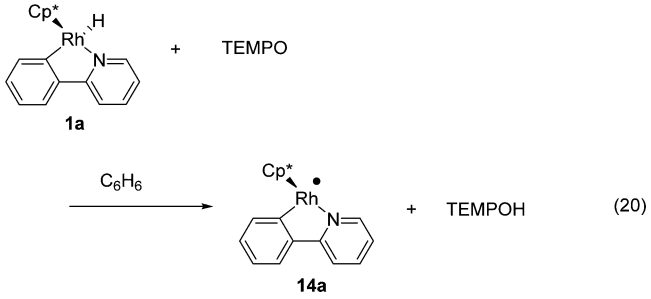
(17)

CH_3CN (relative to Fc^+/Fc) of its conjugate base **13a** and use eq 18,[2b,23] we can obtain ΔG (the "BDFE") for eq 17; from the same measurements we can also, with eq 19,[2b,23] obtain ΔH (the "BDE") for eq 17.

$$\text{BDFE(kcal/mol)} = 1.364\text{p}K_a + 23.06E^\circ_{ox}(\mathbf{13a}) + 53.6 \quad (18)$$

$$\text{BDE(kcal/mol)} = 1.364\text{p}K_a + 23.06E^\circ_{ox}(\mathbf{13a}) + 59.5 \quad (19)$$

The high pK_a of **1a** has made it impossible to isolate **13a** and thus difficult to examine its oxidation electrochemically. However, it has proven easy to remove H• from **1a** with 1 equiv of the stable radical TEMPO in benzene (eq 20) (see next section) and thus to isolate the Rh(II) radical **14a**; under N_2 **14a** is quite stable in solution and as a solid. Unfortunately **14a** is insoluble in CH_3CN and electrochemical studies in this solvent are not possible. DuBois et al. have shown that "half-wave potentials measured in benzonitrile provide reliable estimates of half-wave potentials in acetonitrile".[24] Under standard



(20)

conditions ([**14a**] = 0.001 M, ν = 100 mV/s) in benzonitrile only a broad, featureless cyclic voltammetry (CV) wave is observed, from which no reliable data can be extracted. However, at much higher concentration (0.01 M) and faster scan rate (ν = 500 mV/s), **14a** has a reversible one-electron reduction wave at −1.85 V vs Fc^+/Fc in benzonitrile (Figure 4). The CV of a THF solution (0.001 M) also shows a reversible wave (SI-6) for the reduction of **14a**, with a one-electron potential of −1.98 V vs Fc^+/Fc in THF. This reduction is most likely metal based.[25]

If we assume that the difference in potentials between **14a** and Fc^+ is the same in acetonitrile as in benzonitrile, the BDFE (ΔG) of the Rh−H bond in **1a** is 52.3(3) kcal/mol, and the BDE (ΔH) of that bond is 58.2(3) kcal/mol.

The smooth H• transfer in eq 20 confirms that the Rh−H bond in **1a** is very weak. Our Rh−H BDE, and an estimate for the BDE in TEMPO−H as 70 kcal/mol,[26] implies that reaction 20 is downhill by 12 kcal/mol.

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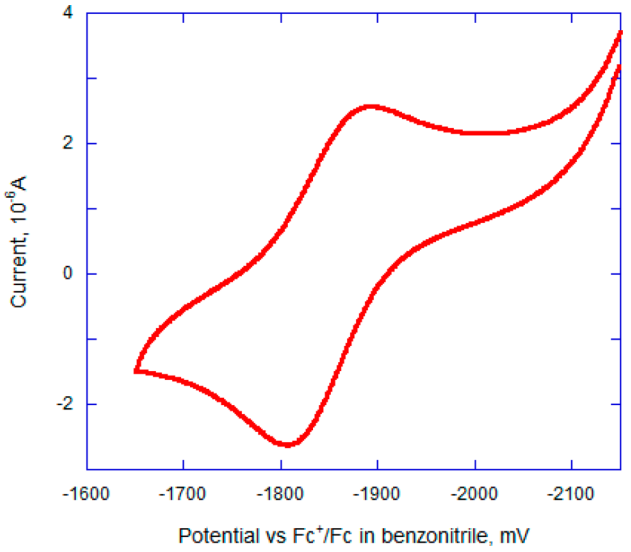


Figure 4. Cyclic voltammogram of the rhodium radical **14a** (0.01 M) in benzonitrile at room temperature, with a 0.20 M $[Bu_4N]PF_6$ supporting electrolyte, a Pt disk electrode (d = 1.6 mm), and a voltage sweep rate ν = 500 mV/s.

H• Transfer from 1a to TEMPO. The Norton group has used TEMPO to suppress H/Cl exchange between CpRu(dppp)H (**15**) (dppp =1,3-bis(diphenylphosphino)propane) and CD_2Cl_2 when measuring the kinetics of H^- transfer from **15** in that solvent.[19] (Presumably exchange occurs by a radical chain mechanism like that for the reduction of RX by Bu_3SnH and the addition of TEMPO quenches the chain.) However, with **1a** the same strategy (treatment with TEMPO in CD_2Cl_2) gives immediate formation of the rhodium chloride complex Cp*Rh(2-(2-pyridyl)phenyl)Cl and TEMPOH.

In C_6D_6 **1a** immediately transfers H• to TEMPO, forming TEMPOH and leaving the 17-electron rhodium radical **14a** (eq 20). That radical (**14a**) does not dimerize and remains paramagnetic. (Only the signal of TEMPOH is detected by ^1H NMR.) Isolated **14a** is a red powder, soluble in C_6H_6 and THF but insoluble in CH_3CN. Its EPR spectrum at room temperature in benzene is shown in Figure 5. If we use as internal standard the

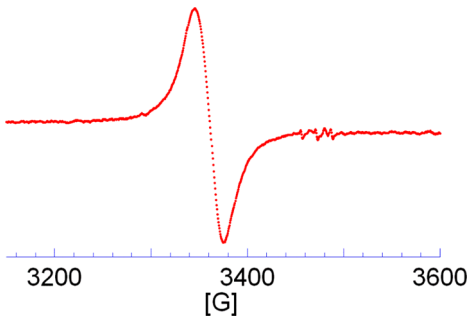


Figure 5. EPR spectra of the rhodium radical **14a** in C_6H_6 at room temperature; trace of TEMPO acts as internal standard; g = 2.0704.

trace of TEMPO that remains, we determine a g value of 2.0704 for **14a** at room temperature—far enough from 2 to imply that the spin density resides mainly on the rhodium.

The rhodium radical **14a** can activate H_2 at atmospheric pressure to regenerate **1a**, and we know from eq 20 that **1a** can transfer H• to TEMPO at room temperature in benzene. In combination these processes catalyze the hydrogenation of TEMPO to TEMPOH (eq 21).

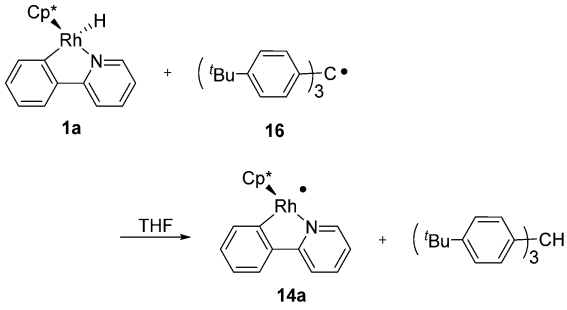
$$\text{TEMPO} \xrightarrow[C_6D_6,\ \text{rt}]{\textbf{14a}\ (2\ \text{mol}\ \%),\ H_2\ (1\ \text{atm})} \text{TEMPOH} \qquad (21)$$

While complexes of Rh(I) and Rh(III) are familiar,[27] monomeric Rh(II) complexes have been very rare, "with their synthesis and isolation hindered by disproportionation reactions."[28]

Charge discourages dimerization, and several cationic complexes of Rh(II) have been reported. Mirkin and co-workers have synthesized a Rh(II) cation with a bisphosphine η^6-arene ligand.[29] De Bruin et al. have made (DPA)M(II)$(COD)^{2+}$ (M = Rh, Ir), with the fac-coordinating ligand *N,N*-bis(2-pyridylmethyl)amine (DPA).[30] Milstein and co-workers have prepared Rh(II) cations with the 2,6-bis((di-*tert*-butylphosphino)-methyl)pyridine ligand and the corresponding phosphinite ligand.[31] The groups of Reek and Vlugt have developed Rh(II) cations with C_3-symmetric tripodal tetraphosphine ligands.[32]

Neutral Rh(II) monomers dimerize readily unless discouraged by steric encumbrance around the metal. The first neutral complexes of Rh(II) were reported with heavily substituted porphyrin ligands some years ago.[33] In 2001 the groups of Tilley and Bergman made neutral Rh(II) complexes with bis(oxazoline) ligands.[34] More recently Ozerov and co-workers have reported a series of Rh(II) complexes (PNP)Rh(X) (where X = OAc, $OSiPh_3$, OC_6H_4F, Cl) with diarylamido/bis(phosphine) PNP pincer ligands.[28a] Most recently, the groups of de Bruin and Schneider have prepared the Rh(II) pincer complex $[Rh(Cl)\{N(CHCHP^tBu_2)_2\}]$.[35] The stability of our neutral Rh(II) radical **14a** is a bit surprising, as the X-ray structure of **1a** does not show much crowding near the hydride ligand.[10]

Rate of H• Transfer from 1a to Tris(4-(*tert*-butyl)-phenyl)methyl Radical (Ar_3C•, 16). The para-substituted trityl radical **16** is monomeric in solution and known to abstract H• from many transition-metal hydrides,[36] so it should be able to replace TEMPO in reaction 20. (The Ar_3C–H BDE is about 74 kcal/mol.)[37] Indeed, the reaction of **16** with **1a** gives tris(*p*-*tert*-butylphenyl)methane and the rhodium radical **14a** (eq 22).



(22)

We have measured the rate of this H• transfer in an anaerobic stopped-flow apparatus at room temperature. (We chose THF as the solvent because **1a** is not very soluble in benzene.) Unfortunately the broad absorbance of **14a** overlaps with the sharp absorbance peak of the trityl radical **16** at 523 nm, making ΔA relatively small at that wavelength. We therefore made **1a** the limiting reagent (under pseudo-first-order conditions) and monitored the greatest absorbance change for the reaction at 430 nm.

In the presence of a large (>10-fold) excess of the radical **16** the reaction obeyed first-order kinetics (SI-7). The linearity of

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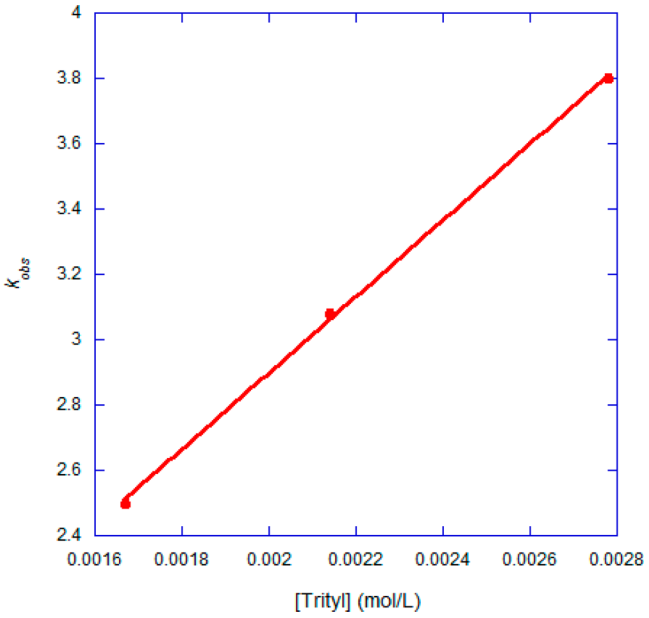


Figure 6. Plot of k_{obs} vs concentration of the trityl radical **16** at room temperature.

plots of k_{obs} versus [**16**] (Figure 6) confirmed that reaction 22 is also first order in **16** (as expected from previous studies[36] of such reactions). Thus, reaction 22 obeys the rate law in eq 23, with $k_{H\bullet} = 1.17(3) \times 10^3\ M^{-1}\ s^{-1}$.

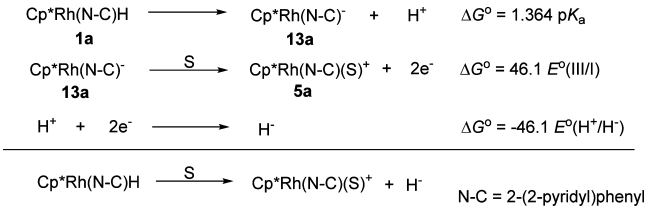
$$-\frac{d[\mathbf{1a}]}{dt} = k_{H\bullet}[\mathbf{1a}][\mathbf{16}] \tag{23}$$

DISCUSSION

Thermodynamic and Kinetic Hydricities of Cp*Rh(2-(2-pyridyl)phenyl)H (1a). A $\Delta G^\circ_{H^-}$ of 54.9 kcal/mol in water has been reported for a highly charged rhodium(III) porphyrin hydride, $[HRh(TSPP)(H_2O)]^{4-}$, where TSPP is tetra(*p*-sulfonatophenylporphyrin).[38] However, as is to be expected from a glance at eq 8, these "hydricities" vary considerably with solvent. DuBois and co-workers have reported values of $\Delta G^\circ_{H^-}$ in acetonitrile for several neutral rhodium(I) hydride complexes $HRh(P{-}P)_2$[9,24] and several cationic rhodium(III) dihydrides $[H_2Rh(P{-}P)_2]^+$.[39] For $HRh(P{-}P)_2$ the hydricities vary from 45 to 26.4 kcal/mol,[9,24] and for $[H_2Rh(P{-}P)_2]^+$ they vary from 71.6 to 50.4 kcal/mol.[39] The present work provides the first thermodynamic hydricity in acetonitrile of a neutral rhodium(III) hydride ($\Delta G^\circ_{H^-,\,MeCN}$ for Cp*Rh(2-(2-pyridyl)phenyl)H (**1a**) is 49.5 kcal/mol). The hydride donor ability of **1a** thus, unsurprisingly, lies between those of the cationic dihydrides $[H_2Rh(P{-}P)_2]^+$ and those of the neutral Rh(I) hydrides $HRh(P{-}P)_2$.

We can calculate other potentials of the Cp*Rh(2-(2-pyridyl)phenyl) system from the thermodynamic hydricity ($\Delta G^\circ_{H^-}$) of **1a**. In principle $\Delta G^\circ_{H^-}$ is available from the thermochemical cycle in Scheme 1, which involves the potential (E°(III/I)) associated with the two-electron oxidation (to **5a**) of the conjugate base (**13a**) of **1a**.[18a] However, that potential cannot be determined by CV (SI-9) because the cation **5a** is solvated and the anion **13a** is not. From eq 24 and our $\Delta G^\circ_{H^-}$ for **1a** we can calculate E°(III/I) (for the reduction of the solvated cation to the unsolvated anion) as −1.55 V vs Fc^+/Fc; use of the one-electron reduction potential E°(II/I) for the rhodium

Scheme 1. Hydricity Determination of 1a

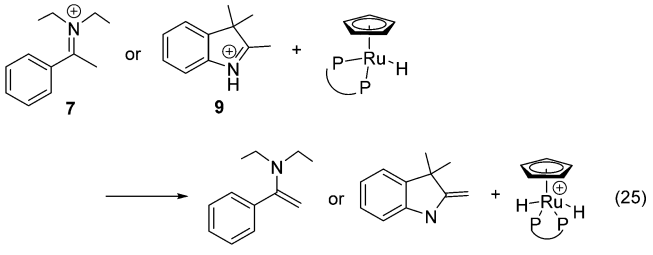


radical **14a**, measured above as −1.85 V vs Fc^+/Fc, implies that E°(III/II) (for the reduction of the solvated cation to the neutral radical) is around −1.2 V vs Fc^+/Fc.

$$\Delta G^\circ_{H^-}(\text{kcal/mol}) = 1.364pK_a + 46.1E^\circ(\text{III/I}) + 79.6 \tag{24}$$

Second-order rate constants for hydride transfer to $[Ph_3C]BF_4$ from various neutral hydrides (MH) have been reported earlier, ranging from $k_{H^-} = 7.2 \times 10^{-1}\ M^{-1}\ s^{-1}$ (from $(C_5H_4CO_2Me)(CO)_3WH$) to $k_{H^-} = 4.6 \times 10^6\ M^{-1}\ s^{-1}$ (from *trans*-$Cp(CO)_2(PMe_3)MoH$).[14b] With the iminium cation **4** as hydride acceptor, transfer of H^- from the Rh hydride **1a** ($k_{H^-} = 3.5(1) \times 10^5\ M^{-1}\ s^{-1}$) has proven around 10^6 times faster than transfer from our best Ru H^- donor, CpRu(dppm)H ($k_{H^-} = 6.4 \times 10^{-1}\ M^{-1}\ s^{-1}$).[40] It is not possible, however, to compare the hydricities of our Rh and Ru hydrides, as we have been unable to measure them in the Ru case (CH_3CN coordination is too strong, and the measurement of E°(2+/0) has proven impossible). Hydricities were reported in 2012 for two other Ru hydrides.[41]

Activity of 1a as a Hydrogenation Catalyst. Its rate constant for hydride transfer suggested that **1a** would be more efficient than any of our Ru hydrides at catalyzing the ionic hydrogenation of iminium cations[1e]—a suggestion verified by the results in Table 1. The cations **7**−**11** are difficult to hydrogenate with Ru hydride catalysts; for example, the cations **7** and **9** are easily deprotonated to the corresponding enamines and transfer H^+ to the Ru hydrides more rapidly than they abstract H^- from them, converting these catalysts to the inactive dihydride cations RuH_2^+ (eq 25).[1e,42] However, <1 mol % of the



(25)

Rh hydride **1a** catalyzes the quantitative hydrogenation of **7** and **9** within 4 h. Similarly, the Ru hydrides are extremely slow as catalysts for the hydrogenation of the iminium cations **10** and **11**,[43] whereas **1a** is fast and efficient. The hydrogenation of the cyclohexyl-substituted cation **8** is catalyzed slowly even by **1a**, but its operation is still much more efficient than that of the Ru hydrides.[1e] The Rh catalyst **1a** can even catalyze the ionic hydrogenation of the iminium cation **4** slowly in coordinating solvents like acetonitrile, while the Ru ones cannot.

Thermodynamic and Kinetic Acidities of Cp*Rh(2-(2-pyridyl)phenyl)H (1a). The pK_a values of several Rh(III) dications, $[HRh(P{-}P)_2(CH_3CN)]^{2+}$, in acetonitrile have been reported, ranging from 5.8 to 18.9 as a function of the

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diphosphine (P−P).[39] Less acidic are neutral Rh(I) hydrides $HRh(P-P)_2$ (the pK_a of $HRh(dppb)_2$ is 35[9a]) and cationic Rh(III) dihydrides $[(H)_2Rh(P-P)_2]^+$ (the pK_a of $[(H)_2Rh(depx)_2]^+$ is 30.6[24]). The neutral Rh(III) hydride **1a** is a much weaker acid thermodynamically (pK_a (**1a**) in CH_3CN = 30.3) than the dicationic Rh(III) hydrides $[HRh(P-P)_2(CH_3CN)]^{2+}$.

The rhodium hydride **1a** is a poor proton donor both thermodynamically and kinetically. The transfer in eq 14 is approximately thermoneutral, but the rate constant k_f is quite small in comparison to those for other such M → N transfers.[44]

Bond Dissociation Energies of the Rh−H in 1a. Rate Constants for H• Transfer. The bond dissociation enthalpy of the Rh−H bond in **1a**, 58.2 kcal/mol, is among the weakest reported for Rh−H bonds, all of which also involve Rh(III). (We use the BDE instead of the BDFE for comparison because most of the previous data are BDE.) In 1983 Drago and co-workers obtained an average Rh(III)−H BDE of 58 kcal/mol by calorimetric methods for various $RhClB(P(p\text{-tolyl})_3)_2(H)_2$ (the ligands B are various N, P, and S donors).[45] In 1988 Wayland and co-workers estimated the BDE of the Rh−H bond in (OEP)RhH (OEP = octaethylporphyrin) as 62 kcal/mol from the rate of dissociation they measured for $[(OEP)Rh]_2$.[46] Wayland and co-workers subsequently (1991) assumed a linear correlation between the BDE of Rh(III)−H bonds and their ν_{Rh-H} ($\nu(Rh(Cl)(P(p\text{-tolyl})_3)_3(H)_2)$ = 2034 cm^{-1}, $\nu((OEP)Rh-H)$ = 2220 cm^{-1}, $\nu((TMP)Rh-H)$ = 2095 cm^{-1}),[47] and estimated the BDE of (TMP)RhH (TMP = tetramesitylporphyrinato) as 60 kcal/mol;[47] ν_{Rh-H} for **1a** (1935 cm^{-1})[10] gives an estimate of 55 kcal/mol for the Rh(III)−H BDE of **1a**, 3 kcal/mol lower than our experimental value (58.2 kcal/mol).

The Norton group has measured rate constants $k_{H•}$ for H• transfer to $Ar_3C•$ from a variety of metal hydrides. Usually they range from 3 to 1030 M^{-1} s^{-1} at room temperature,[36] although $HFe(CO)_2Cp$ is considerably faster, with a $k_{H•}$ of 12000 M^{-1} s^{-1}.[36] Presumably $HFe(CO)_2Cp$ is so fast because of its lack of steric congestion, as its M−H bond is relatively strong (its Fe−H BDE is 68 kcal/mol).[48] (We have found that $k_{H•}$ values reflect steric factors more than bond strengths.) The Rh−H bond in **1a** is much weaker than the Fe−H bond in $HFe(CO)_2Cp$, but k_H for **1a** ($1.17(3) \times 10^3$ M^{-1} s^{-1}) is an order of magnitude lower—presumably because the Rh center is so crowded (as is reflected in the stability of the Rh(II) radical **14a**). However, $k_{H•}$ for **1a** lies at the upper end of the range for other transition-metal hydrides.[36]

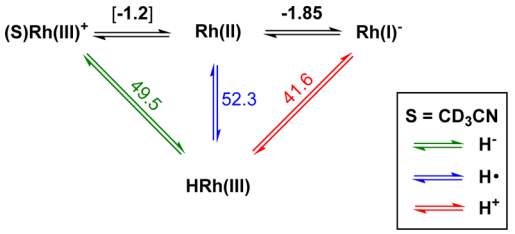
Relationships among the Three Cleavage Modes of the Rh−H in 1a (to produce H$^+$, H•, H$^-$). Bullock and co-workers concluded from data available in 1998 that there is no general correlation, both kinetically and thermodynamically, between the hydricity and the acidity of a transition-metal hydride complex.[49] Often "relative propensities of proton transfer and hydride transfer [are] roughly the opposite of each other."[49] For example, $Cp^*(CO)_3MoH$ is faster at H$^-$ transfer than $Cp(CO)_3MoH$, while the Cp hydride is faster at H$^+$ transfer; $(CO)_4(PPh_3)MnH$ is faster at H$^-$ transfer than $(CO)_5MnH$, while the unsubstituted hydride is faster at proton transfer. In contrast, however, some hydride complexes are both very acidic and very hydridic. For example, "the palladium hydride $[HPd(PNP)_2^+$ (PNP = $Et_2PCH_2N(Me)CH_2PEt_2)]$ is both [more] acidic and more hydridic than either of the platinum or nickel analogues".[50]

An opposing (complementary) relationship is also common between the ability to transfer H$^-$ and the ability to transfer H•. Bullock and co-workers have examined $(CO)_5MnH$, $Cp(CO)_3MoH$, $Cp^*(CO)_3MoH$, and $Cp(CO)_3WH$ and found that "$(CO)_5MnH$ has the highest rate constant for hydrogen atom transfer, but it is the slowest at hydride transfer"[49] and that "$Cp(CO)_3MoH$ is 37 times faster at hydrogen atom transfer than $Cp^*(CO)_3MoH$, but the Cp*complex has a higher rate constant for hydride transfer."[49]

The pattern we see with the rhodium hydride **1a** (Cp*Rh(2-(2-pyridyl)phenyl)H) is different. The rate constants above show that **1a** is relatively reactive as a hydride donor, at least more so than the Ru hydrides we have previously examined.[19] The Rh−H bond of **1a** is relatively weak, and it transfers H• to the acceptor **16** more rapidly than most transition-metal hydride complexes.[36,51] However, **1a** is a poor proton donor both thermodynamically and kinetically.

We can see the reasons for this unusual pattern if we examine the thermodynamics of the Rh system (Scheme 2). The free

Scheme 2. Hydricity, BDFE, and Acidity of 1a[a]



[a]Numbers in bold are reduction potentials in volts vs Fc$^+$/Fc. Numbers near arrows are $\Delta G°$ values for the indicated hydride, hydrogen atom, or proton transfer reaction in kcal/mol.

energies of H• and H$^-$ dissociation are determined by eqs 18 and 26, respectively. The high pK_a of **1a** is more than offset by the ease of oxidation of the Rh(I) anion **13a** ($E°$(II/I) = −1.85 V vs Fc$^+$/Fc), so H• and H$^-$ transfers (52.3 kcal/mol, 49.5 kcal/mol) are more favorable thermodynamically from **1a** than from many other transition-metal hydrides.

$$\mathrm{BDFE(kcal/mol)} = 1.364\mathrm{p}K_a + 23.06E^\circ_{ox}(\mathbf{13a}) + 53.6 \quad (18)$$

$$\Delta G^\circ{}_{H^-}\mathrm{(kcal/mol)} = 1.364\mathrm{p}K_a + 46.1E^\circ_{2e\ ox}(\mathbf{13a}) + 79.6 \quad (26)$$

CONCLUSIONS

The hydride, hydrogen atom, and proton donor abilities of the newly reported Rh(III) hydride, Cp*Rh(2-(2-pyridyl)phenyl)H (**1a**), have been studied both thermodynamically and kinetically. This Rh(III) hydride is both a good hydride donor and a good hydrogen atom donor, but a poor proton donor. This previously unobserved combination of properties is due to the high energy of **1a**'s conjugate base, [Cp*Rh(2-(2-pyridyl)phenyl)]$^-$ (**13a**). Its exceptional hydride donor ability makes Cp*Rh(2-(2-pyridyl)phenyl)H (**1a**) a very efficient catalyst for the ionic hydrogenation reactions of iminium cations.

EXPERIMENTAL SECTION

General Procedures. All air-sensitive compounds were prepared and handled under an N_2/Ar atmosphere using standard Schlenk and inert-atmosphere box techniques. CD_2Cl_2 was deoxygenated and stored over 4 Å molecular sieves. CD_3CN was dried successively over P_2O_5 and CaH_2, degassed by three freeze−pump−thaw cycles, and then purified by vacuum transfer. C_6D_6 was dried over CaH_2, degassed, and purified by vacuum transfer. MeOH was deoxygenated and dried by two successive columns (Q-5, activated alumina). THF was distilled from

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sodium/benzophenone under an N_2 atmosphere. *n*-Pentane was distilled from sodium under an N_2 atmosphere. CH_3CN was distilled successively from P_2O_5 and CaH_2 under an N_2 atmosphere. Cp*Rh(2-(2-pyridyl)phenyl)H (**1a**),[10] [Cp*Rh(2-(2-pyridyl)phenyl)-(CH_3CN)]PF_6 (**5a**),[10] 1-(1-phenylethylidene)pyrrolidinium tetrafluoroborate (**4**),[52] *N*-(1-phenylethylidene)diethylammonium tetrafluoroborate (**7**),[1e] *N*-(1-cyclohexylethylidene)pyrrolidinium tetrafluoroborate (**8**),[1e] 2,3,3-trimethyl-3H-indolium tetrafluoroborate (**9**),[53] *N*-[1-(*o*-methoxyphenyl)ethylidene]pyrrolidinium tetrafluoroborate (**10**),[53] 1-methyl-6,7-dimethoxy-3,4-dihydroisoquinolinium tetrafluoroborate (**11**),[53] and tris(*p-tert*-buty1phenyl)methyl radical (**16**)[36] were prepared by literature methods.

Electrochemical Study of 14a in Benzonitrile. The supporting electrolyte for the measured solution was 0.20 M [Bu_4N]PF_6 in benzonitrile. The cell consisted of a 1.6 mm diameter platinum disk working electrode, a platinum wire auxiliary electrode, and a silver wire reference electrode (0.01 M $AgNO_3$ + 0.20 M [Bu_4N]PF_6 in benzonitrile). The reference electrode was separated from the sample solutions with a porous Vycor tip. Ferrocene (Fc^+/Fc) was used as an external reference and was found to be +0.05 V with respect to our reference electrode. The sample was prepared under an N_2/Ar atmosphere and further purged with N_2 before measurement. The analyte concentration was 0.01 M. The scan rate was 500 mV/s. All potentials are reported in volts (V) vs Fc^+/Fc.

Stopped-flow Experiments Determining the Rate Constant for H^- Transfer from Cp*Rh(2-(2-pyridyl)phenyl)H (1a) to the Iminium Cation 4. In a typical experiment, 5.1 mg **1a** (0.013 mmol) was dissolved in 25 mL CH_3CN (limited by the solubility of **1a** in CH_3CN), and the concentration of **1a** was confirmed from the absorbance at 400 nm in the UV−vis spectra. One reservoir syringe was then filled with this solution and the other with an iminium cation **4** solution whose concentration is twice the concentration of **1a**. The two solutions were mixed in a stopped-flow apparatus under anaerobic conditions at room temperature (22 °C). The reaction was monitored at 400 nm—the λ_{max} of **1a**. The absorbance data within the first 20 ms were averaged over 23 injections, and k_{H^-} was determined by fitting the A_p *t* data to the second-order rate law (eq 12). The second-order rate constant at room temperature (22 °C) is equal to the slope divided by the initial concentration of **1a**.

Stopped-flow Experiments Determining the Rate Constant for H• Transfer from 1a to Tri(*t*-butylphenyl)methyl Radical (Ar_3C•, 16). Under the pseudo-first-order condition, the Rh hydride **1a** was chosen as the limiting reagent. In a typical experiment an approximate 0.0056 mmol sample of **1a** was prepared in 10 mL of THF. One reservoir syringe was then filled with this solution and the other with a THF solution containing tri(*t*-butylphenyl)methyl radical at least a 10-fold excess of **1a**. The greatest absorbance change for the reaction was found at 430 nm. The average rate constant at room temperature (22 °C) was determined by averaging the rate constants from 15 injections.

Catalysis of the Hydrogenation of Iminium Cations by 1a. A solid iminium salt (0.6 mmol) and Cp*Rh(2-(2-pyridyl)phenyl)H (0.003−0.006 mmol) were added to a Fisher-Porter bottle under an argon atmosphere. The bottle was flushed several times with hydrogen gas. Then 10 mL CH_3OH was added by syringe under a flow of hydrogen, and the resulting solution stirred under 50 psig of hydrogen. When the reaction was complete (3.5−18 h), the solvent was removed under vacuum. Then a saturated aq NaOH solution (10 mL) was added to the residue, and the resulting amine was removed by ether extraction (3 × 20 mL). The combined organic layers were dried over $MgSO_4$, and then the ether was removed by vacuum to afford light yellow oil. The results are summarized in Table 1. The ^{1}H NMR spectra of the corresponding amine products were consistent with those reported in the literature.[54]

pK_a of 1a in Acetonitrile. Cp*Rh(2-(2-pyridyl)phenyl)H (**1a**) (1.0 mg, 2.54×10^{-3} mmol) and the phosphazene base **12** (from 2.56×10^{-3} to 6.72×10^{-3} mmol) were dissolved in 0.7 mL CD_3CN in a J-young tube. After the tube was left overnight at room temperature the ^{1}H NMR spectrum showed that equilibrium had been established. The concentrations of the hydride **1a** and the corresponding rhodium anion **13a** were then determined by the integration of the appropriate resonances in the aromatic range. The phosphazene base and the corresponding conjugated Lewis acid concentrations at equilibrium were then calculated from the amount of phosphazene added and the reaction stoichiometry. The equilibrium constant for the deprotonation reaction was then calculated and was used to determine the pK_a value for the hydride complex **1a**. The final pK_a value was then determined by averaging the values from five independent experiments.

Thermodynamic Hydricity Measurement of 1a. Equilibrium Studies of the 1a/5a System with Hydrogen and Et_3N. Cp*Rh(2-(2-pyridyl)phenyl)H (**1a**) (1.0−1.2 mg, 0.0025−0.0031 mmol), [Et_3NH]BF_4 (0.7−1.3 mg, 0.0037−0.0069 mmol), and Et_3N (3.5−9.2 mg, 0.034−0.0091 mmol) were accurately weighed into three NMR tubes, and 0.7 mL CD_3CN was added to each. The tubes were capped with septa, and H_2 was slowly bubbled through a needle into each solution for 15 min, to produce a solution saturated with H_2 under 1 atm pressure. The reactions were monitored by ^{1}H NMR spectroscopy until equilibrium was reached (7 h). The ratio of **1a** to **5a** at equilibrium was determined by integrating the Cp* signals of these complexes. The concentrations of the four components at equilibrium were then calculated from their initial concentrations and the stoichiometry of the reaction. The average value for the equilibrium constant from the three samples was 3.6 (6) atm, which gives a hydride donor ability for **1a** of 49.5 (1) kcal/mol in CD_3CN.

[Cp*Rh(2-(2-pyridyl)phenyl)(*u*-H)Rh(2-(2-pyridyl)phenyl)-Cp*]PF_6 (6/6′). Under an argon atmosphere, 13.1 mg Cp*Rh(2-(2-pyridyl)phenyl)H (**1a**) (0.033 mmol) was mixed together with 18.9 mg [Cp*Rh(2-(2-pyridyl)phenyl)(CH_3CN)]PF_6 (**5a**) (0.032 mmol). Then 2 mL C_6H_6 was added to the mixture. After the resulting suspension was stirred at room temperature for 4h, a red precipitant forms, which was decanted and washed with C_6H_6 three times, and then dried under vacuum to give a red powder **6/6′** (22.4 mg, 75% yield) which contains three dinuclear complexes with the (μ_2-H)Rh_2 structure (ratio is 0.03:1:0.1). IR (ATR) of the mixture **6/6′**: 1689 (br) cm^{-1} (Rh−H−Rh). ^{1}H NMR (400 MHz, THF-d_8) of the major product: δ −19.94 (t, J = 24.2 Hz, 1H, RhHRh), 1.41 (s, 30H, Cp*), 6.80−6.83 (m, 4H), 7.12 (t, J = 7.0 Hz, 2H), 7.28 (t, J = 7.4 Hz, 2H), 7.35 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.4 Hz, 2H), 7.56 (d, J = 7.4 Hz, 2H), 7.88 (d, J = 7.4 Hz, 2H). ^{13}C{^{1}H} NMR (400 MHz, THF-d_8) of the major complex in **6/6′**: δ 9.1 (Cp*), 98.1 (Cp*), 118.8, 122.5, 123.5, 125.8, 129.1, 137.8, 137.9, 144.3, 151.8(HC═N), 164.6, 176.8 (d, J = 144 Hz, Rh−C)). The Rh deuteride Cp*Rh(2-(2-pyridyl)phenyl)D (**1a-*d***) was prepared by stirring Cp*Rh(2-(2-pyridyl)phenyl)Cl with excess $NaBD_4$ in MeOD overnight at room temperature. IR (KBr): 1390 cm^{-1} (Rh−D). [Cp*Rh(2-(2-pyridyl)phenyl)(μ-D)Rh(2-(2-pyridyl)phenyl)Cp*]PF_6 (**6,6′-*d***) was then prepared by reacting Cp*Rh(2-(2-pyridyl)phenyl)D with [Cp*Rh(2-(2-pyridyl)phenyl)(CH_3CN)]PF_6 using the same method as described above. IR (ATR): 1224 (br) cm^{-1} (Rh−D−Rh).

■ ASSOCIATED CONTENT

Supporting Information

^{1}H NMR spectra of equilibrium studies, stopped-flow traces, CV scans, and the statistics of data fitting to appropriate equations. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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