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Thermodynamic Studies of $[H_2Rh(diphosphine)_2]^+$ and $[HRh(diphosphine)_2(CH_3CN)]^{2+}$ Complexes in Acetonitrile

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Thermodynamic studies of a series of $[H_2Rh(PP)_2]^+$ and $[HRh(PP)_2(CH_3CN)]^{2+}$ complexes have been carried out in acetonitrile. Seven different diphosphine (PP) ligands were selected to allow variation of the electronic properties of the ligand substituents, the cone angles, and the natural bite angles (NBAs). Oxidative addition of H_2 to $[Rh(PP)_2]^+$ complexes is favored by diphosphine ligands with large NBAs, small cone angles, and electron donating substituents, with the NBA being the dominant factor. Large pK_a values for $[HRh(PP)_2(CH_3CN)]^{2+}$ complexes are favored by small ligand cone angles, small NBAs, and electron donating substituents with the cone angles playing a major role. The hydride donor abilities of [H₂Rh(PP)₂]⁺ complexes increase as the NBAs decrease, the cone angles decrease, and the electron donor abilities of the substituents increase. These results indicate that if solvent coordination is involved in hydride transfer or proton transfer reactions, the observed trends can be understood in terms of a combination of two different steric effects, NBAs and cone angles, and electron-donor effects of the ligand substituents.

Introduction

Transition metal hydride complexes are important in a broad range of catalytic and stoichiometric reactions. Examples include biological catalysts such as hydrogenase enzymes, industrial catalysts such as those involved in hydroformylation of olefins, and catalysts used in the synthesis of L-Dopa for treating Parkinson's disease.¹⁻⁶ As a result, more quantitative models for understanding and predicting the thermodynamic properties of transition metal hydrides are important. For example, knowledge of the pK_a value and hydride donor ability of a transition metal hydride allows one to predict the pH range over which a transition metal hydride will be stable.⁷ Similarly, hydricity of transition metal hydrides have been used to predict which hydrides generated

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from H_2 gas in the presence of a base will transfer a hydride ligand to coordinated CO or to BX₃ compounds.⁸⁻¹¹ A quantitative understanding of hydride acceptor abilities is also useful in designing electrocatalysts for H_2 production and oxidation.¹²⁻¹⁷

Considerations such as these have inspired efforts to measure both the kinetic and the thermodynamic hydricity of transition metal hydrides.^{7,8,12,13,18–28} Many transition metal hydrides contain monodentate or bidentate phosphine ligands, and the steric and electronic properties of these

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Article

ligands play an important role in determining the reactivity of the complexes. The steric and electronic effects can be understood in terms of parameters such as the ligand cone angle Θ and substituent parameters χ introduced by Tolman.²⁹ In addition to these parameters, Casey and Whiteker introduced the concept of the natural bite angle (NBA) for diphosphines as a measure of the chelate angle preferred by a given ligand backbone.³⁰ This concept has been elaborated extensively by van Leeuwen, Weigand, and others.^{31–38} Of particular relevance to the studies reported in this work are previous thermodynamic studies of five-coordinate monohydride complexes of the type $HM(PP)_2$ (where M = Co or Rh and PP is a chelating diphosphine ligand) and $[HM'(PP)_2]^+$ (where M' = Ni, Pd, and Pt). These studies have shown the hydride donor abilities of these complexes depend on the electron donor abilities of the substituents of the diphosphine ligand,¹⁴ the nature of the metal,³⁹ and the natural bite angle (NBA) of the diphosphine ligand.⁷ In contrast to these extensively studied HM(PP)₂ and $[HM'(PP)_2]^+$ complexes, the factors controlling the hydride donor abilities of [H₂M- $(PP)_2$ ⁺ complexes are not known. Just as for their fivecoordinate monohydride analogues, it is expected that knowledge of the factors controlling the hydride donor abilities of this class of hydrides will allow for a more rational approach to the development of catalytic and stoichiometric reactions. In this paper we interpret the thermodynamic properties of $[H_2Rh(PP)_2]^+$ and $[HRh(PP)_2(CH_3CN)]^2$ complexes in terms of electronic substituent effects, ligand cone angles, and the NBAs of the diphosphine ligands.

Results

Rhodium(I) cations of the type $[Rh(PP)_2]^+$ (where PP = a diphosphine ligand) are convenient for equilibrium studies because they lie near thermoneutrality for the oxidative addition and reductive elimination of several substrates.

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 ΔG° (kcal/mol)

Scheme 1

$[H_2Rh(PP)_2]^+ \Longrightarrow [Rh(PP)_2]^+ + H_2$	$1.37 pK_{eq(1)}$	(1)
$[Rh(PP)_2]^+ + H^+ + CH_3CN \implies [HRh(PP)_2(CH_3CN)]^{2+}$	-1.37pK _a	(2)
$\underline{\mathrm{H}}_2$ \longrightarrow H^+ + H^-	76.0	(3)
$[H_2Rh(PP)_2]^+ \longleftarrow [HRh(PP)_2(CH_3CN)]^{2+} + H^-$		(4)
$\Delta G^{\circ}_{H^-} = 1.37 p K_{eq(1)} - 1.37 p K_a + 76.0$		

Chart 1. List of Diphosphine (PP) Ligands and Their Abbreviations



These substrates include dihalogens, $^{40-42}$ alkyl halides, 43 dioxygen, 41,42 and dihydrogen. $^{12-14,41}$ In addition, these cations can be reversibly protonated with appropriate acids in a variety of solvents.^{12–14,41} Diphosphine ligands offer flexibility in backbone and substituent selection, allowing variation in the ligand bite angle as well as the steric and electronic features of the substituents.

The determination of hydride donor abilities of transition metal hydride complexes relies on the use of thermodynamic cycles such as the one shown in Scheme 1. The sum of reactions 1-3 is reaction 4, the heterolytic cleavage of the Rh-H bond of $[H_2Rh(PP)_2]^+$ to form $[HRh(PP)_2(CH_3-$ (CN)²⁺, and the free energy associated with this reaction is the sum of the free energies corresponding to reactions 1-3 as shown in eq 5. The determinations of the equilibrium constants associated with reaction 1 and the pK_a values for reaction 2 for complexes containing the diphosphine ligands in Chart 1 are discussed below. The free energy for the heterolytic cleavage of H₂ in acetonitrile (reaction 3, 76.0 kcal/mol) was taken from reference 49. The stereochemistry for reaction 1 is shown in reaction 1' below.



Determination of the Free Energy of Hydrogen Elimination (ΔG°_{-H2}) from $[H_2Rh(PP)_2]^+$ Complexes. It was

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Table 1. ³¹P{¹H} NMR Data and ¹H NMR Hydride Data and Assignments for [Rh(PP)₂]⁺, [H₂Rh(PP)₂]⁺, and [HRh(PP)₂(CH₃CN)]²⁺ Complexes

complex	31 P NMR (δ)	¹ H NMR hydride peak (δ)
[Rh(dmpe) ₂] ⁺	36.4, ¹ J _{RhP} 123 Hz	N/A
$[Rh(depe)_2]^+$	$63.2, {}^{1}J_{\rm RhP}$ 126 Hz	N/A
$[Rh(dppe)_2]^+$	58.5, ¹ J _{RhP} 133 Hz	N/A
$[Rh(dcpe)_2]^+$	67.1, ¹ J _{RhP} 131 Hz	N/A
$[Rh(dppb)_2]^+$	$62.5, {}^{1}J_{\rm RhP}$ 134 Hz	N/A
$[Rh(depp)_2]^+$	$5.0, {}^{1}J_{\rm RhP}$ 126 Hz	N/A
$[Rh(dppp)_2]^+$	$8.4, {}^{1}J_{\rm RhP}$ 132 Hz	N/A
$[Rh(depx)_2]^{+a}$	12.7, ¹ J _{RhP} 134 Hz	N/A
$[H_2Rh(dmpe)_2]^+$	38.0 br, 26.4 br	-10.3 br d, <i>trans</i> $^{2}J_{PH}$ 145 Hz
$[H_2Rh(depe)_2]^+$	64.5 br, 47.5 br	-10.7 br d, <i>trans</i> $^{2}J_{PH}$ 132 Hz
$[H_2Rh(dppe)_2]^+$	63.3 br, 46.9 br	-9.0 br d, <i>trans</i> $^{2}J_{PH}$ 152 Hz
$[H_2Rh(dcpe)_2]^+$	74.6 dt, ${}^{1}J_{RhP}$ 96 Hz, ${}^{2}J_{PP}$ 14 Hz, 50.5 br	-12.5 br d, <i>trans</i> ${}^{2}J_{\rm PH}$ 140 Hz
$[H_2Rh(dppb)_2]^+$	N/A	N/A
$[H_2Rh(depp)_2]^+$	15.0 dt, ¹ J _{RhP} 94 Hz, ² J _{PP} 30 Hz	-10.8 br d, <i>trans</i> $^{2}J_{\rm PH}$ 140 Hz
	$-6.1 \text{ dt}, {}^{1}J_{\text{RhP}} 81 \text{ Hz}, {}^{2}J_{\text{PP}} 30 \text{ Hz}$	
$[H_2Rh(dppp)_2]^+$	$18.9 \text{ dt}, {}^{1}J_{\text{RhP}}$ 100 Hz, ${}^{2}J_{\text{PP}}$ 30 Hz	-8 . br d, trans $^2J_{\rm PH}$ 141 Hz
	7.0 dt, ${}^{1}J_{RhP}$ 83 Hz, ${}^{2}J_{PP}$ 30 Hz	
$[H_2Rh(depx)_2]^{+a}$	15.7 br, 3.4 ppm br	-10.8 br d, <i>trans</i> $^{2}J_{PH}$ 142 Hz
$[HRh(dmpe)_2(CH_3CN)]^{2+}$	$38.0, {}^{1}J_{\rm RhP}$ 88 Hz	$-18.5 \text{ dp}, {}^{1}J_{\text{RhH}}$ 14 Hz, ${}^{2}J_{\text{PH}}$ 14 Hz
$[HRh(depe)_2(CH_3CN)]^{2+}$	58.4, ¹ J _{RhP} 87 Hz	$-18.3 \text{ dp}, {}^{1}J_{\text{RhH}}$ 16 Hz, ${}^{2}J_{\text{PH}}$ 12 Hz
$[HRh(dppe)_2(CH_3CN)]^{2+}$	56.0, ¹ J _{RhP} 92 Hz	$-15.9 \text{ dp}, {}^{1}J_{\text{RhH}}$ 11 Hz, ${}^{2}J_{\text{PH}}$ 11 Hz
$[HRh(dcpe)_2(CH_3CN)]^{2+}$	63.9, ¹ J _{RhP} 88 Hz	$-19.1 \text{ dp}, {}^{1}J_{\text{RhH}} 10 \text{ Hz}, {}^{2}J_{\text{PH}} 10 \text{ Hz}$
$[HRh(dppb)_2(CH_3CN)]^{2+}$	56.9, ¹ J _{RhP} 93 Hz	$-14.6 \text{ dp}, {}^{1}J_{\text{RhH}}$ 10 Hz, ${}^{2}J_{\text{PH}}$ 7.5 Hz
$[HRh(depp)_2(CH_3CN)]^{2+}$	$4.8, {}^{1}J_{\rm RhP} 85 {\rm Hz}$	$-17.6 \text{ dp}, {}^{1}J_{\text{RhH}}$ 15 Hz, ${}^{2}J_{\text{PH}}$ 14 Hz
[HRh(dppp) ₂ (CH ₃ CN)] ²⁺	6.2, ¹ J _{RhP} 91 Hz	$-14.9 \text{ dp}, {}^{1}J_{\text{RhH}}$ 12 Hz, ${}^{2}J_{\text{PH}}$ 12 Hz
$[HRh(depx)_2(CH_3CN)]^{2+a}$	<i>cis</i> : 26.4, 9.4, -2.0, -18.3	<i>cis</i> : -10.3 , ${}^{2}J_{\rm PH}$ 163 Hz
	trans: 25.4 and 19.6	<i>trans</i> : -18.6 br s

^{*a*} Data from reference 21.

previously reported that $[H_2Rh(dmpe)_2]^+$ and $[H_2Rh(depe)_2]^+$ reversibly lose hydrogen as shown in reaction 1', with equilibrium constants of 0.6 and 4.0 atm, respectively.¹⁸ The complex $[H_2Rh(dppp)_2]^+$ is also in equilibrium with $[Rh(dppp)_2]^+$ under 1.0 atm of hydrogen, and the ³¹P{¹H} NMR spectrum of $[H_2Rh(dppp)_2]^+$ exhibits two doublets of triplets indicating an AA'XX'M spin system and a *cis* geometry. Integration of the ³¹P NMR resonances of **1** and **2** can be used to determine an equilibrium constant of 0.10 atm for reaction 1 when the diphosphine ligand is dppp. A listing of the observed ³¹P{¹H} NMR resonances and their assignments are provided in Table 1 for the $[Rh(PP)_2]^+$ and $[H_2Rh(PP)_2]^+$ complexes discussed in this paper.

The complex $[Rh(dppe)_2]^+$ does not react with H₂ at 1.0 atm; however, at 110 atm H₂, sufficient $[H_2Rh(dppe)_2]^+$ is observed in equilibrium with $[Rh(dppe)_2]^+$ to permit accurate integration of the two rhodium species. An equilibrium constant of 5.7×10^2 atm was determined, corresponding to a ΔG°_{-H2} value of -3.8 kcal/mol. Similarly measurable amounts of $[H_2Rh(dcpe)_2]^+$ were produced from $[Rh(dcpe)_2]^+$ at H₂ pressures greater than 130 atm. A broad resonance at 50.5 ppm is assigned to the phosphorus atoms trans to the hydride ligands (Px and $P_{X'}$ of structure 1). This assignment is supported by the HSQC NMR data, with the observation of a prominent cross peak between the hydride at -12.5 ppm on the ¹H axis and the resonance at 50.5 ppm on the ³¹P NMR axis. This signal can be assigned with confidence because of the large (~140 Hz) trans ${}^{2}J_{PH}$. The area of the ${}^{31}P$ resonance at 50.5 ppm correlates with a relatively sharp doublet of triplets at 74.6 ppm attributed to P_A and $P_{A'}$ of structure **1**. The *cis* phosphorus atoms (P_A and $P_{A'}$ of structure **1**) did not display a cross peak with the hydride. This is attributed to the smaller cis ${}^2J_{\rm PH}$ (~15 Hz) and H₂ exchange. In addition to the resonances assigned to

 $[H_2Rh(dcpe)_2]^+$ (1) and $[Rh(dcpe)_2]^+$ (2), resonances were observed at 92.6 ppm (${}^1J_{RhP}$ 186 Hz) and at 52.2 ppm with no rhodium coupling. The former is tentatively attributed to $[Rh(dcpe)(CH_3CN)_2]^+$ and the latter to a ligand decomposition product. Despite these additional species, a reproducible equilibrium constant of 1.0×10^3 atm was obtained for reaction 1 over the range of hydrogen pressures studied (110–140 atm).

A solution of $[Rh(dppb)_2]^+$ was subjected to H₂ pressures greater than 130 atm, but no oxidative addition product was observed; hence the dissociation free energy of $[H_2Rh(dppb)_2]^+$ is more negative than -4.4 kcal/mol. At the opposite extreme, $[Rh(depp)_2]^+$ and $[Rh(depx)_2]^+$ add H₂ irreversibly at 1.0 atm H₂. Because no equilibrium is observed, the free energy of hydrogen elimination for $[H_2Rh(depp)_2]^+$ and $[Rh(depx)_2]^+$ must be derived indirectly, as discussed below under the topic of hydride donor abilities. The free energies (ΔG°_{-H2}) associated with reaction 1 for the $[H_2Rh(PP)_2]^+$ complexes discussed in the preceding paragraphs and those available for $[H_2Rh(depx)_2]^+$ from the literature²¹ are summarized in column 5 of Table 2.

Determination of pK_a Values for $[HRh(PP)_2(CH_3-CN)]^{2+}$ Complexes. In addition to the equilibrium constants for reaction 1, determination of the hydride donor abilities of $[H_2Rh(PP)_2]^+$ complexes using Scheme 1 requires pK_a values for the cationic rhodium $[HRh(PP)_2-(CH_3CN)]^{2+}$ complexes. The pK_a values for the complexes containing the ligands in Chart 1 were determined by using Scheme 2. In a typical experiment, an acetonitrile solution of $[Rh(PP)_2]^+$ was treated with a mixture of an acid and its conjugate base, and monitored by ${}^{31}P{}^{1}H{}$ NMR spectroscopy until equilibrium was achieved. Equilibrium constants for eq 6 were determined by integration of the ${}^{31}P$ NMR resonances of the equilibrating rhodium species and mass balance of the acid/conjugate

 ΔG° (kcal/mol)

Table 2. Thermodynamic Data and Ligand Parameters for [Rh(PP)2]⁺, [H₂Rh(PP)2]⁺, and [HRh(PP)2(CH₃CN)]²⁺ Complexes^a

РР	$\Theta_{B}{}^{b}$ (deg)	NBA^{c} (deg)	$TEM^d \Sigma^3 \chi$	$\frac{[H_2Rh(PP)_2]^+ \Delta G^{\circ}_{-H2}}{\text{kcal/mol (eq 1)}}$	$[H_2Rh(PP)_2]^+ \Delta G^{\circ}_{H^-} kcal/mol (eq 5)$	$\frac{[\text{HRh}(\text{PP})_2(\text{MeCN})]^{2+} \Delta G^\circ_{\text{H}+}}{\text{kcal/mol} (pK_a) (\text{eq 9})}$
dmpe	107 (107)	86	7.8	$+0.44^{e}$	50.4	26.0 (18.9)
depe	117 (115)	86	6.2	-0.87^{e}	52.3	22.8 (16.6)
dppe	125 (125)	86	11.2	-3.8	59.6	$12.3(9.0)^{e}$
dcpe	142 (142)	86	2.8	-4.2	63.1	8.7 (6.0)
depp	119	93	6.2	+5.1	61.3	19.8 (14.4)
depx	121	100	6.2	$+11.4^{f}$	71.6 ^f	$15.8 (11.5)^{f} (6:1 cis to trans)$
dppb	125	86	12.9	<-4.4	< 58.7	$12.9 (9.4)^{e}$
dppp	127 (127)	93	11.2	+1.4	69.5	7.9 (5.8)

^a All values are for acetonitrile at 23 \pm 2 °C. ^b From eq 15 as discussed in the Supporting Information, values in parentheses are from reference 29. ^c Ref 37. ^d Tolman electronic parameters from ref 29, as discussed in the Supporting Information. ^e Ref 18. ^f Ref 21, weighted average of *cis* and *trans* values.

Scheme 2

Scheme 3

$[HRh(PP)_2(MeCN)]^{2+} + Base \implies [Rh(PP)_2]^+ + HBase^+ + MeCN$	(6)
$HBase^+$ \implies $Base + H^+$	(7)
$[HRh(PP)_2(MeCN)]^{2+} = [Rh(PP)_2]^+ + H^+ + MeCN$	(8)
$pK_{a}(HRh) = pK_{a}(HBase^{+}) + pK_{aa}(h)$	(9)

 $pK_a(HRh) = pK_a(HBase^+) + pK_{eq(6)}$

base pair. (Details are discussed in the Experimental Section.) These equilibrium constants, together with published p K_a data for acids in acetonitrile (eq 7), ^{9,44–48} were used to calculate the pK_a values of the corresponding $[HRh(PP)_2(CH_3CN)]^{2+}$ complexes using eq 9. The resulting values and the corresponding free energies for deprotonation of [HRh(PP)₂(CH₃CN)]²⁺ are summarized in column 7 of Table 2. It is worth noting that in reactions 6 and 8, deprotonation of the $[HRh(PP)_2(CH_3CN)]^{2+}$ complex is accompanied by loss of acetonitrile. For these reactions, the activity of pure acetonitrile solvent is taken as unity. This choice of standard states results in pK_a values that are internally consistent with pK_a values reported for complexes in acetonitrile that do not involve solvent loss. However, the pK_a values calculated according to Scheme 2 cannot be readily transferred to solvents other than acetonitrile.

Determination of the Hydride Donor Ability ($\Delta G^{\circ}_{H^{-}}$) of $[H_2Rh(PP)_2]^+$ Complexes. The equilibrium constants for H_2 loss and the pK_a values for reaction 2 were used to calculate the hydride donor abilities of the $[H_2Rh(PP)_2]^+$ complexes using Scheme 1, with the exception of [H₂Rh- $(depp)_2]^+$. The $\Delta G^{\circ}_{H^-}$ values are shown in Table 2. Because $[Rh(depp)_2]^+$ reacts irreversibly with H₂, Scheme 1 could not be used to determine the hydride donor ability of $[H_2Rh(depp)_2]^+$. In this case, the hydride donor ability was determined using Scheme 3, where the free energy for the heterolytic cleavage of H_2 in acetonitrile (eq 12) was taken from the literature.⁴⁹ In contrast, [Rh(dppb)₂]⁺ does not react with H₂ even at 140 atm. As a result, the value of $\Delta G^{\circ}_{H^-}$ for this complex can only be determined to be less than 58.7 kcal/mol.

$H_2Rh(PP)_2$	$^{+}$	$HBase^+$	+ MeCN	-

	$\left[HRh(PP)_2(MeCN)\right]^{2+} + Base + H_2$	$1.37 p K_{eq(10)}$	(10)
Base + H^+ \Longrightarrow 1	IBase^+	$-1.37 \text{p}K_{a}(\text{HBase}^{+})$	(11)
$\underline{H}_2 \longrightarrow \underline{H}^+ + \underline{H}^-$		76.0	(12)
$\left[H_2 Rh(PP)_2\right]^+$ + MeC	$N \implies [HRh(PP)_2(MeCN)]^{2+} + H^{-}$		(13)
$(\Delta G^{\circ}_{H^{-}}) = 1.37 p K_{eq}(1)$	$_{00} = 1.37 p K_{2} (HBase^{+}) + 76.0$		(14)

Discussion

The objective of this work is to delineate the ligand parameters controlling various thermodynamic properties of $[H_2Rh(PP)_2]^+$ and $[HRh(PP)_2(CH_3CN)]^{2+}$ complexes. Previous studies of $[HM(PP)_2]^+$ complexes (where M = Ni, Pd, and Pt) have shown that the hydride donor abilities, pK_a values, and homolytic solution bond dissociation free energies depend on three factors. These are the nature of the metal, the electron donor or acceptor ability of the substituents on the diphosphine ligand, and the natural bite angle of the ligand.³⁹ In contrast, although thermodynamic hydride donor abilities have been reported for a small number of six-coordinate metal complexes, ^{19,50–53} there has been no systematic study of this class. The ligands shown in Chart 1 were selected because they provide a range of cone angles, natural bite angles, and electronic parameters as shown in columns 2-4 of Table 2.

Reductive Elimination of H₂ from $[H_2Rh(PP)_2]^+$ Complexes. The reductive elimination of H2 from distorted cisoctahedral $[H_2Rh(PP)_2]^+$ complexes results in the formation of $[Rh(PP)_2]^+$ complexes. The NBAs appear to be the dominant factor influencing this reaction and its reverse, the oxidative addition of H_2 to $[Rh(PP)_2]^+$. For example, elimination of H₂ is favored by 12.3 kcal/mol for [H₂Rh- $(depe)_2]^+$ ($\Delta G^{\circ}_{-H2} = -0.87$ kcal/mol) compared to [H₂- $Rh(depx)_2$]⁺ (11.4 kcal/mol), which have NBAs of 86° and 100°, respectively.³⁷ This effect has been discussed previously and can be understood in terms of simple molecular orbital overlap arguments, in which the tetrahedral distortion from a square-planar geometry associated

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with a larger NBA results in a decrease of the energy of the σ acceptor orbital and an increase in the energies of the π -donor orbitals of the $[Rh(PP)_2]^+$ complex.^{7,12,54} These changes in orbital energies favor the addition of hydrogen to $[Rh(PP)_2]^+$ derivatives as the NBAs increase.

When considering the effect of the steric bulk of the ligand substituents, it is not obvious whether sterically bulky groups will favor either $[H_2Rh(PP)_2]^+$ or [Rh- $(PP)_2$ ⁺. Tolman introduced the concept of cone angle to quantify the bulkiness of various substituents, and values have been published for the cone angles of the diphosphine ligands with ethylene backbones used in this study (shown in parentheses in Table 2). Tolman calculated the cone angle for diphosphine ligands ($\Theta_{\rm B}$) using eq 15, where $\Theta_{\rm M}$ is the cone angle of the corresponding monodentate PR₃ ligand with the same R substituents as the diphosphine ligands and α is the experimentally observed PMP bond angle of the chelating diphosphine ligand. We have extended this method to the other ligands shown in Chart 1 using the experimentally determined bite angles from the work of Aguila et al.³⁷ and the cone angles for the corresponding monodentate ligands used by Tolman (see Supporting Information).²⁹ Our calculated values are the same as those reported by Tolman for the ligands previously reported with the exception of depe for which we calculate a cone angle of 117° versus Tolman's 115°. This approach allows cone angles that are consistent with those used by Tolman to be determined for the additional ligands used in this work.

$$\Theta_{\rm B} = 2/3(\Theta_{\rm M} + 1/2\alpha) \tag{15}$$

A plot of ΔG°_{-H2} versus the cone angle for the data in Table 2 is shown in Figure 1. It can be seen that the data for the ligands with an ethylene backbone are nearly colinear (see solid line), and increasing the steric bulk of the substituents clearly favors reductive elimination of H_2 . It is of interest to note that this steric effect is counter to that observed for increasing the natural bite angle. It is also apparent from Figure 3 that the data point for the dppe complex deviates slightly from the value expected based on pure steric considerations, and this small deviation of -2.1 kcal/mol is attributed to electronic effects. The poorer electron donating ability of the phenyl substituents compared to the alkyl substituents favors reductive elimination of H_2 . This electronic effect has been noted previously.^{55–57} In summary, oxidative addition of H_2 to $[Rh(PP)_2]^+$ complexes is favored by diphosphine ligands with large NBAs, small cone angles, and electron donating substituents, with the NBA being the dominant factor.

 pK_a Values of $[HRh(PP)_2(CH_3CN)]^{2+}$ Complexes. Protonation of $[Rh(PP)_2]^+$ cations in acetonitrile is accompanied by the coordination of a solvent molecule and results in the formation of *trans*-[HRh(PP)_2(CH_3CN)]^{2+} complexes. As a result, it is expected that factors influencing the dissociation of the solvent ligand will influence



Figure 1. Plot of ΔG°_{-H2} versus the cone angle for the data in Table 2. The diphosphine ligands of the corresponding *cis*-[H₂Rh(PP)₂]⁺ complexes are shown adjacent to each data point with the green diamonds corresponding to ligands with ethylene backbones, the blue squares to propylene backbones, and the red triangle to that for depx which contains four carbon atoms.



Figure 2. Plot of ΔG°_{H+} for $[HRh(PP)_2(CH_3CN)]^{2+}$ complexes versus the cone angle of the corresponding diphosphine ligands. The straight line is the best fit line through the data for the diphosphine ligands containing ethylene backbones and alkyl substituents.



Figure 3. Plot of $\Delta G^{\circ}_{H^{-}}$ versus the ligand cone angle. The solid line is the best-fit line through the data for the ligands with ethylene backbones and alkyl substituents.

the free energies (ΔG°_{H+}) and pK_a values associated with deprotonation of the corresponding *trans*-[HRh(PP)₂-(CH₃CN)]²⁺ complexes. These values are shown in column 7 of Table 2, and Figure 2 shows a plot of ΔG°_{H+} versus the cone angles of the diphosphine ligands. The solid line represents the best-fit line for the diphosphine ligands with an ethylene backbone and alkyl substituents. The ΔG°_{H+} value of [HRh(dmpe)₂(CH₃-CN)]²⁺ is 17.3 kcal/mol larger than that of [HRh-(dcpe)₂(CH₃CN)]²⁺, indicating that the cone angles of the diphosphine ligands play a major role in determining the pK_a values of these complexes. Steric interactions between the phosphine substituents and the acetonitrile ligand that coordinates upon protonation of the metal

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apparently results in less stable and more acidic *trans*- $[HRh(PP)_2(CH_3CN)]^{2+}$ complexes. An analogous explanation, based on counterbalancing steric and electronic effects, has been offered to account for the unexpected similarity in the thermodynamic hydride donor abilities of $[HW(CO)_4P(OMe_3)]^-$ (37 kcal/mol) and $[HW(CO)_4-(PPh_3)]^-$ (36 kcal/mol).⁵⁰

Comparison of the values for depe, depp, and depx complexes and of dppe and dppp complexes indicates that an increase in the NBA also increases the acidity of these complexes, but this effect is smaller than the effect of the cone angle. Both trends are understandable in terms of increased steric interactions between the diphosphine ligands, and between the diphosphine ligands and acetonitrile, as the NBA or cone angle increases. In contrast, as discussed above, oxidative addition of H₂ to [Rh- $(PP)_2$ ⁺ complexes is significantly favored by an increase in the NBA of the diphosphine ligands, but disfavored by an increase of the steric bulk of the ligands cone angle. This difference in the dependence of the driving force for the oxidative addition of H₂ to $[Rh(PP)_2]^+$ and protonation of $[Rh(PP)_2]^+$, both of which result in an increase in the formal oxidation state and the coordination number of the metal by two, is thought to arise from the different geometries (cis and trans) of the two products formed.

The value of ΔG°_{H+} for *trans*-[HRh(dppe)₂(CH₃-(CN)²⁺, which has phenyl substituents, is significantly smaller than expected for an alkyl-substituted complex with the same cone angle. The -5.9 kcal/mol difference between the expected and observed values for dppe is attributed to the difference in the electron-donor ability of phenyl groups compared to alkyl groups. For comparison, the ΔG°_{H+} value for $[HM(depe)_2]^+$ is 14 or 10 kcal/ mol larger than that of $[HM(dppe)_2]^+$ for M = Ni and Pt, respectively. These values for nickel and platinum are primarily determined by the electron donor abilities of the substituents, not the NBAs or cone angles. Apparently electronic substituent effects are relatively less important (compared to steric effects) in determining the acidities of $[HRh(PP)_2(CH_3CN)]^{2+}$ complexes than those of the [HM(PP)₂]⁺ complexes of nickel and platinum; presumably this is in large part a consequence of the sixth ligand in the former. In summary, large pK_a values for [HRh- $(PP)_2(CH_3CN)^{2+}$ complexes are favored by small ligand cone angles, small NBAs, and electron donating substituents with both cone angles and electron donor abilities playing a major role.

Hydride Donor Abilities of $[H_2Rh(PP)_2]^+$ Complexes. Column 6 in Table 2 lists the hydride donor abilities $(\Delta G^{\circ}_{H^{-}})$ of $[H_2Rh(PP)_2]^+$ complexes, which measure the thermodynamic driving force for dissociation of a hydride ligand from the dihydride to form [HRh- $(PP)_2(CH_3CN)]^{2+}$. Smaller values of $\Delta G^{\circ}_{H^-}$ indicate a greater driving force for the delivery of a hydride by $[H_2Rh(PP)_2]^+$ complexes. As can be seen from Table 2, the hydride donor abilities of the complexes range from 50.4 kcal/mol for $[H_2Rh(dmpe)_2]^+$ to 71.6 kcal/mol for $[H_2Rh(depx)_2]^+$. Because the pK_a values of $[HRh(PP)_2$ - (CH_3CN) ²⁺ and the ΔG°_{-H2} values of $[H_2Rh(PP)_2]^+$ are used to calculate the $\Delta G^{\circ}_{H^{-}}$ values of $[H_2Rh(PP)_2]^+$, it is anticipated that both electronic and steric effects will make significant contributions to the hydride donor abilities of $[H_2Rh(PP)_2]^+$ complexes.

The observation that $[H_2Rh(dmpe)_2]^+$ is a better hydride donor than $[H_2Rh(dcpe)_2]^+$ by 12.7 kcal/mol suggests that the cone angle of the diphosphine ligand exerts a significant influence on the hydride donor abilities of these complexes. This is illustrated graphically in Figure 3 by the linear dependence of the plot of $\Delta G^{\circ}_{H^{-}}$ versus the ligand cone angle for the ligands with ethylene backbones and alkyl substituents (solid line). Ligands with larger cone angles give complexes with poorer hydride donor abilities or larger $\Delta G^{\circ}_{H^{-}}$ values. This can be understood in terms of increased steric interactions between acetonitrile and diphosphine ligands with larger cone angles. This interaction disfavors the binding of acetonitrile that accompanies hydride ligand loss. For the ethylene bridged ligands, dppe deviates from the best-fit line for the alkyl substituted ligands by 4.0 kcal/mol. This is attributed to electronic effects with phenyl substituents resulting in poorer hydride donors than alkyl substituents, and this electronic effect is comparable to the difference in the ΔG°_{H+} values for the [HRh(PP)₂-(CH₃CN)]²⁺ complexes discussed in the preceding section. The NBA also plays an important role in determining the hydride donor ability of $[H_2Rh(PP)_2]^+$ complexes. The complex $[H_2Rh(depe)_2]^+$ is a better hydride donor than $[H_2Rh(depx)_2]^+$ by 19.3 kcal/mol. If this difference is corrected for electronic effects of ethyl versus benzyl, this difference would be expected to be slightly smaller (1-2 kcal/mol). In summary, the hydride donor abilities of $[H_2Rh(PP)_2]^+$ complexes increase as the NBAs decrease, the cone angles decrease, and the electron donor abilities of the substituents increase. In this case the influence of the NBAs and cone angles appear to be of comparable magnitude and dominate electronic effects of the substituents.

Comparison with Other Metal Hydride Systems. Previously reported thermodynamic studies of metal complexes most relevant to those reported here include the $[H_2Co(dppe)_2]^+$ and $[H_2Pt(EtXantphos)_2]^{2+}$ systems. $[H_2Co(dppe)_2]^+$ is reported to have a ΔG°_{-H2} of 4.6 kcal/mol while $[H_2Rh(dppe)]^+$ has a ΔG°_{-H2} of -4.0 kcal/mol. This indicates that oxidative addition of H₂ to $[Co(dppe)_2]^+$ is favored over the oxidative addition of H₂ to $[Rh(dppe)_2]^+$ by 8.6 kcal/mol. Although this is only one direct comparison, the conclusion that $[Co(PP)_2]^+$ complexes will bind H₂ more strongly than $[Rh(PP)_2]^+$ for the same diphosphine ligand is likely to be generally valid. The pK_a value of 11.3 for $[HCo(dppe)_2(CH_3CN)]^{2+}$ compared to 9.0 for $[HRh(dppe)_2(CH_3CN)]^{2+}$ indicates that rhodium is slightly more acidic than cobalt in these six coordinate structures. $[H_2Co(dppe)]^+ (\Delta G^{\circ}_{H^-} = 65.1)$ kcal/mol) is a significantly less powerful hydride donor than $[H_2Rh(dppe)]^+ (\Delta G^{\circ}_{H^-} = 59.6 \text{ kcal/mol})$, but this difference is smaller than that observed between first and second row metals in five coordinate monohydride $[HM(PP)_2]^+$ complexes, for which palladium complexes are generally 15 kcal/mol better hydride donors than the corresponding nickel complexes.

Group 10 d⁶ bis(diphosphine) dihydrides are uncommon; nonetheless one example, $[H_2Pt(EtXantphos)_2]^{2+}$ [EtXantphos = 9,9-dimethyl-4,5-bis(diethylphosphino)xanthene], has been observed by NMR.²⁰ This complex has a ΔG°_{-H2} of 9.3 kcal/mol. Consistent with the rhodium trends, this $[H_2Pt(PP)_2]^{2+}$ species is one with an extremely large bite angle. Despite the significant driving force for the formation of $[H_2Pt(EtXantphos)_2]^{2+}$, it still takes days for 1 atm of hydrogen to completely consume $[Pt(EtXantphos)_2]^{2+}$. In contrast, the reactions of H_2 with $[Rh(PP)_2]^+$ derivatives are fast (complete prior to taking NMR spectra) in all cases reported here, even those with very little driving force. While reaction kinetics have not been explicitly evaluated in this work, it is clear that there is a significant difference in the intrinsic activation barriers for the addition of hydrogen to $[Rh(PP)_2]^+$ and $[Pt(PP)_2]^{2+}$.

Comparison with Five-Coordinate HRh(PP)₂ Complexes. HRh(PP)₂ complexes can be generated by the deprotonation of $[H_2Rh(PP)_2]^+$, and the hydride donor abilities of the five coordinate hydrides have been investigated for four different ligands; dmpe ($\Delta G^{\circ}_{H^-} = 26.4$ kcal/mol), depe ($\Delta G^{\circ}_{H^-} = 28.1 \text{ kcal/mol}$), dppb ($\Delta G^{\circ}_{H^-} = 33.9 \text{ kcal/mol}$), and depx ($\Delta G^{\circ}_{H^-} = 45 \text{ kcal/mol}$).^{18,21,22} Comparisons of these values with those of the corresponding [H₂Rh(PP)₂]⁺ derivatives indicate that deprotonation of the dihydride complexes results in the formation of a monohydride complex that is approximately a 25 kcal/mol better hydride donor. If both the $[H_2Rh(PP)_2]^+$ and $HRh(PP)_2$ complexes are considered, the hydride donor abilities demonstrated for HRh- $(dmpe)_2$ and $[H_2Rh(depx)_2]^+$ span a range of 45 kcal/ mol. This range of hydride donor abilities can be accessed readily from H₂ gas and bases of various strengths.

Conclusions

The thermodynamic studies described above demonstrate that while both steric and electronic influences of diphosphine ligands are factors, the steric constraints of the cone and bite angle tend to dominate the thermodynamic properties of six-coordinate rhodium hydride complexes. As expected, electron donating substituents on the diphosphine ligands increase pK_a values of $[HRh(PP)_2(CH_3CN)]^{2+}$, correlate with better hydride donor abilities of $[H_2Rh(PP)_2]^+$, and disfavor reductive elimination of H_2 from $[H_2Rh(PP)_2]^+$. Larger NBAs decrease the pK_a values of $[HRh(PP)_2]$ - (CH_3CN) ²⁺, correlate with poorer hydride donor abilities for $[H_2Rh(PP)_2]^+$ derivatives, and disfavor reductive elimination of H_2 from $[H_2Rh(PP)_2]^+$ complexes. Finally, larger cone angles decrease the p K_a of $[HRh(PP)_2(CH_3CN)]^{2+}$, decrease the hydride donor abilities of $[H_2Rh(PP)_2]^+$ derivatives, and favor reductive elimination of H₂ from [H₂Rh- $(PP)_2$ ⁺. The coordination of acetonitrile that accompanies the protonation of $[Rh(PP)_2]^+$ and hydride transfer from $cis-[H_2Rh(PP)_2]^+$ to form trans- $[HRh(PP)_2(CH_3CN)]^{2+}$ results in increased steric interations between the coordinated acetonitrile ligands and the diphosphine ligands. As a result, these reactions are disfavored by an increase in both the NBA and the cone angle. Our results suggest that if solvent coordination is involved in hydride transfer and proton transfer reactions, the observed trends can be understood in terms of two different steric effects, NBAs, and cone angles, and in terms of electronic effects. It is important to emphasize that the two steric effects can be much larger than electronic effects, and that increasing cone angles and NBAs can have the same effect on thermodynamic properties, such as the acidity of $[HRh(PP)_2(CH_3CN)]^{2+}$ complexes and the hydricity of $[H_2Rh(PP)]^+$ complexes, or opposite effects, as in the reductive elimination of H_2 from $[H_2Rh(PP)]^+$ complexes. We believe that these concepts can be applied to a large range of proton and hydride transfer reactions in which solvent coordination is involved, and that they can help guide the development of a more comprehensive and quantitative understanding of the thermodynamic properties of these complexes.

Experimental Section

Syntheses. The $[Rh(PP)_2]^+$ complexes were prepared as yellow to orange powders following standard literature procedures.^{18,58} In a representative preparation, a solution of the ligand dppp (2.15 g, 5.21 mmol) in 20 mL of MeCN was added to a 40 mL MeCN solution of $[Rh(COD)_2]OTf(1.22 g, 2.61 mmol)$, and the reaction mixture was allowed to stir for 2 h at room temperature. The volume of the solution was reduced to 10 mL under vacuum, and 100 mL of Et₂O added to produce a precipitate. The bright orange solid was collected by filtration, washed with 3 100 mL aliquots of petroleum ether, and dried in a vacuum for 12 h. The NMR data for this complex match the literature values reported for $[Rh(dppp)_2]OTf(2.73 g, 2.53 mmol, 97\% yield).⁵⁸ The ³¹P{¹H} NMR data and ¹H NMR hydride data also match the literature values for the remaining <math>[Rh(PP)_2]^+$ complexes used in this study, and these values are listed in Table 1.^{18,22,58}

Equilibrium Measurements. All equilibrium measurements were made at 23 ± 2 °C by recording a series of NMR spectra on three to six different samples until the integration ratios became constant within experimental error. The standard state for H₂ is 1.0 atm, and the standard state for acetonitrile was taken as pure acetonitrile as discussed in the text.

Equilibria of [Rh(dppe)₂][OTf] and [Rh(dcpe)₂][OTf] with H₂ Gas at High Pressure. [Rh(dppe)₂][OTf] (7 mg, 0.007 mmol) and 0.5 mL of CD₃CN were added to a sapphire NMR tube with a volume of 1.6 mL and fitted with a check valve which could be connected to a high pressure gas manifold. This tube was then charged with 1,754 psi (119 atm, ~4.8 mmol) of hydrogen with the pressure measured by a Wikall Transmitter UT-10 pressure gauge integrated into the manifold. Once charged, the NMR tube was inverted several times over a period of minutes to induce mixing. The reaction reached equilibrium within minutes as indicated by a constant ratio of NMR signals for products, [Rh(dppe)₂][OTf] (³¹P{¹H} NMR: 58.5 ppm, int. set to 1.0) and $[H_2Rh(dppe)_2][OTf]$ (³¹P{¹H} NMR: 15.0 ppm, int. 0.104; -6.1 ppm, int. 0.104). The NMR was followed for at least 24 h to ensure the stability of the product ratio and vessel pressure. Integration of each of the resonances of [H₂Rh(dppe)₂][OTf] and [Rh(dppe)₂][OTf] as well as the pressure of the H₂ gas were used to calculate an equilibrium constant for Reaction 1 of $5.7 \times$ 10^2 atm. A total of three experiments were conducted, each charged with hydrogen pressures between 1690 and 1760 psi (115–120 atm, 4.6–4.8 mmol). The integrals were measured, and an average ΔG°_{-H2} of -3.8 kcal/mol was calculated, with none of the values for individual experiments deviating more than 0.01 kcal/mol.

A similar series of three experiments were conducted for $[Rh(dcpe)_2][OTf]$, with hydrogen pressures between 1470 and 2060 psi (100–140 atm, 4.6–4.8 mmol). In the pressurized $[Rh(dcpe)_2][OTf]$ system, two major unknown side products were produced (³¹P{¹H} NMR: 92.6 ppm, d, ¹J_{RhP} 186 Hz; and 52.2 ppm, s) among other minor products in addition to the species attributed to $[H_2Rh(dcpe)_2][OTf]$. All species in the reaction mixture appeared to reach thermodynamically stable ratios within 24 h. The $[H_2Rh(dcpe)_2][OTf]$ species was identified by a hydride signal in the ¹H NMR spectrum at –12.5 ppm,

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m, and by the ³¹P{¹H} NMR: 74.6 ppm, m (P *cis* to hydride), 50.5 ppm, m, ²J_{PH} ~140 Hz (P *trans* to hydride, assignment supported by ³¹P-¹H HSQC). The relative concentrations of reactant and product were determined by integration of the signal assigned to [Rh(dcpe)_2][OTf] and the signals associated with the phosphorus *cis* to hydride in [H₂Rh(dcpe)₂][OTf]. In this series of experiments, an average ΔG°_{-H2} of -4.2 kcal/mol was determined. None of the values for individual experiments deviated more than 0.05 kcal/mol. When [Rh(dppb)₂][OTf] was exposed to high pressures, no reaction was observed.

Equilibrium of [Rh(dppp)₂][OTf] with H₂ Gas. [Rh(dppp)₂]-[OTf] (5 mg, 0.005 mmol) and 0.7 mL of CD₃CN were added to an NMR tube fitted with a septum. The tube was purged with a slow stream of H₂ for 10 min. The reaction reached equilibrium within minutes as indicated by a constant ratio of products, which persisted for more than 24 h. The species observed were [Rh(dppp)₂][OTf] (${}^{31}P{}^{1}H{}$ NMR: 8.4 ppm, d, ${}^{1}J_{RhP}$ 132 Hz) and [H₂Rh(dppp)₂][OTf] (${}^{31}P{}^{1}H{}$ NMR: 18.9 ppm, dt, ${}^{1}J_{RhP}$ 100 Hz, ${}^{2}J_{PP}$ 30 Hz; 7.0 ppm, dt, ${}^{1}J_{RhP}$ 83 Hz, ${}^{2}J_{PP}$ 30 Hz). The signals centered at 8.4 ppm ([Rh(dppp)₂][OTf]) and 7.0 ppm (half of total signal for [H2Rh(dppp)2][OTf]) were not resolved, so the combined integral of 1.2 was compared to the set integral of 1.0 for the signal at 18.8 ppm (the other half of [H₂Rh-(dppp)₂[[OTf] total signal), giving a [Rh(dppp)₂][OTf]/ [H₂Rh(dppp)₂][OTf] ratio of 0.10. This value, combined with the hydrogen pressure of 1 atm, was used to calculate an equilibrium constant for Reaction 1 of 1.0×10^{-1} atm., and a ΔG°_{-H2} of 1.4 kcal/mol. A total of three experiments were conducted with no significant deviation in the integration ratios.

 pK_a Determination of [HRh(dmpe)₂(CH₃CN)][OTf]₂ in Acetonitrile. In a typical experiment, [Rh(dmpe)₂][OTf] (22.8 mg, 0.041 mmol), 1,8-bis(dimethylamino)naphthalene (proton sponge, ps, 51 mg, 0.24 mmol), and the triflate salt of protonated proton sponge (HpsOTf) (24 mg 0.066 mmol) were combined in an NMR tube with 0.6 mL of CD₃CN. The reaction was followed by ³¹P NMR spectroscopy, and a constant ratio of [HRh(dmpe)₂(CH₃CN)][OTf]₂ (15.7 ppm, br; 3.4 ppm, br, int. set to 1) to [Rh(dmpe)₂][OTf] (36.4 ppm, int. 0.85) was observed in less than 1 h. After correction for protonation of [Rh-(dmpe)₂[[OTf], the ratio of H(ps)OTf/ps was determined to be 0.18 based on the initial mass added. Using these two ratios, an equilibrium constant of 1.5×10^{-1} was calculated for reaction 6. Combining this with the pK_a of protonated proton sponge in acetonitrile (18.2),⁹ a p K_a of 18.9 can be calculated for [HRh-(dmpe)₂(CH₃CN)][OTf]₂ using eq 9. This corresponds to a ΔG°_{H+} of 26.0 kcal/mol. Three independent experiments were performed in this manner, and [HRh(dmpe)₂(CH₃CN)][OTf]₂ was found to have an average pK_a of 18.9 and ΔG°_{H+} of 26.0 kcal/mol with none of the experiments deviating from the average by more than 0.16 kcal/mol.

p K_a **Determination of [HRh(depe)₂(CH₃CN)][OTf]₂ in Acetonitrile.** A similar set of three experiments was conducted for [HRh(depe)₂(CH₃CN)][OTf]₂ using the same proton sponge buffer system. For [HRh(depe)₂(CH₃CN)][OTf]₂ an average p K_a of 16.6 and ΔG°_{H+} of 22.8 kcal/mol were found; with none of the experiments deviating from the average by more than 0.05 kcal/mol.

p*K*_a **Determination of [HRh(depp)₂(CH₃CN)][OTf]₂ in Acetonitrile.** Using a anisidine buffer system (acetonitrile $p_{K_a} = 11.9$)⁴⁴ prepared in an analogous way, another trio of experiments was conducted for [HRh(depp)₂(CH₃CN)][OTf]₂ to give an average p_{K_a} value of 14.4 and ΔG°_{H+} of 19.8 kcal/mol, with none of the experiments deviating from the average by more than 0.04 kcal/mol. Use of 2,4-dichloroanilinium triflate as the acid produced the same chemical shifts as protonation with anisidinium triflate, supporting the formation of [HRh(depp)₂(CH₃CN)][OTf]₂ rather than [HRh(depp)₂(base)][OTf]₂.

 pK_a Determination of $[HRh(dppp)_2(CH_3CN)][OTf]_2$ in Acetonitrile. The species $[Rh(dcpe)_2][OTf]$ and $[Rh(dppp)_2][OTf]$

required strong acids. In these cases acid/base buffers were prepared and injected as a solution into the NMR tube containing the complex and 0.6 mL of CD₃CN. A typical experiment involved adding trifluoromethanesulfonic acid (HOTf) (795 mg, 5.30 mmol) to dimethylformamide (DMF, $pK_a = 6.1)^{45}$ (966 mg, 13.2 mmol) to create a buffer with a ratio of H(DMF)-OTf/DMF of 0.67. Then a portion of the buffer (167 mg, H(DMF)OTf, 0.51 mmol, DMF, 0.75 mmol) was injected into the NMR tube containing [Rh(dppp)₂][OTf] (20 mg, 0.019 mmol). The reaction reached equilibrium within minutes as indicated by a constant ratio of products for more than 24 h. The products included [Rh(dppp)₂][OTf] (³¹P{¹H} NMR: 8.4 ppm, d, ${}^{1}J_{RhP}$ 132 Hz, int. 0.66) to [HRh(dppp)₂(CH₃-CN)][OTf]₂ (${}^{31}P{}^{1}H{}$ NMR: 6.2 ppm, d, ${}^{1}J_{RhP}$ 91 Hz, int. set to 1.0). Considering the p K_a of H(DMF)OTf (6.1)⁴⁵ in acetonitrile and following the procedure set out above, a pK_a of 6.5 and ΔG°_{H+} of 8.8 kcal/mol were calculated. This experiment was conducted three times with a DMF buffer and three times with a dimethyl sulfoxide buffer (DMSO $pK_a = 5.8$)⁴⁵ to find that $[HRh(dppp)_2(CH_3CN)][OTf]_2$ had an average pK_a of 6.0 and ΔG°_{H+} of 8.7 kcal/mol with the maximum deviation for an individual experiment of 2.2 kcal/mol. Regardless of whether the acid was protonated DMSO or DMF, the same chemical shifts were observed for [HRh(dppp)2(CH3CN)][OTf]2, suggesting that [HRh(dppp)₂(base)][OTf]₂ is not present in appreciable quantities.

pK_a Determination of [HRh(dcpe)₂(CH₃CN)][OTf]₂ in Acetonitrile. A similar series of experiments was conducted with [Rh(dcpe)₂][OTf], three runs with a DMF buffer, and three runs with a dimethyl sulfoxide buffer. These experiments had the added challenge that [Rh(dcpe)2][OTf] decomposed into species identified as protonated dcpe and [HRh(dcpe)(CH₃CN)₃][OTf]₂ on exposure to strong acid. The addition of excess dcpe completely prevented the formation of [HRh(dcpe)(CH₃CN)₃]-[OTf]₂. Ignoring these side equilibria and focusing on the equilibrium between [Rh(dcpe)₂][OTf], and [HRh(dcpe)₂-(CH₃CN)][OTf]₂, and the buffer, it was found that [HRh- $(dcpe)_2(CH_3CN)$ [OTf]₂ had an average pK_a of 5.8 and ΔG°_{H+} of 7.9 kcal/mol with the maximum deviation for an individual experiment of 1.5 kcal/mol. Regardless of whether the acid was protonated DMSO or DMF, the same chemical shifts were observed for [HRh(dcpe)₂(CH₃CN)][OTf]₂, suggesting that [HRh(dcpe)₂(Base)][OTf]₂ is not present in appreciable quantities.

Equilibrium of [HRh(depp)₂(CH₃CN)][OTf]₂ with H₂ and Base. A solution of [Rh(depp)₂][OTf] (22 mg, 0.033 mmol), anisidine (104 mg, 0.84 mmol), and anisidiniumOTf (31 mg, 0.11 mmol) (p $K_a = 11.9$)⁴⁴ in CD₃CN was prepared and sealed with a septum. This solution was bubbled with hydrogen twice a day for 2 days before reaching a stable equilibrium. The ratio of [H₂Rh(depp)₂][OTf] and [HRh(depp)₂(MeCN)][OTf]₂ was determined from both the ³¹P NMR and the ¹H NMR spectra. ³¹P{¹H} NMR for [HRh(depp)₂(MeCN)][OTf]₂: 4.8 ppm, int 0.2, and for [H₂Rh(depp)₂][OTf]: 15.0 ppm, int. set to 1.0; -6.1 ppm, int 0.5; and for [H₂Rh(depp)₂][OTf]: -10.8 ppm, int. set to 1.0. These data were used to calculate a value for K_{eq} of 1.3 × 10^{-2} for Reaction 10. The value of $\Delta G^{\circ}_{H^-}$ for [H₂Rh(depp)₂]-[OTf] was determined to be 59.9 kcal/mol. This experiment was performed twice.

Another pair of experiments was performed with an aniline buffer ($pK_a = 10.6$)⁴⁶ prepared in a similar way as the DMSO and DMF buffers; however, the aniline was initially diluted in CD₃CN to prevent precipitation of the protonated amine. In these experiments a solution of [Rh(depp)₂][OTf] in CD₃CN was prepared and sealed with a septum. One sample was first purged with hydrogen forming [H₂Rh(depp)₂][OTf] as the dominant species. The buffer solution was added to this H₂-saturated solution, and an equilibrium mixture of [H₂Rh(depp)₂][OTf] and [HRh(depp)₂(MeCN)][OTf]₂ was formed over a period of

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2 days. The other tube was first injected with the buffer solution initially forming [HRh(depp)₂(MeCN)][OTf]₂ as the dominant species. This buffered solution was then purged with hydrogen for 10 min twice a day for 2 days, and progress toward equilibrium monitored. By averaging the values for all four experiments [H₂Rh(depp)₂][OTf] was found to have a $\Delta G^{\circ}_{H^{-}}$ of 61.3 kcal/mol with none of the experiments deviating from the average more than 1.1 kcal/mol.

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Supporting Information Available: Derivation of Tolman cone angles for bidentate ligands used. This material is available free of charge via the Internet at http://pubs.acs.org.