Thermodynamic Studies of $HRh(depx)_2$ and $[(H)_2Rh(depx)_2](CF_3SO_3)$: Relationships between Five-Coordinate Monohydrides and Six-Coordinate Dihydrides

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Four new rhodium complexes, $[Rh(depx)_2](CF_3SO_3)$, $[(H)_2Rh(depx)_2](CF_3SO_3)$, $[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$, and $HRh(depx)_2$ (where depx = α,α′-bis(diethylphosphino)xylene), have been synthesized and characterized. The pK_a values of $[(H)_2Rh(depx)_2]^+$ (30.6 ± 0.3) and $[HRh(depx)_2(CH_3CN)]^{2+}$ (11.5 ± 0.4) in acetonitrile were determined by equilibrium reactions with appropriate bases. The hydride donor ability of $[(H)_2Rh(depx)_2]^+$ (71.6 ± 1.0 kcal/mol) was determined by the heterolytic cleavage of hydrogen by $[HRh(depx)_2(CH_3CN)]^{2+}$ to form $[(H)_2Rh(depx)_2]^+$ in the presence of thioacetamide or benzamide. These equilibrium measurements, the half-wave potentials for the Rh(+1/0) and Rh(0/−1) couples of $[Rh(depx)_2]^+$, and the reversible one-electron oxidation of $HRh(depx)_2$ (all measured at 22 ± 1.5 °C) were used to establish nine heterolytic and homolytic bond-dissociation free energies in acetonitrile. From these relationships, and those established previously for analogous cobalt and platinum complexes, we conclude that the homolytic bond-dissociation free energies of six-coordinate dihydride species are approximately 2 kcal/mol less than those of the corresponding five-coordinate monohydride species derived by deprotonation. Similarly, the pK_a values of six-coordinate dihydride complexes are approximately 2 units lower than the corresponding five-coordinate species formally derived by homolytic bond cleavage.

Introduction

Rhodium hydrides play a central role in a number of important catalytic reactions such as hydrogenation and hydroformylation of olefins. In these reactions, hydrogen is activated by oxidative addition of hydrogen followed by insertion and reductive elimination reactions to produce the alkane or aldehyde products. The hydride intermediates in these reactions may be either five- or six-coordinate with oxidation states of +1 or +3. It is of interest therefore to know how changes in coordination number and oxidation states affect the thermodynamic properties of the Rh−H bond. Understanding those features that determine the various M−H bond-dissociation free energies as a function of coordination number and oxidation state can contribute to our understanding of these reactions as well as a large number of other catalytic reactions.

M−H bonds can be cleaved in one of three ways: $MH \rightarrow M^- + H^+$, $MH \rightarrow M^\bullet + H^\bullet$, or $MH \rightarrow M^+ + H^-$. The free energies associated with these three bond-cleavage reactions in solution are ΔG_{H^+}, $\Delta G_{H^\bullet}$, and ΔG_{H^-}, respectively. Previous studies of $[HM(diphosphine)_2]^+$ complexes (where M = Ni, Pd, or Pt) in acetonitrile solutions have shown that all three of these parameters are dependent on the nature of the metal. The acidities of these complexes follow the order Pd ≥ Ni > Pt; hydride donor abilities, the order Pd ≥ Pt > Ni; and solution homolytic bond-dissociation free energies, the order Pt > Pd > Ni.[1−6] The diphosphine ligands also influence the thermodynamic properties of these complexes. The two heterolytic bond-dissociation free energies are much more sensitive to electron-donating or -withdrawing substituents on the diphosphine ligand than are the homolytic bond-dissociation free energies.[1−6] This is expected, because heterolytic cleavage of the M−H bond results in a change of the charge of the metal complex and a significant redistribution of electron density. As a result, the ability of substituents to stabilize this charge has a significant effect on the free energies of these processes. It has also been shown that the natural bite angle of diphosphine ligands, as defined by previous researchers,[7] exerts a large effect on the hydricity of these complexes, but only minor effects on the pK_a values or the homolytic bond-dissociation free energies.[5] For example, 20 kcal/mol of the measured 27 kcal/mol

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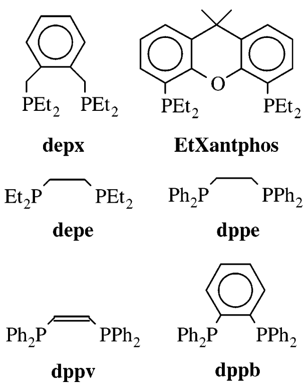
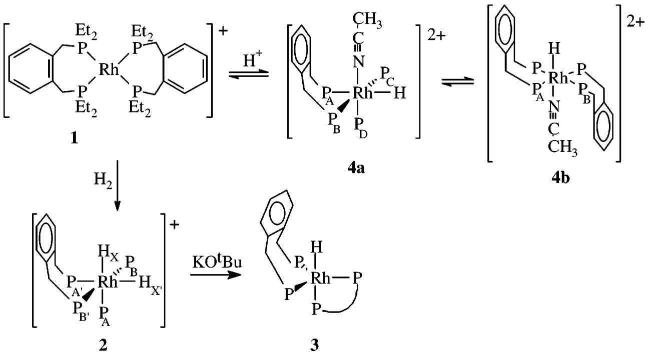
Chart 1



Scheme 1



difference in the hydride donor abilities of $[HPd(EtXantphos)_2]^+$ and $[HPd(depe)_2]^+$ is attributed to the 33° difference in natural bite angles of the two diphophine ligands.[5] (See Chart 1 for structures and abbreviations of diphosphine ligands.) For platinum, this effect is even larger: 28 kcal/mol of the measured 32 kcal/mol difference in hydride donor abilities of $[HPt(EtXantphos)_2]^+$ and $[HPt(depe)_2]^+$ is attributed to the 33° difference in natural bite angles of the two diphosphine ligands.[6] In contrast, the homolytic bond-dissociation free energy in acetonitrile for $[HPd(EtXantphos)_2]^+$ and $[HPd(depe)_2]^+$ is 57 kcal/mol for both complexes.[5] The large effect of the chelate bite angle on hydride donor ability of the $[HM(diphosphine)_2]^+$ complexes can be traced to the energy of the LUMO of the corresponding $[M(diphosphine)_2]^{2+}$ complexes.[8] On the basis of these previous studies, a reasonable understanding of the factors that control the thermodynamic properties of the M−H bond of five-coordinate $[HM(diphosphine)_2]^+$ complexes (where M = Ni, Pd, or Pt) is emerging.

Much less is known about the factors controlling the thermodynamic properties of octahedral dihydride complexes. The objective of the present study is to determine what relationships exist between the thermodynamic properties of the more extensively studied five-coordinate monohydrides and six-coordinate dihydrides. We are also interested in how changes in oxidation state affect the thermodynamic parameters of the M−H bond. An understanding of how M−H bond free energies change as a function of oxidation state, and coordination number could be useful in understanding known catalytic processes and, perhaps, in designing and controlling new ones.

Results

Synthesis and Characterization of Complexes. Reaction of $[Rh(COD)_2]CF_3SO_3$ (where COD is 1,5-cyclooctadiene) with 2 equiv of depx in acetonitrile results in the formation of orange microcrystalline $[Rh(depx)_2]CF_3SO_3$, **1**. A doublet is observed in the ^{31}P NMR spectrum at 12.7 ppm, consistent with coordination of the depx ligand to rhodium, and the ^1H NMR spectrum exhibits the resonances expected for a coordinated depx ligand (see Experimental Section). Elemental analysis and the lack of resonances attributable to the COD ligand are consistent with the formulation of this complex as $[Rh(depx)_2]CF_3SO_3$.

$[Rh(depx)_2]CF_3SO_3$ reacts rapidly and irreversibly with H_2 to form colorless $[(H)_2Rh(depx)_2]CF_3SO_3$, **2**, as shown in the left reaction in Scheme 1. The ^{31}P NMR spectrum exhibits two broad resonances at 15.9 and 3.4 ppm in deuteroacetonitrile at room temperature. Warming this sample to 75 °C results in a sharpening and the splitting of each resonance into a broad doublet, but a high-temperature limit was not reached. Cooling a sample of this complex to −60 °C in CD_2Cl_2 resulted in two doublets of triplets, consistent with a *cis*-octahedral dihydride complex. The triplet structure is attributed to the coupling of the two *trans*-phosphorus atoms (P_B and $P_{B'}$) and two *cis*-phosphorus atoms atoms (P_A and $P_{A'}$) to each other. The doublet structure arises from coupling to rhodium (see Experimental Section for detailed spectral data). The hydride region of the proton NMR spectrum at ambient temperature consists of a broad doublet of pentets, consistent with the XX′ portion of an AA′BB′XX′ spectrum. An infrared band at 2024 cm^{-1} is assigned to a Rh−H stretching vibration. The dynamic process that leads to the broadening of resonances in both the ^1H and ^{31}P NMR spectra is attributed to conformational changes in the depx ligand. This may be due to interconversion between boat and chair conformations of the seven-membered ring formed by coordination of depx to rhodium. Alternatively, three different conformational isomers are possible in which the arene rings of the ligand backbones fold either toward or away from the hydride and phosphorus ligands. Previous structural studies indicate that the boat conformation is common for this ligand.[5,9]

Deprotonation of $[(H)_2Rh(depx)_2](CF_3SO_3)$ with potassium *tert*-butoxide in acetonitrile results in the precipitation of yellow microcrystalline $HRh(depx)_2$, **3**, as shown by the bottom reaction of Scheme 1. The ^{31}P NMR spectrum of this complex at room temperature is a broad resonance at 14.7 ppm. Upon warming to 60 °C, the resonance sharpens to a doublet with $^1J_{RhP} = 145$ Hz. At −80 °C, a broad doublet (17.2 ppm, $^1J_{RhP} = 124$ Hz) and a broad doublet of triplets (13.9 ppm, $^1J_{RhP} = 153$ Hz) are observed. The temperature dependence of the ^{31}P NMR spectra is attributed to conformational changes of the diphosphine ligand, which produces two different environments for the phosphorus atoms of this complex. Similar behavior has been observed previously for closely related palladium and platinum complexes.[5,6]

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The hydride region at room temperature is an overlapping doublet of pentets arising from coupling to four equivalent phosphorus atoms and to rhodium. The infrared spectrum of a Nujol mull of this complex exhibits a band at 1970 cm^{-1} assigned to a Rh−H stretch. These data are all consistent with a fluxional, five-coordinate, 18-electron HMP_4 complex. Hydride complexes of this type typically have distorted trigonal bipyramidal structures with an apical hydride, as shown in Scheme 1.[10]

Protonation of $[Rh(depx)_2]CF_3SO_3$ with triflic acid in acetonitrile followed by precipitation with ether results in the formation of a white crystalline solid that is formulated as $[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$ (**4**, top reaction of Scheme 1). In CD_2Cl_2, the ^{31}P NMR spectrum of $[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$ at −80 °C consists of four broad resonances. The resonance that appears as a doublet of quartets at 22.2 ppm is assigned to P_D in structure **4a**, *cis*-$[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$, of Scheme 1. The resonance at −19.1 ppm is a broad doublet due to coupling to rhodium. A proton-coupled experiment indicates that this resonance is split into a second doublet with $^2J_{PH} = 163$ Hz. On this basis, this resonance is assigned to the phosphorus atom *trans* to the hydride ligand, P_A in structure **4a**. The remaining two phosphorus atoms, P_B and P_C, are *trans* to each other and exhibit a large *trans* coupling of 304 Hz. These doublets are split further into a doublet from coupling to rhodium and a triplet by coupling to phosphorus atoms A and D. The hydride resonance of this complex is a broad doublet of doublets of quartets. The largest doublet coupling of 163 Hz arises from coupling to the *trans*-phosphorus atom, P_A; rhodium coupling to the hydride ligand of 18 Hz produces a second doublet splitting; finally, coupling of the hydride ligand to the three *cis*-phosphorus atoms, P_B, P_C, and P_D ($^2J_{PH} = 12$ Hz), results in a quartet pattern. The infrared spectrum of a Nujol mull of this complex exhibits a band at 2024 cm^{-1} assigned to the Rh−H stretching vibration. These data are all consistent with the formulation of this complex as *cis*-$[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$. In CD_3CN solutions, two additional doublets of triplets are observed in the ^{31}P NMR spectrum at 25.4 and 19.6 ppm that are assigned to the *trans*-isomer, structure **4b** of Scheme 1. The ratio of *cis*- to *trans*-isomers in acetonitrile is approximately 6:1 at room temperature. The nonequivalence of the phosphorus atoms in the *trans*-isomer, **4b**, is attributed to ligand conformations. Consistent with the ^{31}P NMR spectra, a second broad hydride resonance is observed at −18.6 ppm in the ^1H NMR spectrum in acetonitrile. This chemical shift is similar to that observed previously for $[HRh(dppe)_2(CH_3CN)]^{2+}$ (−15.9 ppm, where dppe is 1,2-bis(diphenylphosphino)ethane).[11] In summary, ^{31}P and ^1H NMR data for $[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$ are consistent with a single *cis*-isomer in CD_2Cl_2 and an approximately 6:1 ratio of *cis*- to *trans*-isomers in CD_3CN.

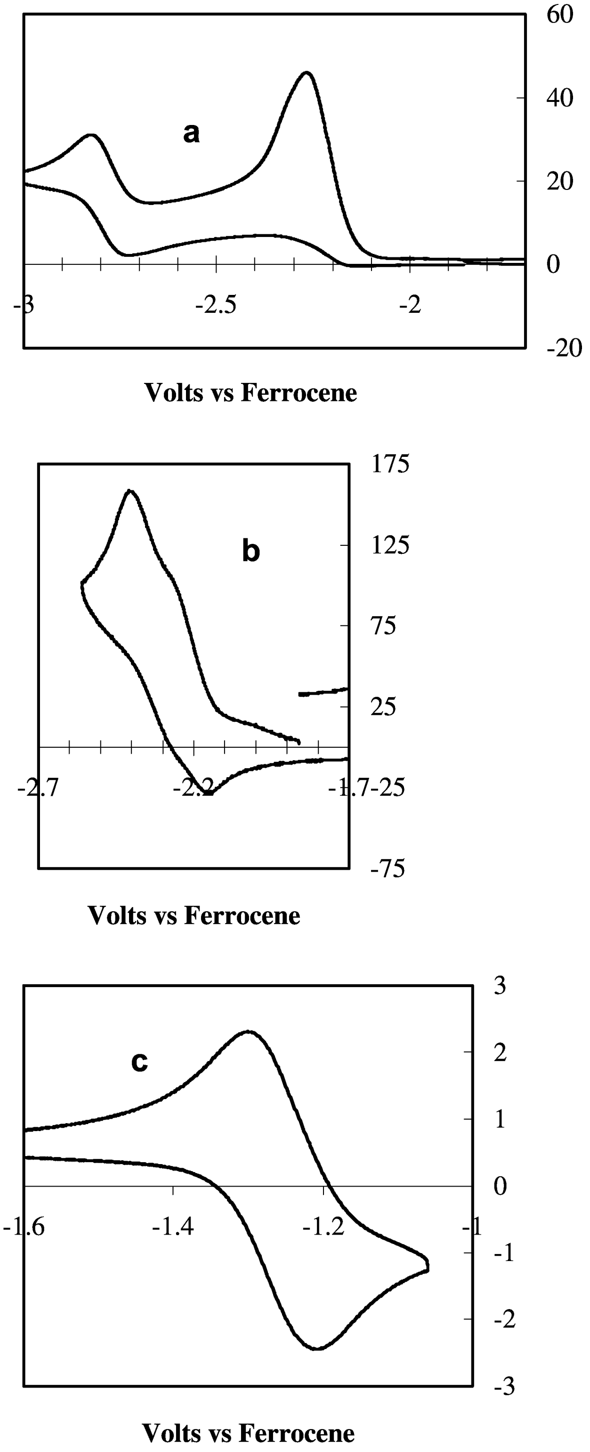

Figure 1. (a) Cyclic voltammogram of a 4×10^{-3} M solution of $[Rh(depx)_2]CF_3SO_3$ in 0.2 M NBu_4PF_6/acetonitrile at a scan rate of 0.1 V/s. (b) Cyclic voltammogram of a 2.4×10^{-3} M solution of $[Rh(depx)_2]CF_3SO_3$ in 0.2 M NBu_4PF_6/acetonitrile at a scan rate of 4 V/s. (c) Cyclic voltammogram of a 1.3×10^{-3} M solution of $HRh(depx)_2$ in 0.2 M NBu_4PF_6/benzonitrile at a scan rate of 0.1 V/s.

Electrochemical Studies. Cyclic voltammograms of $[Rh(depx)_2](CF_3SO_3)$ in acetonitrile (22 ± 1.5 °C) are shown in Figure 1, traces a and b. Trace a was recorded at a scan rate of 0.1 V/s, and trace b was recorded at 4 V/s. In trace a, one irreversible reduction ($E_P = -2.26$ V) is observed. At the higher scan rate of 4 V/s shown in trace b, this wave splits into two incompletely resolved waves. These two waves are assigned to the Rh(+1/0) couple ($E_{1/2} = -2.21 \pm 0.02$ V, $\Delta E_p = 120$ mV) and Rh(0/−1) couple ($E_{1/2} = -2.33 \pm 0.02$ V, $\Delta E_p = 140$ mV).

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The potentials of the two waves associated with the Rh(+1/0) and Rh(0/−1) couples in acetonitrile are used in the calculation of various solution bond-dissociation free energies (see Supporting Information for details). The 0.12 V difference in the half-wave potentials is similar to the 0.08 V difference in half-wave potentials observed for the Pd(+2/+1) and Pd(+1/0) couples of $[Pd(depx)_2](BF_4)_2$.[5] In tetrahydrofuran, these couples are more completely resolved. A reversible Rh(+1/0) couple is observed at −2.14 V, and a quasi-reversible Rh(0/−1) couple is observed at −2.39 V. In previous studies of $[M(diphosphine)_2]^+$ complexes, it has been found that these two couples are typically separated by an additional 120 mV in less polar solvents such as tetrahydrofuran and dichloromethane.[5,8a]

The irreversible nature of the reduction wave in acetonitrile at 0.1 V/s, trace a, is attributed to rapid protonation following the reduction of $Rh(depx)_2$ to $[Rh(depx)_2]^-$. When the initial scan direction is negative and the Rh(0/−1) couple is traversed first, a new reversible wave at −1.27 V is observed in acetonitrile. As discussed in the next paragraph, $HRh(depx)_2$ exhibits a reversible wave at −1.26 V in benzonitrile, and the $[Rh(depx)_2]^-$ species is a powerful base that should be capable of deprotonating either the $NBu_4{}^+$ cation of the supporting electrolyte or acetonitrile (see Discussion, Acidities of Rhodium Complexes).

In addition to the irreversible wave associated with the reduction of $[Rh(depx)_2]^+$ to form $HRh(depx)_2$, shown in trace a of Figure 1, a reversible reduction wave is observed at −2.77 V ($\Delta E_p = 95$ mV) that is assigned to the reduction of the depx ligand. The ratio of the peak height of the irreversible two-electron reduction wave at −2.26 V to the peak height of the wave at −2.77 V is 2.8, which is consistent with a quasi-reversible one-electron reduction for the wave at −2.77 V.[12] Finally, an irreversible oxidation wave ($E_{pa} = +0.16$ V at 0.1 V/s) and an associated irreversible cathodic wave ($E_{pc} = -0.68$ V) are also observed for $[Rh(depx)_2]^+$ (not shown in Figure 1). These irreversible processes were not studied in any further detail.

The complex $HRh(depx)_2$ is not soluble in acetonitrile, and electrochemical studies in this solvent were not possible. In previous studies of $Pd(depx)_2$, $[Pd(depx)_2](BF_4)_2$, and other $Pd(diphosphine)_2$ and $[Pd(diphosphine)_2](BF_4)_2$ complexes, it was found that half-wave potentials in benzonitrile and acetonitrile were the same within experimental error (±0.02 V), which indicates that half-wave potentials measured in benzonitrile provide reliable estimates of half-wave potentials in acetonitrile.[2,5] A reversible one-electron oxidation wave is observed at −1.26 V for $HRh(depx)_2$ in benzonitrile, trace c of Figure 1. This wave is diffusion-controlled, as indicated by a linear plot of the peak current versus the square root of the scan rate. In addition, ΔE_p is 77 mV compared to a ΔE_p of 72 mV for the oxidation of permethylferrocene in the same solution. Reversible one-electron oxidations of the closely related $HRh(dppe)_2$ and $HRh(CO)(PPh_3)_3$ complexes have also been reported.[13,14] An irreversible oxidation is also observed with a peak potential at −0.83 V. This peak did not become reversible at scan rates up to 10 V/s, and this oxidation process was not studied further. In tetrahydrofuran, the same two oxidation waves are observed, and an additional quasi-reversible reduction wave is observed at −3.0 V that is attributed to reduction of the depx ligands.

Equilibrium Studies. The reaction of $[(H)_2Rh(depx)_2](CF_3SO_3)$ with $(Me_2N)_3P{=}NMe$ to form $HRh(depx)_2$ is reversible, as shown in eq 1. This reaction was monitored by ^1H and ^{31}P NMR spectroscopy in both directions in benzonitrile at 22 ± 1.5 °C, and the hydride resonances of $[(H)_2Rh(depx)_2]^+$ and $HRh(depx)_2$ were integrated to determine the ratios of these two compounds. The ratio of protonated base to base was determined from the stoichiometry of the reaction. These ratios were used to calculate an equilibrium constant of $9 \times 10^{-4} \pm 2 \times 10^{-4}$ for reaction 1 $\{K_{eq}(1) = [\mathbf{3}][(Me_2N)_3P{=}NHMe^+]/[\mathbf{2}][(Me_2N)_3P{=}NMe]\}$. The uncertainties indicated for all equilibrium measurements reported in this work represent 2 standard deviations. Addition of $pK_{eq}(1)$ to the pK_a of $[(Me_2N)_3P{=}NHMe](BF_4)$ (27.6 in acetonitrile)[15] gives a pK_a value of 30.6 ± 0.3 for $[(H)_2Rh(depx)_2](CF_3SO_3)$. In this calculation, it is assumed that the *difference* in pK_a values measured in benzonitrile and acetonitrile is the same. Previous studies of Ni and Pt complexes indicate that this is an accurate assumption.[2,4]

$$\underset{\mathbf{2}}{[(H)_2Rh(depx)_2]^+} + (Me_2N)_3P{=}NMe = \underset{\mathbf{3}}{HRh(depx)_2} + [(Me_2N)_3P{=}NHMe]^+ \quad (1)$$

An equilibrium is also observed for the reaction of $[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$ with anisidine in acetonitrile, as shown in reaction 2. This reaction is slow and requires about a week to come to equilibrium. In addition to deprotonation at rhodium, loss of acetonitrile also occurs. An equilibrium constant for this reaction $\{K_{eq}(2) = [\mathbf{1}][p\text{-}CH_3OC_6H_4NH_3{}^+]/[\mathbf{4}][p\text{-}CH_3OC_6H_4NH_2] = 0.6 \pm 0.3\}$ was determined from an integration of the ^{31}P NMR spectra and stoichiometric relationships. Addition of $pK_{eq}(2)$ to the pK_a of $p\text{-}CH_3OC_6H_4NH_3{}^+$ (11.3 in acetonitrile)[16] gives a pK_a value of 11.5 ± 0.4 for $[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$. The equilibrium expression does not show the acetonitrile concentration, because the activity of the solvent was taken as 1. This choice of a standard state has the advantage that two acids in equilibrium with each other will have the same equilibrium constant (and same pK_a), even if solvent coordination occurs for one and not the other. However, because solvent coordination occurs in reaction 2 and the strength of the metal−solvent interaction may vary

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Scheme 2

	ΔG (kcal/mol)	
	$PhC(O)NH_2$	$CH_3C(S)NH_2$
$\mathbf{2} + CH_3CN + [Hamide]^+ \rightarrow \mathbf{4} + amide + H_{2(g)}$	1.2 ± 0.2	1.5 ± 0.2
$amide + H^+ \rightarrow [Hamide]^+$	-5.1 ± 0.3	-6.4 ± 0.3
$H_{2(g)} \rightarrow H^+_{(CH3CN)} + H^-_{(CH3CN)}$	76.0	76.0
$[(H)_2Rh(depx)_2]^+ + CH_3CN \rightarrow [HRh(depx)_2(CH_3CN)]^{2+} + H^-$	72.1 ± 0.5	71.1 ± 0.5
	average = 71.6 ± 1.0	

with solvent, these pK_a values are not readily transferred to another solvent.

$$\underset{\mathbf{4}}{[HRh(depx)_2(CH_3CN)]^{2+}} + p\text{-}CH_3OC_6H_4NH_2 = \underset{\mathbf{1}}{[Rh(depx)_2]^+} + p\text{-}CH_3OC_6H_4NH_3{}^+ + CH_3CN \quad (2)$$

In acetonitrile, reaction 3 reaches an equilibrium in 1−4 h under 1.0 atm of H_2, as indicated by a constant integration ratio of the hydride resonances of $[HRh(depx)_2(CH_3CN)]^{2+}$ to $[(H)_2Rh(depx)_2]^+$ for nearly 24 h. The reverse of this reaction is the heterolytic cleavage of hydrogen in which thioacetamide acts as a base. Similarly, reaction 4 (under 1.0 atm of H_2) is observed if benzamide is used as a base. However, in the reverse of reactions 3 and 4, unidentified hydrides (e.g., a complex multiplet in the ^1H NMR spectrum at −16.5 ppm for benzamide) are produced that became the dominant hydrides before the reactions reached equilibrium. These new hydrides are believed to be $[HRh(depx)_2(amide)]^{2+}$ complexes. The same hydrides were observed when running reactions 3 and 4 in the forward directions; however they are not dominant prior to reaching an equilibrium.

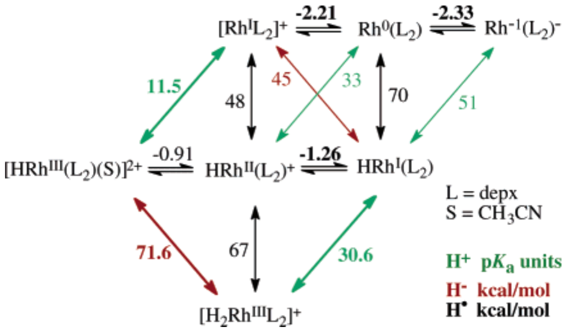
$$\underset{\mathbf{2}}{[(H)_2Rh^{III}(depx)_2]^+} + CH_3C(S)NH_3{}^+ + CH_3CN = \underset{\mathbf{4}}{[HRh^{III}(depx)_2(CH_3CN)]^{2+}} + CH_3C(S)NH_2 + H_2 \quad (3)$$

$$\underset{\mathbf{2}}{[(H)_2Rh^{III}(depx)_2]^+} + PhC(O)NH_3{}^+ + CH_3CN = \underset{\mathbf{4}}{[HRh^{III}(depx)_2(CH_3CN)]^{2+}} + PhC(O)NH_2 + H_2 \quad (4)$$

Using the ratios obtained in both the forward and reverse directions, equilibrium constants of 0.08 ± 0.02 and 0.13 ± 0.04 atm were obtained for reactions 3 and 4, respectively, using the expression $K_{eq} = [\mathbf{4}][H_2][amide]/[\mathbf{2}][Hamide^+]$. In this case, the activity of hydrogen at 1 atm is taken as unit activity. This choice of standard state is made to remain internally consistent with the choice of standard states used for the heterolytic cleavage of hydrogen in acetonitrile (see third reaction of Scheme 2).[17,18]

Solution Bond-Dissociation Free Energies. The equilibrium data for the protonation of $[(H)_2Rh(depx)_2]^+$ to form H_2 (reactions 3 and 4), the pK_a values of the protonated bases (thioacetamide, 4.7; benzamide, 3.7),[19] and the energy required for the heterolytic cleavage of hydrogen in acetonitrile (76.0 kcal/mol)[17,18] can be used in a thermodynamic cycle to calculate a hydride donor ability of 71.6 ± 1.0 kcal/mol for $[(H)_2Rh(depx)_2]^+$, **2**, as shown in Scheme 2. As indicated in this scheme, coordination of acetonitrile to rhodium occurs when $[(H)_2Rh(depx)_2]^+$ acts as a hydride donor. As discussed above for the acidity of $[HRh(depx)_2(CH_3CN)]^{2+}$, **4**, the activity of the solvent is taken as unity, because this choice of standard state has the advantage that two hydrides in equilibrium with each other in acetonitrile via a hydride-transfer reaction will have the same hydricity regardless of whether solvent coordination occurs. It is the ability of hydride complexes to donate a H^- ion in acetonitrile that is of interest, not whether solvent coordination occurs. However, as with the acidity measurements associated with reaction 2, even relative hydricity values should not be transferred to different solvents for complexes in which solvent coordination accompanies hydride transfer.

Scheme 3



Similar thermodynamic cycles (all of which are shown in the Supporting Information) can be used to calculate the thermodynamic parameters shown in Scheme 3. In Scheme 3, black vertical arrows represent homolytic bond-dissociation reactions. The associated numbers are the homolytic solution bond-dissociation free energies in units of kcal/mol. Green arrows pointing up and to the right indicate proton-transfer reactions, and the pK_a values shown are for the corresponding acids in aceto-

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nitrile. Red arrows pointing up and to the left represent hydride-transfer reactions, and the free energies associated with these reactions are given in kcal/mol. Reversible arrows between columns indicate one-electron-transfer reactions. The corresponding half-wave potentials are in volts, and they are referenced to the ferrocene/ferrocenium couple. The parameters shown in bold represent the values obtained by direct experimental measurements. Normal text indicates values determined using the thermodynamic cycles (given in the Supporting Information). The uncertainties shown in Scheme 3 are ±0.4 pK_a units for the measured pK_a values and ±2 pK_a units for those calculated from thermodynamic cycles. The uncertainties on the homolytic bond-dissociation free energies and the hydride donor abilities are estimated to be ±3 kcal/mol. A more complete discussion of the estimated errors is also provided in the Supporting Information.

Discussion

Hydricity of $HRh(depx)_2$ and $[(H)_2Rh(depx)_2]^+$. Two hydride-transfer reactions are indicated by red arrows in Scheme 3, one for $HRh(depx)_2$ (45 kcal/mol) and the other for $[(H)_2Rh(depx)_2]^+$ (72 kcal/mol). The lower value for the hydride donor ability of $HRh(depx)_2$ compared to $[(H)_2Rh(depx)_2]^+$ indicates that $HRh(depx)_2$ is the better hydride donor by 27 kcal/mol. Similarly, the hydride donor abilities of $[(H)_2Co(dppe)_2]^+$ (65 kcal/mol) and $HCo(dppe)_2$ (49 kcal/mol) indicate the five-coordinate hydride is a 16 kcal/mol better hydride donor than the corresponding six-coordinate dihydride.[20] A number of factors contribute to the difference in hydride donor abilities of these five- and six-coordinate hydrides (e.g., charge, solvation of the product, chelate bite size), and a detailed quantitative understanding will require more systematic studies. However, the two results for rhodium and cobalt indicate that protonation of a five-coordinate hydride will produce a large (15−30 kcal/mol) decrease in hydricity.

The only other rhodium hydrides for which the hydride donor ability has been reported is $HRh(dppb)_2$ (34 kcal/mol in acetonitrile, where dppb is 1,2-bis(diphenylphosphino)benzene)[11] and $[HRh(TSPP)(H_2O)]^{4-}$ (54.9 kcal/mol in water, where TSPP is tetra(*p*-sulfonatophenyl)porphyrin).[21] Solvation effects are expected to be large in water because of hydrogen bonding between the protons of water molecules and the hydride ligand. In addition, solvent coordination to the metal will also contribute to differences in hydricity. For these reasons, direct comparisons of the values obtained for $[HRh(TSPP)(H_2O)]^{4-}$ in water with those obtained for rhodium diphosphine complexes in acetonitrile are not meaningful.

The hydride donor abilities of $HRh(dppb)_2$ and $HRh(depx)_2$ (both in acetonitrile) differ by 11 kcal/mol. This difference is reasonable when previously studied contributions of natural bite angles and ligand substituents are taken into account. A comparison of the hydride donor abilities of $[HPd(depx)_2]^+$ (62 kcal/mol) and $[HPd(depe)_2]^+$ (43 kcal/mol) in acetonitrile indicates that there is a 19 kcal/mol difference in the hydride donor ability produced by these ligands for palladium.[5] If a similar difference is observed for rhodium complexes, $HRh(depe)_2$ should have a hydride donor ability of 26 kcal/mol. Similarly, the hydride donor abilities of $[HNi(dppv)_2]^+$ (66 kcal/mol where dppv is 1,2-bis(diphenylphosphino)ethene) and $[HNi(depe)_2]^+$ (56 kcal/mol) differ by 10 kcal/mol.[2] Because the electronic and natural bite angles of dppb and dppv should be very similar, it is anticipated that changing from depe to dppb should result in an approximately 10 kcal/mol increase in the free energy for hydride loss from $HRh(depe)_2$ compared to $HRh(dppb)_2$ or an estimated 9 kcal/mol difference in the hydride donor abilities of $HRh(depx)_2$ and $HRh(dppb)_2$. The observed 11 kcal/mol difference in the hydride donor abilities of $HRh(dppb)_2$ and $HRh(depx)_2$ is in good agreement with this estimated 9 kcal/mol difference that is based on previously observed chelate bite effects for palladium and substituent effects for nickel.

Besides $[(H)_2Rh(depx)_2]^+$, hydride donor abilities have been measured for only four other six-coordinate metal hydrides in acetonitrile: $[HW(CO)_4(PPh_3)]^-$ (36 kcal/mol), $[HW(CO)_4P(OMe)_3]^-$ (37 kcal/mol), $[HW(CO)_5]^-$ (40 kcal/mol), and $[(H)_2Co(dppe)_2]^+$ (65 kcal/mol).[20,22] Because of the relatively few examples for six-coordinate hydrides, the factors controlling hydricity for this class of complex are not well understood. The six-coordinate rhodium and cobalt complexes are much poorer hydride donors than the tungsten complexes. The positive charge on these complexes compared to the negative charge on the tungsten complexes probably plays a major role in the observed differences in hydricity. It is somewhat surprising that $[(H)_2Co(dppe)_2]^+$, which has more electron-withdrawing substituents, is a better hydride donor than $[(H)_2Rh(depx)_2]^+$, but the contributions of substituents, metal, and chelate bite size in six-coordinate complexes have not been systematically studied. In addition, differences in cobalt−acetonitrile and rhodium−acetonitrile bond energies will also contribute to the difference in the hydride donor abilities of these two complexes.

Solution Homolytic Bond-Dissociation Free Energies. The free energies for the homolytic cleavage of the Rh−H bonds of $[(H)_2Rh(depx)_2]^+$, $[HRh(depx)_2]^{2+}$, and $HRh(depx)_2$ are 67, 48, and 70 kcal/mol, respectively (see Scheme 3). These values indicate that protonation of $HRh(depx)_2$ to form $[(H)_2Rh(depx)_2]^+$ results in a small decrease in the homolytic bond-dissociation free energy. Similar results have been obtained previously for cobalt and platinum complexes. The homolytic bond-dissociation free energy of $[(H)_2Pt(EtXantphos)_2]^{2+}$ (68 kcal/mol) is 1 kcal/mol less than that of $[HPt(EtXantphos)_2]^+$ (69 kcal/mol), and the homolytic bond-dissociation free energy of $[(H)_2Co(dppe)_2]^+$ (58 kcal/mol) is 1 kcal/mol less than that of $HCo(dppe)_2$ (59 kcal/mol).[6,20] On this basis, it is expected that protonation of five-coordinate hydrides to produce six-coordinate dihydrides will produce a small (approximately 2 kcal/mol) decrease in the homolytic bond-dissociation free energy. In contrast, oxidation of $HRh(depx)_2$ to form $[HRh(depx)_2]^+$

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results in a large (22 kcal/mol) decrease in the homolytic bond-dissociation free energy. Large decreases of 24 and 9 kcal/mol are also observed upon oxidation of $[HPt(EtXantphos)_2]^+$ and $HCo(dppe)_2$, respectively.[6,20] These data are consistent with homolytic bond-dissociation free energies being much more sensitive to changes in electron count than to changes in charge produced by protonation. Oxidation of seven-coordinate $CpCr(CO)_2(L)H$ complexes (where Cp = C_5H_5 and L = CO, $P(OMe)_3$, PPh_3, and PEt_3) and $TpM(CO)_3H$ complexes (where Tp = hydridotris(pyrazolyl)borate and M = Cr, Mo, and W) produces a 6−11 kcal/mol decrease in homolytic bond-dissociation enthalpies.[23,24]

The sum of the two successive homolytic bond-dissociation free energies for $[(H)_2Rh(depx)_2]^+$ (115 kcal/mol) indicates that the oxidative addition of hydrogen to $[Rh(depx)_2]^+$ is downhill by approximately 11 kcal/mol, because the free energy for the homolytic cleavage of gaseous hydrogen to form hydrogen atoms in acetonitrile is estimated to be 103.6 kcal/mol.[17] This is consistent with the observed irreversible addition of H_2 to $[Rh(depx)_2]^+$. Similarly, disproportionation of $[HRh^{II}(depx)_2]^+$ to form $[H_2Rh^{III}(depx)_2]^+$ and $[Rh^{I}(depx)_2]^+$ should be favored by 9 kcal per mol of $[HRh^{II}(depx)_2]^+$. Although $[HRh^{II}(depx)_2]^+$ forms reversibly upon oxidation of $HRh(depx)_2$ in benzonitrile and THF, it is thermodynamically unstable.

A Rh−D homolytic bond-dissociation *free energy* of 60 kcal/mol has been reported for $[DRh(TSPP)(D_2O)]^{4-}$ in water and a homolytic bond-dissociation *enthalpy* value of 62 kcal/mol for HRh(OEP) (where OEP is octaethylporphyrin) in benzene.[21,25] These values suggest that the homolytic bond-dissociation enthalpies are largely solvent independent and that solvent coordination does not have a large effect on these energies. If so, HRh(OEP) would be expected to have a bond-dissociation enthalpy in acetonitrile of 62 kcal/mol, which would correspond to a free energy of approximately 57 kcal/mol after correcting for entropy effects ($T\Delta S = 4.8$ kcal/mol).[17] This value is approximately 10 kcal/mol less than the value observed for $[(H)_2Rh(depx)_2]^+$. An average bond-dissociation enthalpy of 58 kcal/mol has been reported for $(H)_2Rh[P(4\text{-tolyl})_3]_3Cl$ in toluene.[26] Because this value was obtained from the oxidative addition of hydrogen, only average bond-dissociation enthalpies could be obtained, and the free energies of the first and second bond cleavage reactions can differ markedly, as shown in Scheme 3.

Acidities of Rhodium Complexes. The four pK_a values shown in Scheme 3 for $[HRh(depx)_2(CH_3CN)]^{2+}$, $[HRh(depx)_2]^+$, $HRh(depx)_2$, and $[(H)_2Rh(depx)_2]^+$ range from 11.5 to 51 in acetonitrile. For comparison, the pK_a values of $[HRh(dppe)_2(CH_3CN)]^{2+}$ and $[HRh(dppb)_2(CH_3CN)]^{2+}$ are 9.0 and 9.4, respectively. The latter two complexes with phenyl substituents are somewhat more acidic than $[HRh(depx)_2(CH_3CN)]^{2+}$ (pK_a = 11.5). From a comparison of $[HRh(depx)_2(CH_3CN)]^{2+}$, $[HRh(depx)_2]^+$, and $HRh(depx)_2$, it can be seen that sequential reduction of the metal results in strongly increasing pK_a values. These increases in pK_a values upon reduction by 21 and 18 pK_a units are comparable to those reported for $CpM(CO)_2(L)H$ hydrides (where M = Cr, Mo, W and L = CO or PR_3) and their oxidized partners, which are in the range of 20−25 pK_a units.[24,27] The very high pK_a value of $HRh(depx)_2$ (51) is consistent with the interpretation that the irreversible reduction of $Rh(depx)_2$ to $[Rh(depx)_2]^-$ observed at slow sweep rates by cyclic voltammetry involves a protonation of the metal. Because the acidity of five-coordinate 18-electron metal hydrides follows the order second row > first row > third row,[1] the reduction of $[Ir(diphosphine)_2]^+$ complexes to $[Ir(diphosphine)_2]^-$ complexes should generate extremely powerful bases.

It is also apparent from Scheme 3 that the oxidation of $HRh(depx)_2$ produces a slightly smaller decrease in the acidity than protonation; that is, the pK_a of $[(H)_2Rh^{III}(depx)_2]^+$ is 2 or 3 units less than that of $[HRh^{II}(depx)_2]^+$. Similarly, the pK_a value of $[(H)_2Pt(EtXantphos)_2]^{2+}$ (7) is the same as that of $[HPt(EtXantphos)_2]^{2+}$ (7), and the pK_a value of $[(H)_2Co(dppe)_2]^+$ (23) is 1 unit less than that of $[HCo(dppe)_2]^+$ (24).[6,20] On this basis, it appears that adding 1 or 2 pK_a units to the pK_a value of a six-coordinate dihydride may provide a reasonable estimate of the pK_a of the corresponding five-coordinate 17-electon complexes. The pK_a values of these five- and six-coordinate hydrides appear to be sensitive to the charge on the complex, but they are relatively insensitive to electron count.

Summary

Four new rhodium complexes, $[Rh(depx)_2](CF_3SO_3)$, $[(H)_2Rh(depx)_2](CF_3SO_3)$, $[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$, and $HRh(depx)_2$, have been synthesized and characterized. The reversible deprotonation reaction of $[(H)_2Rh(depx)_2]^+$ with $(Me_2N)_3P{=}NMe$ to produce $HRh(depx)_2$ was used to establish the pK_a of $[(H)_2Rh(depx)_2]^+$. Similarly, the reversible protonation of $[Rh(depx)_2]^+$ with $p\text{-}CH_3OC_6H_4NH_3^+$ was used to determine the pK_a of $[HRh(depx)_2(CH_3CN)]^{2+}$. Finally, the heterolytic cleavage of hydrogen by $[HRh(depx)_2(CH_3CN)]^{2+}$ to form $[(H)_2Rh(depx)_2]^+$ in the presence of thioacetamide or benzamide was used to determine the hydride donor ability of $[(H)_2Rh(depx)_2]^+$. These equilibrium measurements together with the half-wave potentials for the two quasi-reversible one-electron reductions of $[Rh(depx)_2]^+$ and the reversible one-electron oxidation of $HRh(depx)_2$ were used to establish nine heterolytic and homolytic bond-dissociation free energies that relate seven different species to each other, as shown in Scheme 3. From these relationships, and those established previously for related cobalt and platinum complexes, it appears that the homolytic bond-dissociation free energies of six-coordinate dihydrides are approximately 2 kcal/mol less than the corresponding five-coordinate monohydrides formed by deprotonation. Similarly, the acidity of five-coordinate 17-electron monohydrides are 1−3 pK_a units larger than the corresponding dihydride complexes from which they are derived by homolytic bond cleavage. These preliminary results suggest that the thermodynamic properties of six-

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coordinate dihydride species are related to those of the corresponding five-coordinate hydride species derived by homolytic bond cleavage and deprotonation by predictable amounts. These relationships can be used to estimate pK_a values and homolytic bond-dissociation free energies for one class of compounds if those of the other are known. Also from Scheme 3, it is apparent that electron-transfer reactions can be used to trigger large changes in the solution bond-dissociation free energies of these complexes. It may be possible to use such changes in oxidation state to turn catalytic reactions on and off in a controlled and predictable manner.

Experimental Section

Physical Measurements. NMR spectra were recorded on a Varian Inova 400 MHz spectrometer. ^{1}H chemical shifts are reported relative to tetramethylsilane using residual solvent protons as a secondary reference. ^{31}P chemical shifts are reported relative to external phosphoric acid, and all ^{31}P NMR spectra were proton decoupled unless stated otherwise. All electrochemical measurements were carried out under an N_2 atmosphere in 0.3 M Et_4NBF_4 in acetonitrile or in 0.2 M Bu_4NBF_4 in benzonitrile or dichloromethane. Cyclic voltammetry experiments were carried out on a Cypress Systems computer-aided electrolysis system. The working electrode was a glassy carbon disk (2 mm diameter), and the counter electrode was a glassy carbon rod. A platinum wire immersed in a permethylferrocene/permethylferrocenium solution was used to fix the potential. Ferrocene was used as an internal standard, and all potentials are referenced to the ferrocene/ferrocenium couple.

Syntheses. All manipulations were performed under an inert atmosphere using standard Schlenk techniques or a glovebox. Solvents were distilled under nitrogen using standard procedures. Bis(1,5-cyclooctadiene)rhodium(I) triflate, [Rh(COD)$_2$]CF$_3$SO$_3$, was purchased from Strem Chemicals, Inc. The ligand, α,α′-bis(diethylphosphino)xylene (depx), was prepared as previously described.[5] Anisidinium tetrafluoroborate and (Me$_2$N)$_3$P═NHMe(BF$_4$) were prepared by reacting either anisidine or (Me$_2$N)$_3$P═NMe[15] with HBF$_4$·OMe$_2$ in ether and washing the resulting solid with ether. Thioacetamide was recrystallized from acetone, and benzamide was recrystallized from water prior to use.

[Rh(depx)$_2$]CF$_3$SO$_3$, [1]CF$_3$SO$_3$. A solution of 0.48 g (1.7 mmol) of depx in 10 mL of MeCN was added to a solution of 0.40 g (0.85 mmol) of [Rh(COD)$_2$]CF$_3$SO$_3$ in 7 mL of MeCN. The resulting orange solution was stirred for 1 h. The volume of the solution was reduced to about 10 mL, and ether (100 mL) was added. After standing overnight, the product that formed was collected by cannula filtration, washed with 2 × 30 mL of ether, and dried under vacuum. Yield = 0.56 g (80%) of an orange, microcrystalline solid. ^{1}H NMR (CD$_3$CN): δ 7.12−7.09 (m, Ar-*H*), 7.03−7.00 (m, Ar-*H*), 3.09 (s, ArC*H*$_2$P), 1.63 (s, br, PC*H*$_2$CH$_3$), 1.06 (br, m, PCH$_2$C*H*$_3$). ^{31}P NMR (CD$_3$CN): δ 12.74 (d, $J_{\mathrm{P-Rh}}$ = 134 Hz). Anal. Calcd for $C_{33}H_{56}F_3O_3P_4RhS$: C, 48.53; H, 6.91; P, 15.17. Found: C, 48.55; H, 7.02; P, 15.01.

[HRh(depx)$_2$(CH$_3$CN)](CF$_3$SO$_3$)$_2$, [4]CF$_3$SO$_3$. Triflic acid (18 μL, 0.20 mmol) was added to a solution of [Rh(depx)$_2$]CF$_3$SO$_3$ (0.150 g, 0.184 mmol) in acetonitrile (8 mL). The reaction was stirred for 5 h, during which time the solution became very pale yellow. The solution was layered with 60 mL of ether and allowed to stand overnight. The white, crystalline solid that formed (0.17 g, 92%) was isolated by cannula filtration, washed with ether (2 × 15 mL), and dried under vacuum. ^{1}H NMR (CD$_3$CN): δ 7.4−6.6 (br, m's, Ar-*H*), 3.8−3.0 (br, m's, PC*H*$_2$Ar), 2.2−0.4 (br, m's, C*H*$_2$C*H*$_3$), −10.33 (br, ddq, $^{2}J_{\mathrm{P(A)-H}}$ = 163 Hz, $^{1}J_{\mathrm{RhH}}$ = 18 Hz, $^{2}J_{\mathrm{P(B,C,D)-H}}$ = 12 Hz, Rh*H* of *cis*-[*H*Rh(depx)$_2$(CH$_3$CN)]CF$_3$SO$_3$), −18.6 (br, s, Rh*H* of *trans*-[*H*Rh(depx)$_2$(CH$_3$CN)]CF$_3$SO$_3$). ^{31}P NMR (CD$_3$CN at ambient temperature, *cis*-isomer, see structure **4a** of Scheme 1 for atom labeling): δ 26.4 (br, d, $^{1}J_{\mathrm{RhP}}$ = 107 Hz, P$_{\mathrm{D}}$), 9.4 (br, dd, $^{2}J_{\mathrm{PP}}$ = 306 Hz, $^{1}J_{\mathrm{RhP}}$ = 84 Hz, P$_{\mathrm{c}}$), −2.0 (br, d, $^{2}J_{\mathrm{PP}}$ = 306 Hz, P$_{\mathrm{B}}$), −18.3 (br, d, $^{1}J_{\mathrm{RhP}}$ = 79 Hz, P$_{\mathrm{A}}$). ^{31}P NMR (CD$_3$CN at −20 °C, *trans*-isomer, see structure **4b** of Scheme 1 for atom labeling): δ 25.4 (dt, $^{1}J_{\mathrm{RhP}}$ = 87 Hz, $^{2}J_{\mathrm{PP}}$ = 32 Hz, P$_{\mathrm{A}}$), 19.6 (br, dt, $^{1}J_{\mathrm{RhP}}$ = 93 Hz, $^{2}J_{\mathrm{PP}}$ = 32 Hz, P$_{\mathrm{B}}$). ^{31}P NMR (CD$_2$Cl$_2$ at −80 °C, *cis*-isomer): δ 22.2 (br, dq, $^{1}J_{\mathrm{RhP}}$ = 115 Hz, $^{2}J_{\mathrm{PP}}$ = 18 Hz, P$_{\mathrm{D}}$), 9.2 (br, ddt, $^{2}J_{\mathrm{PP}}$ = 304 Hz, $^{1}J_{\mathrm{RhP}}$ = 85 Hz, $^{2}J_{\mathrm{PP}}$ = 18 Hz, P$_{\mathrm{c}}$), −10.3 (br, ddm, $^{2}J_{\mathrm{PP}}$ = 304 Hz, P$_{\mathrm{B}}$), −19.1 (br, d, $^{1}J_{\mathrm{RhP}}$ = 77 Hz, P$_{\mathrm{A}}$). IR (Nujol): 2024 cm^{-1} (Rh−H). Anal. Calcd for $C_{36}H_{60}F_6NO_6P_4RhS_2$: C, 42.90; H, 6.00; N, 1.39; P, 12.29. Found: C, 43.07; H, 6.14; N, 1.71; P, 12.43.

[(H)$_2$Rh(depx)$_2$]CF$_3$SO$_3$, [2]CF$_3$SO$_3$. A solution of [Rh(depx)$_2$]CF$_3$SO$_3$ (0.20 g, 0.24 mmol) in acetonitrile (10 mL) was sparged with hydrogen gas for 10 min. The solution turned from orange to colorless within 1 min of H_2 sparging. The volume of the solution was reduced by half under vacuum, and the remaining solution was layered with 40 mL of ether. The off-white powder that formed (0.136 g, 68%) was isolated by cannula filtration, washed with ether (3 × 10 mL), and dried under vacuum. ^{1}H NMR (CD$_3$CN): δ 7.20−7.17 (br, m, Ar-*H*), 7.08−7.05 (br, m, Ar-*H*), 3.3−2.9 (br, m's, ArC*H*$_2$P), 2.0−0.7 (br, m's, PC*H*$_2$C*H*$_3$), −11.3 (apparent doublet of pentets, br, $^{2}J_{\mathrm{PH}} \approx 142$, $^{2}J_{\mathrm{PH}} \approx {}^{1}J_{\mathrm{RhH}} \approx 14$ Hz, XX′ portion of AA′BB′XX′ spectrum, Rh*H*). ^{31}P NMR (CD$_3$CN ambient temperature): δ 15.9 (br, P$_{\mathrm{B}}$), 3.4 (br, P$_{\mathrm{A}}$). ^{31}P NMR (CD$_3$CN at 75 °C): δ 15.7 (br, d, $^{1}J_{\mathrm{RhP}}$ = 91 Hz, P$_{\mathrm{B}}$), 3.4 (br d, $^{1}J_{\mathrm{RhH}}$ = 93 Hz, P$_{\mathrm{A}}$). ^{31}P NMR (CD$_2$Cl$_2$ at −60 °C): δ 15.8 (dt, $^{1}J_{\mathrm{RhP}}$ = 96 Hz, $^{2}J_{\mathrm{PP}}$ = 25 Hz, P$_{\mathrm{B}}$), 4.4 (dt, $^{1}J_{\mathrm{RhP}}$ = 87 Hz, P$_{\mathrm{A}}$). IR (Nujol): 1973 cm^{-1} (Rh−H). Anal. Calcd for $C_{33}H_{58}F_3O_3P_4RhS$: C, 48.41; H, 7.14; P, 15.13. Found: C, 48.73; H, 6.96; P, 15.02.

HRh(depx)$_2$, 3. A solution of [Rh(depx)$_2$]CF$_3$SO$_3$ (0.18 g, 0.22 mmol) in acetonitrile (10 mL) was sparged with hydrogen gas for 10 min to form the dihydride. Then a solution of potassium *tert*-butoxide (0.050 g, 0.45 mmol) in acetonitrile (20 mL) was added. The reaction mixture was stirred overnight, during which time a yellow microcrystalline precipitate formed (0.103 g, 70%). The solid was isolated by cannula filtration, washed with acetonitrile (3 × 15 mL), and dried under vacuum. ^{1}H NMR (toluene-*d*$_8$): δ 6.98 (m, Ar-H), 6.89 (m, Ar-*H*), 2.82 (br, ArC*H*$_2$P) 1.43 (br, PC*H*$_2$CH$_3$), 0.92 (br, PCH$_2$C*H*$_3$), −13.16 (dp, $^{2}J_{\mathrm{PH}}$ = 14 Hz, $^{1}J_{\mathrm{RhH}}$ = 10 Hz, Rh*H*). ^{31}P NMR (toluene-*d*$_8$): δ 14.7 (d, br). IR (Nujol): 1970 cm^{-1} (Rh−H). Anal. Calcd for $C_{32}H_{57}P_4Rh$: C, 57.49; H, 8.59; P, 18.53. Found: C, 57.49; H, 8.72; P, 18.36.

Equilibrium Measurements. All equilibrium measurements and electrochemical measurements were made at 22 ± 1.5 °C. A series of NMR spectra were recorded over a period of time on three to five different samples to determine each equilibrium constant. The error bars shown for all equilibrium constants reflect 2 standard deviations for the precision of the measurements. The error bars for the pK_a values calculated from these equilibrium constants reflect both this uncertainty and the uncertainty of the pK_a value of the reference protonated base.

pK_a of [(H)$_2$Rh(depx)$_2$]CF$_3$SO$_3$. NMR equilibrium experiments were used to determine the pK_a, using (Me$_2$N)$_3$P═NMe and its conjugate acid (pK_a = 27.6),[15] according to equilibrium reaction 1. In one of two experiments in the forward direction, [(H)$_2$Rh(depx)$_2$]CF$_3$SO$_3$ and 40 equiv of (Me$_2$N)$_3$P═NMe were accurately weighed into an NMR tube and dissolved in 0.7 mL of PhCN. The solution was mixed and monitored by ^{1}H NMR (unlocked). The reaction came to equilibrium in about 1 h, as indicated by a constant ratio of the integrals of the hydride resonances of [(H)$_2$Rh(depx)$_2$]$^{+}$ and HRh(depx)$_2$ for 24 h. For the reverse reaction, HRh(depx)$_2$, 1 equiv of (Me$_2$N)$_3$P═NHMe(BF$_4$), and 41 equiv of (Me$_2$N)$_3$P═NMe were dissolved in 0.7 mL of CD$_3$CN and allowed to come to equilibrium. An average equilibrium constant of $9 \times 10^{-4} \pm 2 \times 10^{-4}$ was used to calculate a pK_a for $[(H)_2Rh(depx)_2]$ CF_3SO_3 of 30.6 ± 0.3.

pK_a of $[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$. NMR equilibrium experiments were used to determine the pK_a, using anisidine and its conjugate acid (pK_a = 11.3),[16] according to equilibrium reaction 2. In one of three experiments in the forward direction, $[Rh(depx)_2]CF_3SO_3$ and p-$CH_3OC_6H_4NH_3$-(BF_4) were accurately weighed into an NMR tube and dissolved in 0.7 mL of CD_3CN. The solution was mixed and monitored by ^{31}P NMR. The reaction came to equilibrium in about 1 week. For the reverse reaction, $[HRh(depx)_2(CH_3CN)](CF_3SO_3)_2$ and 2.0 equiv of *p*-anisidine were mixed in 0.7 mL of CD_3CN and allowed to come to equilibrium (11 days). The signals of $[HRh(depx)_2(CH_3CN)]^{2+}$ and $[Rh(depx)_2]^+$ were integrated to determine an equilibrium constant of 0.6 ± 0.3 for reaction 2. Using the pK_a of *p*-anisidinium and the equilibrium constant, the pK_a of the hydride was calculated to be 11.5 ± 0.4.

Heterolytic Cleavage of H_2 by $[HRh(depx)_2(CH_3CN)]^{2+}$. In one of two forward experiments, $[(H)_2Rh(depx)_2]CF_3SO_3$ and 10 equiv of base (thioacetamide or benzamide) were dissolved in 0.7 mL of CD_3CN in an NMR tube. Then 5 equiv of triflic acid was added via a gastight syringe to generate 5 equiv of protonated thioacetamide (pK_a = 4.7)[19] or benzamide (pK_a = 3.7),[19] and the headspace of the tube was purged with hydrogen for 10 min. The NMR tubes were placed on a shaker to ensure thorough mixing, and the reactions were followed by ^1H NMR for 7 days. The hydride resonances of $[(H)_2Rh(depx)_2]^+$ and $[HRh(depx)_2(CH_3CN)]^{2+}$ were integrated to determine the ratio of $[HRh(depx)_2(CH_3CN)]^{2+}$ to $[(H)_2Rh(depx)_2]^+$. This ratio became constant after a period of 1−4 h and remained invariant for at least 24 h. For both bases, two reactions were run in the forward direction and one in the reverse direction. Both reactions were observed to proceed in the reverse direction with formation of $[(H)_2Rh(depx)_2]^+$. Data from the two forward and one reverse reaction were used to calculate equilibrium constants of 0.08 ± 0.02 and 0.13 ± 0.04 atm for reactions 3 and 4, respectively. For the reverse reaction, new hydrides, believed to be $[HRh(depx)_2(amide)]^{2+}$ (e.g., a complex multiplet in the ^1H NMR spectrum at −16.5 ppm for benzamide), were produced that became the dominant hydrides after 4 days. The same hydrides were observed when running reactions 3 and 4 in the forward direction; however they did not dominate prior to reaching an equilibrium.

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Supporting Information Available: Thermodynamic cycles that were used in the calculation of various solution bond-dissociation free energies. This information is available free of charge via the Internet at http://pubs.acs.org.

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