Protonation and H₂ Heterolysis Reactions of Electrophilic (η⁵-C₅R₅)Ru(dfepe)(X) (R = H, Me; X = H, OTf) Complexes

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Addition of excess $HOSO_2CF_3$ (HOTf) to CpRu(L)H (**1**) (L = dfepe = $PR_2CH_2CH_2PR_2$, R = C_2F_5) in CD_2Cl_2 under N_2 produces a mixture of $[CpRu(L)(H)_2]^+$ (**2a**), $[CpRu(L)(H_2)]^+$ (**2b**), and CpRu(L)(OTf) (**3**) in a ratio of 1:5:2. Salts of the acid $[HOEt_2]^+$ are not strong enough to protonate **1**. Complexes **2** slowly eliminate H_2 to give **3**; this reaction is slowed by adding excess HOTf. Of all such complexes $[CpRu(PR_2CH_2CH_2PR_2)(H_2)]^+$, R = alkyl and aryl, the dihydrogen complex **2b** has the greatest acidity (similar to that of HOTf) and the related HD complex has the greatest J_{HD} (29.1 Hz) because of the electron-withdrawing substituents R = C_2F_5. The reaction of **3** with 1 atm H_2(g) proceeds much faster in the presence than in the absence of 1 equiv of HOTf to produce **1** and HOTf. This is a rare example of the production of a strong acid from H_2(g) where the intermediate dihydrogen complex has been characterized. Reaction of Cp*Ru(L)Cl (**4**), Cp* = C_5Me_5, in dry CH_2Cl_2 at −78 °C with AgX salts under H_2(g) (1 atm) gives mixtures of Cp*Ru(L)H (**5**) and $[Cp*Ru(L)(H)_2]^+$ (**6**), which have been identified by ^1H NMR. **6** is deprotonated by traces of water or by PPh₃ to give Cp*Ru(L)H (**5**). The addition of excess HOTf to mixtures of **5** and **6** under H_2(g) produces **6**. Complexes **3**, **4**, and **5** have been characterized by single-crystal X-ray diffraction. Complexes CpRu(L)Cl, **1**, **4**, and **5** have very positive redox potentials that indicate that the dfepe ligand has the electron-withdrawing power close to that of two carbonyl ligands.

Introduction

The activation of molecular hydrogen by transition metal centers is a reaction of fundamental importance to catalysis. Since Kubas' seminal demonstration of discrete nonclassical ("arrested oxidation state") M(η²-H₂) complexes,[1] numerous studies concerning interconversion equilibria between M(H)₂ and M(η²-H₂) complexes and their dependence on the nature of the metal center as well as the ancillary ligand environment have been reported.[2−7] For cationic dihydride and dihydrogen complexes derived via protonation of neutral hydride precursors, interconversion equilibria as well as the relative thermodynamic and kinetic Brønsted acidities have also been detailed.[8−15] $M(H)_2^+$ and/or $M(η^2\text{-}H_2)^+$
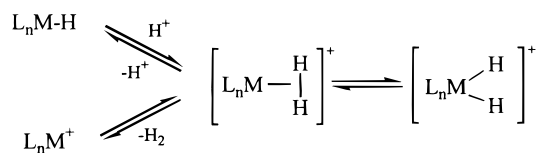
Scheme 1

intermediates are generally implicated in the heterolysis of H₂ by M⁺ in many metal hydride syntheses, but these precursor species have been characterized in only a few cases (Scheme 1).[16−22]

An extensive series of cationic ruthenium piano stool dihydrogen complexes containing Cp or Cp* ligands

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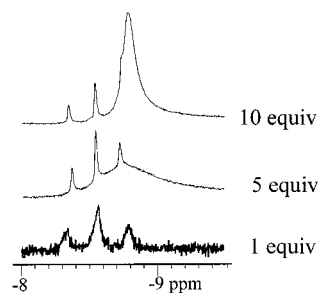(22) Bianchini, C.; Moneti, S.; Peruzzini, M.; Vizza, F. *Inorg. Chem.* **1997**, *36*, 5818.

have been reported.[4] These complexes can undergo a stereochemical change from a three-legged piano stool (octahedral) dihydrogen complex to a transoid-square-based four-legged piano stool (SPS-7) dihydride (eq 1; L, L' = phosphine, carbonyl, isonitrile).

(1)
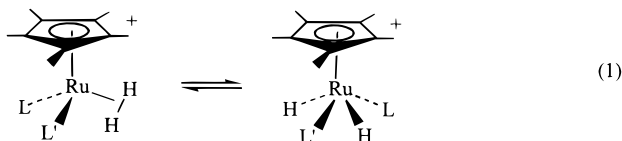
The position of the dihydride/dihydrogen equilibrium for these ruthenium complexes is dependent upon the steric interactions between the ligands (L) and the Cp or Cp* rings. In dihydrogen complexes $(Ru(H_2)^+)$, the ancillary ligands are brought closer to the Cp or Cp* rings. Thus complexes with larger ancillary ligands and Cp* ligands favor the dihydride form $(Ru(H)_2^+)$. In the absence of differences in ligand size, the electronic properties of the ligands influence the equilibrium. In the series of complexes $[CpRu(PR_2CH_2CH_2PR_2)(H_2)]^+$, the equilibrium shifts toward the dihydride as R = p-$C_6H_4CF_3$ < C_6H_5 < p-C_6H_4OMe.[12] Therefore, electron-donating ligands favor the formation of dihydride tautomers. The pK_a values of the dihydride complexes referenced to $HPCy_3^+$ at 9.7 in THF also increase as p-$C_6H_4CF_3$ (4.6) < C_6H_5 (7.2) < p-C_6H_4OMe (8.6).[12] The use of Cp* instead of Cp in corresponding complexes resulted in a 2−3 unit increase in pK_a values.[11] These trends are expected on the basis of the inductive effect of the substituents on phosphorus or Cp ligands. Studies of cationic ruthenium piano stool complexes $[(\eta^5\text{-}C_5R_5)Ru(L)_2(L')]^+$ (L = CO or R_3P; L' = H_2 or $(H)_2$) have been reported where the dihydrogen complexes exhibit a wide range of ancillary ligand-dependent acid−base properties, varying from the strong acid $[(\eta^5\text{-}C_5Me_5)Ru(CO)_2(\eta^2\text{-}H_2)]^+$ (pK_a(CH_2Cl_2) < 0, vs $HOEt_2^+$ at −2 in CH_2Cl_2) to weakly acidic $[(\eta^5\text{-}C_5Me_5)Ru(dmpe)(\eta^2\text{-}H_2)]^+$ (pK_a(MeCN) = 17.6 vs $HNEt_3^+$ at 18.5 in MeCN or pK_a(THF) ~ 10 vs $HNEt_3^+$ at 10.8 in THF).[10−12] In the previously reported synthesis of CpRu(dfepe)H,[23] preliminary observations suggested that the protonated derivative, CpRu(dfepe)(H)_2^+, was highly acidic: (1) No protonolysis of CpRu(dfepe)H by HBF_4·Et_2O in dichloromethane was observed, and (2) chloride abstraction from CpRu(dfepe)Cl by $AgBF_4$ under 1 atm H_2(g) in the presence of diethyl ether resulted in the isolation of the neutral hydride CpRu(dfepe)H rather than [CpRu(dfepe)(H)_2]^+BF_4^-. In this paper we report more detailed protonation studies of CpRu(dfepe)H as well as the permethylated derivative Cp*Ru(dfepe)H and some observations regarding the role of acid-assistance in the heterolysis of dihydrogen by CpRu(dfepe)(OTf).

Results and Discussion

Protonation of CpRu(dfepe)H. Protonations of neutral hydride complexes have typically been accomplished by addition of a slight excess of HBF_4·(Et_2O). However, addition of excess $HBF_4(Et_2O)$ or $[H(OEt_2)_2]^+B[3,5\text{-}(CF_3)_2C_6H_3]_4^-$ to CpRu(dfepe)H (**1**) in dichloromethane under N_2 showed no evidence for

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Figure 1. ^{1}H NMR hydride region for the addition of 1, 5, and 10 equiv of HOTf to CpRu(dfepe)H in CD_2Cl_2 (10 mM).

protonation by ^{1}H NMR. The protonolysis behavior of **1** by the stronger Brønsted acid HOTf was therefore examined. In acetonitrile, no protonation was observed with excess (6 equiv) HOTf. Protonation of CpRu(dfepe)(H) by HOTf in the absence of competing Lewis bases does, however, occur. No acid or hydride resonances were observed by ^{1}H NMR after the addition of 0.5 equiv of HOTf to **1** in CD_2Cl_2 (19 mM) due to rapid proton exchange between **1** and free acid (Figure 1). A small downfield shift for the Cp resonance of **1** from 5.18 to 5.26 ppm was accompanied by the appearance of a small (ca. 5%) peak at 5.48 ppm attributable to the loss of H_2 and the formation of CpRu(dfepe)OTf (**3**) (*vide infra*). After 1 equiv of HOTf was added, the amount of **3** increased to 25%, the major Cp resonance shifted further downfield to δ 5.35, and a small (ca. 5%) new Cp resonance appeared at δ 5.94 together with an associated new hydride triplet at δ −8.68 ($^2J_{PH}$ = 31 Hz), which integrated 2:5 with respect to the δ 5.94 singlet. The peak with the averaged chemical shift of 5.35 (Cp) is assigned to a rapidly equilibrating mixture of **1** and a dihydrogen complex **2b** (the broad hydride resonance is not observed), while those at 5.94 and −8.68 are assigned to a dihydride complex **2a** (vide infra). Attempts to directly observe **1** and any rapidly exchanging protonation product(s) such as **2b** by VT-NMR were not successful due to solubility limitations of HOTf in dichloromethane below −20 °C.

After the addition of a total of 2 equiv of HOTf, a further downfield shift of the main Cp resonance to δ 5.53 was observed along with a slight increase in intensities for the δ 5.94 cyclopentadienyl ruthenium hydride product and **3**. At this point, the three cyclopentadienyl resonances reached a steady 5:1:2 ratio (δ 5.53 to δ 5.94 to **3**), which remained essentially constant with further addition of acid. No observable low field acid resonances were observed. In the presence of ≥5 equiv HOTf, the major downfield Cp resonance reached a limiting downfield value at 5.80 ppm, and no changes in the relative intensities for the other Cp product resonances were noted. At this point, a new hydride resonance appeared as a broad singlet at −8.78 ppm, and an acid peak at 11.90 ppm was also observed. After 10 equiv of added HOTf, a protic resonance appears at 10.78 ppm, and the hydride resonance at −8.78 ppm integrated 2:5 relative to the δ 5.80 cyclopentadienyl resonance.

The hydride resonances at −8.68 and −8.78 ppm are assigned to the classical and nonclassical dihydrides $[CpRu(dfepe)(H)_2]^+$ (**2a**) and $[CpRu(dfepe)(\eta^2\text{-}H_2)]^+$ (**2b**), respectively, on the basis of T_1 relaxation times at 20 °C (400 MHz; 7 equiv added HOTf: T_1(**2a**) 2.91 s; T_1(**2b**)

(a)

(b)
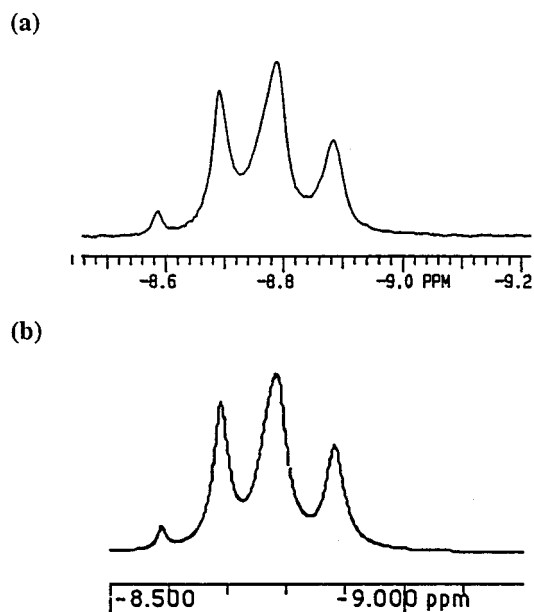
Figure 2. (a) Observed and (b) simulated ^{1}H NMR spectra in the high-field region of **1** in CD_2Cl_2 treated with DOTf. The mixture consists of **2a**:**2b**:**2b-d_1** in a ratio of 1:3:16. δ(**2a**) −8.69 (J_{HP} = 30.6 Hz), δ(**2b**) −8.77 br, δ(**2b-d_1**) −8.79 (J_{HD} = 29.1 Hz).

69 ms) and integration data and the absence of resolvable $^2J_{PH}$ coupling for **2b**. The short T_1 value associated with **2b** falls within the range (10−160 ms) generally found for nonclassical dihydrogen coordination.[4,5,7] The binomial triplet observed for **2a** is in accord with a transoid piano-stool geometry (eq 2).

1

(δ(Cp) = 5.18)

$$ \text{(2)} $$

2a (13%)   **2b** (63%)   **3** (24%)

(δ(Cp) = 5.94)   (δ(Cp) = 5.80)
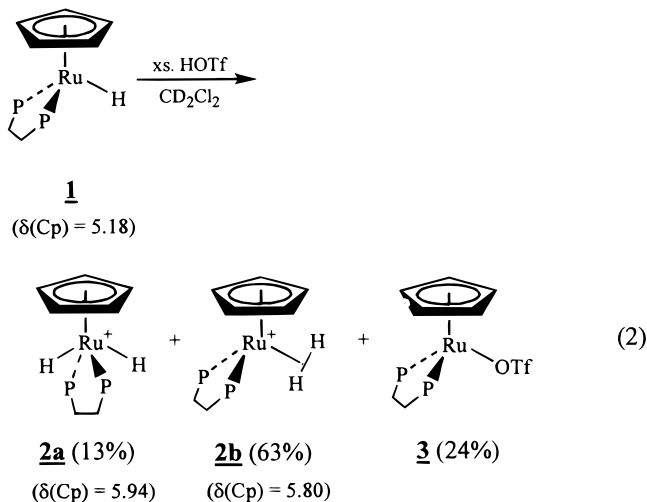
Addition of deuterated triflic acid to **1** resulted in a mixture of **2a**, **2b**, and their HD analogues. Four unsymmetrical peaks are observed in the ^{1}H NMR in the region δ −9.0 to −8.5 arising from the overlap of peaks from the four complexes (Figure 2a). Using an NMR simulation program,[24] the hydride region was simulated (Figure 2b) and the $^1J_{HD}$ of the HD analogue of **2b** (**2b-d_1**) was calculated to be 29.1 Hz, corresponding to a hydrogen−hydrogen distance of 0.93 Å.[25]

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Scheme 2
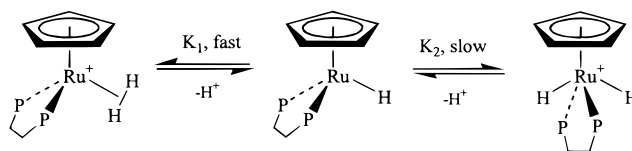
Compared to carbonyl analogues, complex **2b** is exceptionally stable. In the presence of 20 equiv of added HOTf, only slow conversion to the triflate complex CpRu(dfepe)OTf was observed at 20 °C over the course of several days. $Cp^*Ru(CO)_2(\eta^2$-$H_2)^+$ is reported to rapidly dimerize with loss of acid to form $\{[Cp^*Ru(CO)_2]_2(\mu$-H)$\}^+$ at temperatures above 235 K.[10] The stability of **2b** toward bimolecular decomposition is likely due to the steric protection afforded by the bulky dfepe ligand.

NMR observations for the protonation of CpRu(dfepe)H may be accommodated by a mechanism involving competitive protonation equilibria between **1** and the cations **2a** and **2b** (Scheme 2). The appearance of a classical dihydride cation **2a** which does not exhibit exchange broadening in the presence of excess HOTf is consistent with earlier studies that have demonstrated the kinetic acidity of classical dihydride cations to be much lower than that for the related nonclassical tautomer.[8,9,11] Proton exchange in systems involving M−H bonds is often quite slow due to structural and electronic rearrangements.[26] In the present case, protonation of CpRu(dfepe)H to form **2b** retains a cisoid piano stool geometry, while the formation of the **2a** cation involves a rearrangement to a transoid chelate coordination geometry.

Proton exchange between [CpRu(dfepe)(η^2-H_2)]$^+$ and OTf$^-$ and/or unprotonated CpRu(dfepe)H (self-exchange) is fast on the NMR time scale at ambient temperatures. In the presence of excess HOTf, the equilibrium K_1 is driven toward the nonclassical isomer, and the appearance of a broad hydride singlet at −8.78 ppm for **2b** is observed. The extent of protonation to form **2b** is also reflected in the acid-dependent chemical shift of the major cyclopentadienyl resonance, which appears as a weighted average between CpRu(dfepe)H (δ 5.18) and [CpRu(dfepe)(η^2-H_2)]$^+$ (δ 5.80). The solvation and self-association behavior of HOTf in dichloromethane is not well understood, and therefore the thermodynamic acidity of **2b** could not be quantified in this solvent. Qualitatively, however, [CpRu(dfepe)(η^2-H_2)]$^+$ must have a comparable pK_a to triflic acid (p$K_a \approx -5$)[27] in this solvent. In any case, the failure of CpRu(dfepe)H (**1**) to protonate in the presence of diethyl ether qualitatively indicates that [CpRu(dfepe)(η^2-H_2)]$^+$ is a stronger acid than Et_2OH^+ (p$K_a \approx -2.4$).[28] It is also a stronger acid than HOTf/CH_3CN (pK_a 2.6 in CH_3CN or ≈ -5 on the pseudoaqueous scale[27]).[29]

Synthesis and Structure of CpRu(dfepe)OTf (3). The triflate complex CpRu(dfepe)OTf (**3**) is most likely

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Table 1. Summary of Crystallographic Data for CpRu(dfepe)OTf (3), Cp*Ru(dfepe)Cl (4), and Cp*Ru(dfepe)H (5)

	3	4	5
formula	$C_{16}H_9F_{23}O_3P_2RuS$	$C_{20}H_{19}ClF_{20}P_2Ru$	$C_{20}H_{20}F_{20}P_2Ru$
cryst size (mm)	$0.52 \times 0.40 \times 0.24$	$0.40 \times 0.30 \times 0.15$	$0.32 \times 0.40 \times 0.15$
cryst syst	monoclinic	monoclinic	monoclinic
space group	$P2_1/c$	$P2/c$	$P2_1/c$
temp (K)	173	294	173
a (Å)	9.216(2)	19.220(4)	18.422(2)
b (Å)	18.486(3)	11.482(2)	8.671(2)
c (Å)	14.896(3)	12.770(3)	16.789(4)
β (deg)	90.640(10)	91.24(3)	91.37(3)
V (Å^3)	2537.6(9)	2817.5(10)	2681.1(8)
Z	4	4	4
ρ_{calc} (g/cm^3)	2.307	1.975	1.990
wavelength (Å)	0.710 73	0.710 73	0.710 73
mol wt	881.3	837.81	803.4
μ (mm^{-1}) (Mo Kα)	0.996	0.910	0.855
T_{max}/T_{min}	0.4131/0.6244	0.5390/0.5720	0.3335/0.9392
2θ range (deg)	4.0−55.0	4.8−54.0	5.0−54.0
scan type	$2\theta-\theta$	ω	ω
no. of reflns measd	8107	5923	6452
no. of unique reflns	5724	5338	5844
no. of $F > 4.0\sigma(F)$	4455	3216	3246
R_F (%)	3.84	6.40	6.89
R_{WF} (%)	5.54	8.77	6.79
goodness of fit	1.28	2.05	1.37

formed via loss of dihydrogen directly from **2b**. On a preparative scale, the reaction of **1** with excess HOTf in dichloromethane and with periodic removal of evolved hydrogen gas under vacuum afforded **3** in 61% yield (eq 3). Yellow crystalline **3** is moderately soluble in both polar and nonpolar solvents, consistent with covalent triflate coordination. ^{19}F NMR and IR data confirm the presence of a coordinated triflate ligand. In particular, ^{19}F NMR spectra of **3** exhibit a triflate CF_3 singlet at −77.9 ppm, upfield from free triflate ion (−79.0 ppm). IR $\nu(SO_3)$ bands for **3** appearing at 1325 and 1013 cm^{-1} are shifted in the expected manner from ionic triflate stretches and are consistent with unidentate triflate coordination.[30−33]

$$\text{(3)}$$
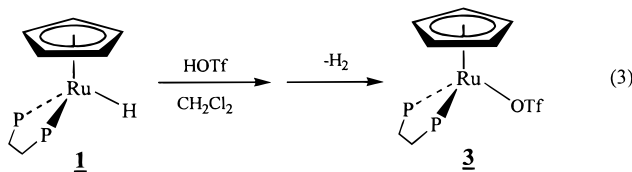
The crystal structure of **3** has been determined in order to provide comparisons with other metal−triflate systems (Figure 3). A summary of data collection parameters, atomic coordinates, and metrical parameters are tabulated in Table 1, and selected bond distances and angles are given in Table 2. The Ru−P bond distances of 2.253(1) and 2.265(1) Å are essentially identical to those reported for CpRu(dfepe)Cl[23] and are significantly shorter than alkylphosphine Ru−P bond lengths. Despite the lower labilities generally found in electron-poor dfepe systems, the observed Ru−O distance of 2.171(3) Å is similar to that in (η^5-C$_5$Me$_5$)Ru-(Ph)(NO)(OTf) (2.146(4) Å)[34] and shorter than the 2.22−
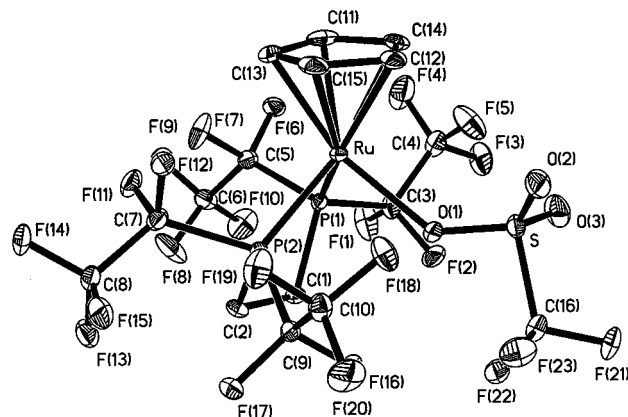
Figure 3. Structure of CpRu(dfepe)OTf (**3**) with atom-labeling scheme (hydrogen atoms omitted for clarity).

Table 2. Selected Distances (Å) and Angles (deg) for CpRu(dfepe)OTf (3)

Bond Distances			
Ru−O	2.171(1)	Ru−C(12)	2.227(4)
Ru−P(1)	2.253(1)	Ru−C(13)	2.169(4)
Ru−P(2)	2.265(1)	Ru−C(14)	2.215(4)
Ru−C(11)	2.181(4)	Ru−C(15)	2.232(4)
Bond Angles			
O−Ru−P(1)	86.2(1)	O−Ru−P(2)	89.0(1)
P(1)−Ru−P(2)	82.3(1)	Ru−O−S	135.4 (2)

2.31 Å range associated with octahedral Ru(II) triflate systems[35−37] and thus does not reflect any unusual strengthening of the Ru−OTf interaction due to the electrophilic nature of the CpRu(dfepe) moiety.

Acid-Promoted H$_2$ Heterolysis by CpRu-(dfepe)(OTf). The initial appearance of **3** during protonation experiments at low acid concentrations fol-

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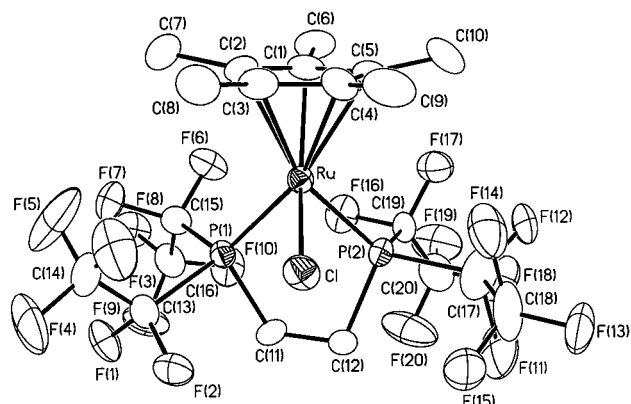
Scheme 3
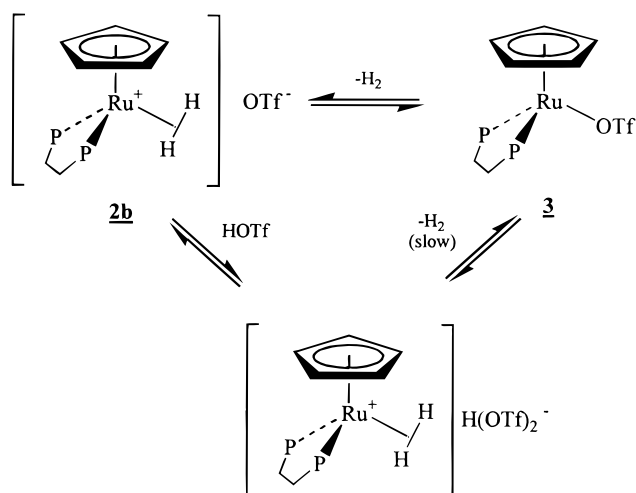
lowed by slower H$_2$ loss in the presence of excess HOTf suggested that H$_2$ loss is inhibited by free triflic acid. Additional NMR experiments have shown that excess acid samples take significantly longer to completely convert to the neutral triflate than do samples containing only a slight excess of acid. For example, in the presence of 3 equiv of HOTf, the complete conversion of **1** to **3** requires 1 week at 20 °C, whereas conversion is complete after 24 h when 1.1 equiv of HOTf is employed. It is probable that H$_2$ loss from **2b** is inhibited by the presence of excess triflic acid due to homoconjugation of the triflate counterion with additional acid. Hydrogen bonding to form [H(O$_3$SCF$_3$)$_2$]$^-$ should reduce the nucleophilicity of the triflate anion and disfavor the displacement of the H$_2$ from **2b** (Scheme 3). The presence of [H(O$_3$SCF$_3$)$_2$]$^-$ is consistent with observed dependence of δ(HOTf) on the [HOTf]/CpRu ratio in dichloromethane.

The inhibition effect observed for **2b** suggested that the reverse reaction, heterolytic cleavage of hydrogen by **3** to form CpRu(dfepe)H (**1**) and HOTf, might similarly show an acid dependence. A comparison of H$_2$ heterolysis rates for **3** with and without added HOTf in CD$_2$Cl$_2$ under 1 atm of hydrogen was assessed by ^{1}H NMR. Upon addition of 1 equiv of HOTf, formation of **1** occurred quickly at room temperature, as noted by the appearance of an exchange-averaged Cp resonance characteristic of **1**,[38] with quantitative conversion to a neutral hydride/HOTf mixture after 1 day. In the absence of HOTf, no H$_2$ cleavage was noted after 3 days. After 60 h at 50 °C, however, complete conversion of **3** to **1** had occurred. In a control experiment, the thermolysis of **3** in CD$_2$Cl$_2$ at 80 °C did not give **1**, but rather Cl abstraction from solvent took place to give CpRu-(dfepe)Cl. These results are consistent with earlier observations by Trogler and co-workers, who found that an increase in the solution acidity enhanced the kinetic rate of substitution of (CO)$_5$Mn(OTf) by donor molecules (Scheme 4).[39]

Synthesis and Structure of Cp*Ru(dfepe)Cl (4). The synthesis of Cp*Ru(dfepe)Cl involves a straightforward reduction of the Ru(III) metal complex

(38) The exchange-averaged Cp chemical shift for **1/2b** varies due to changing **1**: HOTf ratios over the course of reaction.
(39) Nitschke, J.; Schmidt, S. P.; Trogler, W. C. *Inorg. Chem.* **1985**, *24*, 1972.

Figure 4. Structure of Cp*Ru(dfepe)Cl (**4**) with atom-labeling scheme (hydrogen atoms omitted for clarity).

Table 3. Selected Distances (Å) and Angles (deg) for Cp*Ru(dfepe)Cl (4) and Cp*Ru(dfepe)H (5)

	4	**5**
Bond Distances		
Ru–Cl	2.413(3)	
Ru–H(1RU)		1.43(9)
Ru–P(1)	2.256(3)	2.198(3)
Ru–P(2)	2.238(3)	2.192(3)
Ru–C(1)	2.219(9)	2.282(10)
Ru–C(2)	2.256(11)	2.262(9)
Ru–C(3)	2.209(11)	2.242(10)
Ru–C(4)	2.215(11)	2.254(9)
Ru–C(5)	2.258(10)	2.260(9)
H(6)–F(6)[a]	2.429	
H(7B)–F(8)[a]		2.429
H(8B)–F(3)[a]	2.4929	
H(8C)–F(5)[a]		2.193
H(9C)–F(14)[a]	2.359	2.426
H(10C)–F(17)[a]	2.443	
H(10B)–F(12)[a]		2.453
Bond Angles		
Cl–Ru–P(1)	87.8(1)	
Cl–Ru–P(2)	86.5(1)	
H(1RU)–Ru–P(1)		79(4)
H(1RU)–Ru–P(2)		80(4)
P(1)–Ru–P(2)	82.1(1)	83.8(1)
CNT–Ru–Cl[b]	118.4	
CNT–RuH–(1RU)[b]		116.4
CNT–Ru–P(1)[b]	134.6	137.0
CNT–Ru–P(2)[b]	131.9	136.1

^{a} Calculated distances; atoms are not bonded. ^{b} CNT: centroid of cyclopentadienyl ring.

[Cp*RuCl$_2$]$_x$ by zinc in the presence of dfepe (eq 4). Complex **4** dissolves in CH$_2$Cl$_2$ to produce an air-stable orange solution. The ^{1}H resonance for the Cp* ligand appears at δ 1.82, with a multiplet at δ 2.55 due to the dfepe backbone. The ^{31}P{^{1}H} NMR spectrum shows a single fluorine-coupled multiplet at 108.1 ppm.

$$2[Cp^*RuCl_2]_x + 2dfepe + Zn \xrightarrow{\text{toluene}}$$
$$2Cp^*Ru(dfepe)Cl + ZnCl_2 \quad (4)$$
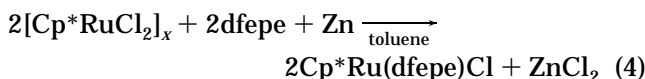
An X-ray diffraction study confirmed the expected three-legged piano stool geometry for complex **4** (Figure 4). Selected crystallographic data for **4** are shown in Table 1, and selected bond distances and angles and atomic coordinates are given in Table 3.
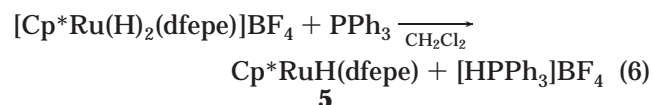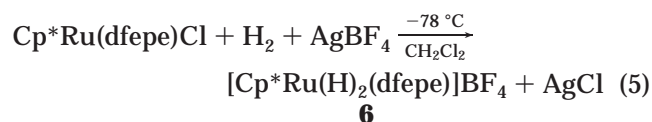
Some of us have reported the crystal structure of CpRu(dfepe)Cl.[23] The observed Ru–Cl bond length (2.415(2) Å) and the Ru–P bond lengths (2.256(2) and 2.239(3) Å) of Cp*Ru(dfepe)Cl are virtually identical to
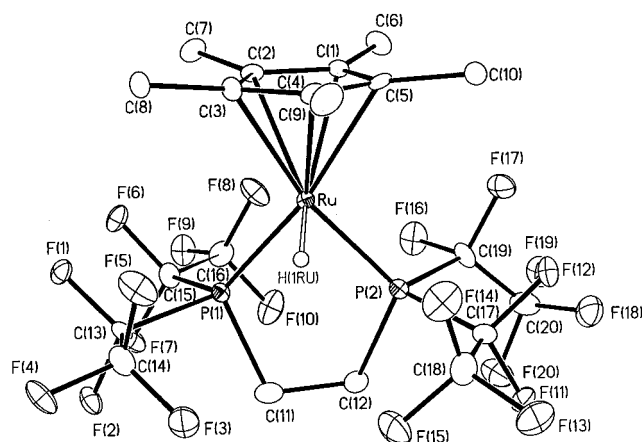
Scheme 4
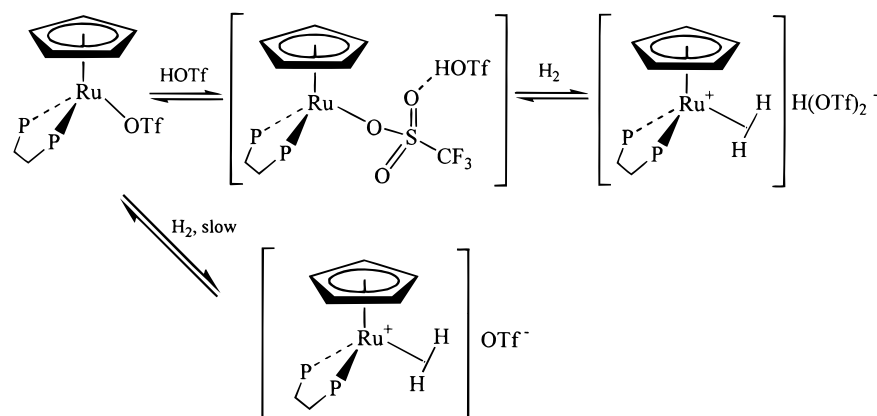
the Ru–Cl bond length (2.406(1) Å) and Ru–P bond lengths (2.248(2) and 2.236(2) Å) found for the Cp complex. In principle, the increased electron density afforded by the Cp* ligand should contribute to enhanced back-bonding to the dfepe ligand and perhaps result in Ru–P bond shortening, whereas increased steric bulk would be expected to counter this effect. The similar Ru–P bond lengths suggest a balancing of these factors. Regarding other structural features, steric effects may cause the bond angle P–Ru–P in Cp*Ru-(dfepe)Cl (81.82(9)°) to be slightly smaller than that for CpRu(dfepe)Cl (83.1(1)°). Also observed for **4** are slightly larger CNT–Ru–P(1) (134.6°) and CNT–Ru–P(2) (131.9°) angles than those of the Cp analogue (CNT–Ru–P(1) (130.8°) and CNT–Ru–P(2) (129.0°)) (where CNT is the centroid of the cyclopentadienyl ring) due to close contacts between the hydrogens on the methyl groups of the Cp* ring and those of the F atoms of the dfepe ligand (Table 3), the closest contact being between H(9C) and F(14) with a distance of 2.359 Å. These close contacts are less than the sum of the van der Waals radii of H (1.20 Å) and F (1.47 Å).

Synthesis and Characterization of Cp*Ru-(dfepe)H (5). The synthesis of Cp*Ru(dfepe)H is thought to proceed via the formation of the dihydride complex (**6**) (vide infra), which is subsequently deprotonated by triphenylphosphine (eqs 5 and 6):

$$\text{Cp*Ru(dfepe)Cl} + \text{H}_2 + \text{AgBF}_4 \xrightarrow[\text{CH}_2\text{Cl}_2]{-78\ °\text{C}}$$

$$[\text{Cp*Ru(H)}_2\text{(dfepe)}]\text{BF}_4 + \text{AgCl} \quad (5)$$
$$\mathbf{6}$$

$$[\text{Cp*Ru(H)}_2\text{(dfepe)}]\text{BF}_4 + \text{PPh}_3 \xrightarrow{\text{CH}_2\text{Cl}_2}$$

$$\text{Cp*RuH(dfepe)} + [\text{HPPh}_3]\text{BF}_4 \quad (6)$$
$$\mathbf{5}$$

Complex **5** dissolves readily in benzene to produce an air-sensitive yellow solution. The proton NMR spectrum shows peaks at δ 2.52 (m), 1.94 (s), and −14.0 (t, J_{HP} = 36.8 Hz), corresponding to the dfepe ligand, Cp* ligand, and the hydride, respectively. The hydride resonance is similar to that of related complexes Cp*Ru(L₂)H such as Cp*Ru(dppp)H (−13.0 ppm, 31.5 Hz)[11] and Cp*Ru-(PMePh₂)₂H (−12.5 ppm, 35.3 Hz).[12] A multiplet at 110.9 ppm is observed for **5** in the ³¹P{¹H} NMR spectrum.

The structure of **5** is a distorted three-legged piano stool (Figure 5). Selected crystallographic data and

Figure 5. Structure of Cp*Ru(dfepe)H (**5**) with atom-labeling scheme (hydrogen atoms omitted for clarity).

selected bond distances and angles are given in Tables 1 and 3, respectively. The hydride was located with a bond length d(Ru–H) = 1.43(9) Å. A large CNT–Ru–P angle of 136.5° is observed for **5**. As with complex **4**, there are close contacts of F atoms of the dfepe ligand with the hydrogens on the methyl groups of the Cp* ligand (Table 3), the closest contact distance being between H(8C) and F(5) (2.193 Å). Lemke and Brammer have studied the geometries of Cp′L₂MH (Cp′ = C₅H₅, C₅Me₅, C₅H₄Me; L₂ = diphosphines, M(d⁶)) and [Cp′L₂M(η²-H₂)]⁺ (M(d⁶)) three-legged and Cp′L₂M(H)₂ (M(d⁴)) four-legged piano stool structures.[40] From their studies, the mean angles between the Cp′ plane and the ML₂ plane are 68(1)°, 56.1(8)°, and 87.6(4)° for Cp′L₂MH, [Cp′L₂M(η²-H₂)]⁺, and Cp′L₂M(H)₂, respectively. On the basis of this interplanar angle, monohydrides, dihydrides, and dihydrogen complexes can be distinguished from each other in the absence of accurate M–H metrical data. Complex **5** has an interplanar angle of 78.1°, which is larger than the mean angle of 68(1)° for related Cp′L₂MH (M(d⁶)) complexes but similar to the value of 79.2° for the sterically crowded complex [Cp*RhH(PPh₃)₂]⁺.[40] Close contacts between the F atoms of the dfepe ligand and the methyl groups of the Cp* ligand probably contribute to the increased interplanar angle. The interplanar angle of **4** (65.7°) is significantly smaller than that found for complex **5**.

Synthesis and Characterization of [Cp*Ru-(dfepe)(H)₂]BF₄ (6). Removal of solvent from the red-

(40) Lemke, F. R.; Brammer, L. *Organometallics* **1995**, *14*, 3980.

Table 4. $E_{1/2}$ Values for Complexes 1, 4, 5, and 7

complex	$E_{1/2}$ obs[a]	$E_{1/2}$ calc[b]	reversibility
CpRu(dfepe)Cl (7)	0.94	0.79	reversible
CpRu(dfepe)H (1)	0.94	0.95	irreversible
Cp*Ru(dfepe)Cl (4)	0.72	0.71	reversible
Cp*Ru(dfepe)H (5)	0.52	0.55	reversible
	0.71		reversible

[a] In V vs FeCp$_2^{+/0}$ with 0.2 M n-Bu$_4$NPF$_6$/CH$_2$Cl$_2$. [b] By use of Lever's method.[41] $E_{1/2}$ calc = ΣE_L − 0.6 (to convert from NHE to FeCp$_2^+$/0); E_L(Cp$^-$) = 3 × 0.03, E_L(Cp^{*-}) = 3 × −0.05, E_L(Cl$^-$) = −0.24, E_L(H$^-$) = −0.4, E_L(dfepe) = 0.85 V.

brown mixture of **5** and **6** obtained from eq 5 produces a moisture-sensitive residue which slowly decomposes to the monohydride (**5**) after several days. Since any traces of water in the reaction medium result in the formation of the monohydride, it is qualitatively concluded that the pK_a of [Cp*Ru(dfepe)(H)$_2$]BF$_4$ is less than that of H$_3$O$^+$. Cp* complexes usually have pK_a values that are 2−3 units greater than their Cp analogue.[11] This would place the pK_a of **5** between 0 and −3 (assuming that **2** is −5, vide supra), in accord with the observed acidity of **6**.

In the ^{1}H NMR spectrum, the hydride resonance of the complex [Cp*Ru(dfepe)(H)$_2$]BF$_4$ appears as a triplet at −8.90 ppm ($^2J_{HP}$ = 34.4 Hz), similar to the triplet observed for the dihydrides [Cp*Ru(dppp)(H)$_2$]BF$_4$ (−8.67 ppm, 29 Hz) and [Cp*Ru(PMePh$_2$)$_2$(H)$_2$]BF$_4$ (−8.13 ppm, 28.2 Hz).[11] The long T_1(min) of 0.59 s (−60 °C, 400 MHz) suggests that complex **6** is a dihydride and not a dihydrogen complex. Any cisoid dihydrogen complex [Cp*Ru(dfepe)(η^2-H$_2$)]BF$_4$ formed initially under the conditions of eq 5 must undergo facile isomerization to **6** due to unfavorable steric interactions between the Cp* and the dfepe ligands (see the Introduction). [Cp*Ru-(dfepe)(H)$_2$]BF$_4$ cannot be synthesized in a pure state; the presence of the monohydride **5** (−14.5 ppm) and acid (7.68 ppm) is always detected in ^{1}H NMR spectra. When the acid peak is not observed, only the resonances of **5** are observed. We assume that any HBF$_4$ generated from **6** is present as [H$_3$O]$^+$[BF$_4$]$^-$, since the proton resonance for HBF$_4$·Et$_2$O generally appears at ~12 ppm.

When AgOTf was used instead of AgBF$_4$ in an attempt to make the Cp* dihydride complex [Cp*Ru-(dfepe)(H)$_2$](O$_3$SCF$_3$), a mixture of monohydride and dihydride similar to that found for the AgBF$_4$ reaction was observed by ^{1}H NMR. Addition of excess HOTf to this solution under H$_2$ does convert the mixture exclusively to the dihydride; however, all attempts to isolate the dihydride triflate salt gave instead the monohydride **5**. If an excess of either silver salt is used in the synthesis of **5,** a multitude of peaks are observed between 1 and 4 ppm in the ^{1}H NMR spectrum.

Cyclic Voltammetric Studies of Complexes, 1, 4, 5, and CpRu(dfepe)Cl (7).[23] All of the complexes except **1** display a reversible Ru(III)/Ru(II) couple (Table 4). CpRu(dfepe)H (**1**) has an oxidation threshold at the same place (0.94 V) as the reversible oxidation of CpRu(dfepe)Cl (**7**). The Cp* monohydride complex **5** in CH$_2$Cl$_2$ exhibits two reversible waves with $E_{1/2}$ of 0.52 and 0.71 V vs FeCp$_2^{+/0}$. The oxidation and reduction peaks with $E_{1/2}$ of 0.52 V are significantly larger than those of the redox couple at 0.71 V. The latter couple is very similar to that observed for Cp*Ru(dfepe)Cl ($E_{1/2}$ = 0.72 V) and may be ascribed to a competing formation

of Cp*Ru(dfepe)Cl by the reaction of **5** with the chlorinated solvent. The oxidation wave of **5** in THF is masked by the peak for the oxidation of the solvent. The application of Lever's ligand additivity method[41] with an E_L value of 0.85 V for ^{1}/$_2$dfepe allows the calculation of redox potentials for these complexes that agree with the observed values (Table 5). Thus, the dfepe ligand is more π-acidic and electron-withdrawing than two dinitrogen ligands (2 × E_L = 2 × 0.68 V) and is almost as π-acidic as two carbonyl ligands (2 × E_L = 2 × 0.99 V).[42] For comparison, we have also prepared Cp*Ru(depe)Cl, depe = PEt$_2$CH$_2$CH$_2$PEt$_2$, and determined its $E_{1/2}$ to be −0.54 V vs FeCp$_2^{+/0}$. The four C$_2$F$_5$ substituents in Cp*Ru(dfepe)Cl ($E_{1/2}$ 0.72 V, Table 4) thus produce an increase in $E_{1/2}$ of 1.26 V relative to the compound with four C$_2$H$_5$ substitutents. This dramatic anodic shift in oxidation potentials going from donor phosphine complexes to dfepe analogues has been observed previously in (η^6-arene)Mo(dfepe)(L) systems.[43]

Concluding Comments

Earlier studies showed that the complex CpRu-(dfepe)H displays chemistry more like that of a carbonyl complex (i.e., CpRu(CO)$_2$H) than of a phosphine complex.[23] For example, the anion [CpRu(dfepe)]$^-$ is readily prepared. Here we show that protonation properties of CpRu(dfepe)H in excess triflic acid are comparable to those found for the carbonyls (η^5-C$_5$Me$_5$)Os(CO)$_2$H and (η^5-C$_5$Me$_5$)W(CO)$_3$H.[18] A measure of the extent of protonation of CpRu(dfepe)H is given by the weighted chemical shift average for the Cp resonances for **1** and **2b**. In the presence of 2 equiv of HOTf, the extent of CpRu(dfepe)H protonation to form CpRu(dfepe)(η^2-H$_2$)$^+$ is 55%. Since triflic acid has a pK_a of roughly −5 in CH$_2$Cl$_2$,[27] we tentatively take this value as the pK_a of **2** in this solvent. The major equilibrium species in the CpRu(dfepe)H$_2^+$ system is the dihydrogen complex **2b**, which indicates a slightly greater thermodynamic acidity for the dihydride tautomer, **2a**, in this particular system.

Table 5 lists some properties of hydride and dihydrogen complexes of ruthenium in order from easiest to oxidize to most difficult. The electrochemical potentials are measured or estimated by use of the known additive ligand parameters and Lever's method.[41,42] The anodic peak potential for complex **1** of 1.5 V vs NHE (Table 5) is the most positive observed for a complex of the type CpRu(L)H. Earlier work has demonstrated that the pK_a of a dihydrogen complex can be calculated if the $E_{1/2}$ value for the monohydride and the bond dissociation energy to remove a hydrogen atom from the dihydrogen unit are known: 1.37pK_a{M(H$_2$)} = BDE{M(H$_2$)} − 23.1$E_{1/2}$(MH/MH$^-$) − 66.[13] It has also been suggested that the BDE value should increase as H−H bonding in the dihydrogen complex increases.[13] Table 5 shows that this is indeed the case. There may be a slight increase in BDE from 72 to 74 kcal/mol as the H−H bond becomes stronger and shorter as judged by a larger J_{HD} value (Table 5). The pK_a decrease along with the $E_{1/2}$ value increase and the value of −7 calculated for

(41) Lever, A. B. P. *Inorg. Chem.* **1990**, *29*, 1271−1285.
(42) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471.
(43) Ernst, M. F.; Roddick, D. M. *Organometallics* **1990**, *9*, 1586−1594.

Table 5. Electrochemical Potentials of Cp′RuLH and pK_a of [Cp′RuLH$_2$]$^+$ and Related Data, Cp′ = Cp, Cp*

Cp′	L^a	$E_L{}^b$	$E_{1/2}$(calc)^c	$E_{1/2}$ or E_a(obs)^d	pK_a(calc)^e	pK_a(obs)^f	BDE^g	$J_{HD}{}^h$	$d_{HH}{}^i$	ref
Cp	dippe	0.3	0.29		9.6		72	20.5	1.08	19
Cp	dmpe	0.3	0.29		9.6	10	72	22	1.05	9
Cp	dape^l	0.33	0.35	0.38	8.6	8.6	72	24	1.01	12
Cp	dppe^l	0.36	0.41	0.41	7.6	7.2	72	24.9	1.00	12, 54
Cp	dppm^l	0.43	0.55	0.55	6.9	7.5	75	21.9	1.05	12
Cp	dtfpe^l	0.47	0.63	0.77	4.6	4.6	73	25.3	1.00	12
Cp	CO/P^{i}Pr$_3{}^j$	0.65^k	0.99		−0.7		74	28.5	0.94	55
Cp	dfepe^m	0.85	1.39	1.5	−7	−5	74	29.1	0.93	this work
Cp*	dippe	0.3	0.05		14	<HO^{t}Bu	72	21	1.07	19
Cp*	dppm^l	0.43	0.31	0.35	9.3	8.8	72	21.5	1.06	56
Cp*	CO/PPh$_3{}^j$	0.68^k	0.81		2.3		74	24	1.02	9
Cp*	dfepe^m	0.85	1.15	1.12	−3	<H$_3$O$^+$				this work
Cp*	CO/CO^m	0.99	1.43		−7.4	<0	75	32	0.89	10

^{a} PR$_2$CH$_2$CH$_2$PR$_2$, R = ^{i}Pr (dippe), Me (dmpe), MeO-4-C$_6$H$_4$ (dape), Ph (dppe), CF$_3$-4-C$_6$H$_4$ (dtfpe), C$_2$F$_5$ (dfepe); PPh$_2$CH$_2$PPh$_2$ (dppm). ^{b} Lever's additive electrochemical parameter (V).[12,41,42] ^{c} $E_{1/2}$ calc for CpRuLH or Cp*RuLH = ΣE_L; vs NHE; Lever's method;[41] E_L(H$^-$) −0.4,[42] E_L(Cp$^-$) 3 × 0.03 = 0.09, E_L(Cp*$^-$) 3 × −0.05 = −0.15. ^{d} In CH$_2$Cl$_2$ or THF vs NHE (−0.6 V vs Fc$^+$/Fc). E_a is the anodic peak potential for an irreversible oxidation. ^{e} pK_a{CpRuL(H$_2$)$^+$} = (BDE{CpRuL(H$_2$)$^+$} − 23.1$E_{1/2}$(CpRuLH) − 66)/1.37; BDE in kcal/mol, E$_{1/2}$ vs Fc$^+$/Fc, pK_a vs HPCy$_3{}^+$ at 9.7. ^{f} pK_a vs HPCy$_3{}^+$ at 9.7. ^{g} BDE in kcal/mol listed for [CpRu(L)H$_2$]$^+$ are chosen so that pK_a(calc) and pK_a(obs) agree. ^{h} J_{HD} in Hz for [CpRuL(HD)]$^+$ or [Cp*RuL(HD)]$^+$. ^{i} d_{HH} = −0.167J_{HD} + 1.42.[25] ^{j} [CpRu(H$_2$)(PR$_3$)(CO)]$^+$. ^{k} Average of E_L(CO) = 0.99 and E_L(PR$_3$). ^{l} Observed pK_a and $E_{1/2}$ values were measured in THF. ^{m} Observed pK_a and $E_{1/2}$ values were measured in CH$_2$Cl$_2$; differences between measured values in THF and CH$_2$Cl$_2$ are generally not significant.[12]
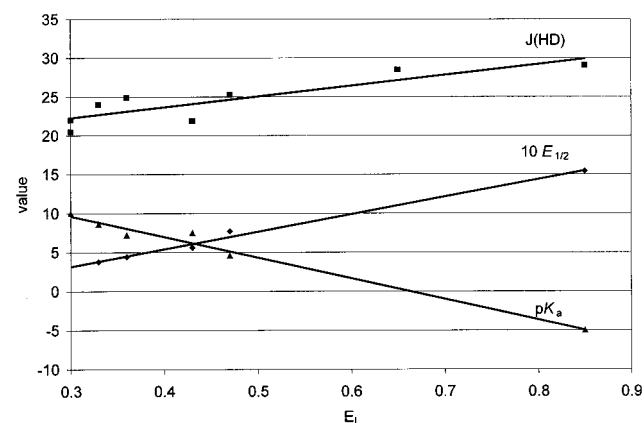
Figure 6. Plot of J_{HD} (in Hz) of [CpRuL(HD)]$^+$, E(d^5/d^6) (in V) of CpRuH(L) multiplied by 10, and pK_a of [CpRuL(H$_2$)]$^+$ (relative to HPCy$_3{}^+$ at 9.7) vs Lever's parameter E_L.

complex **2** matches well the experimental estimate of −5 based on $E_{1/2}$(calc) = 1.39 V vs NHE and a reasonable bond dissociation energy of 74 kcal/mol. It is impressive that changes of the substituents on phosphorus from isopropyl to pentafluoroethyl result in more than a 15 unit increase in pK_a of the dihydrogen complex [CpRu(PR$_2$CH$_2$CH$_2$PR$_2$)(H$_2$)]$^+$. Figure 6 shows the linear decrease in pK_a with the increase in E_L of the phosphine ligand. It also shows a rough trend in increasing J_{HD} with increasing E_L, a result of less back-donation to the HD ligand.[12]

The unobserved dihydrogen tautomer of **6** is expected to have a pK_a value of about −3 (Table 5). It should be more acidic than the dihydride tautomer, which we have shown is deprotonated readily by traces of water. Therefore the acidity of **6** is approaching that of the dicarbonyl complex [Cp*Ru(CO)$_2$(H$_2$)]$^+$, which is deprotonated by diethyl ether.[10]

A significant aspect of the present work is that the very acidic dihydrogen complex **2** and the transient dihydrogen tautomer of **6** can be generated directly from H$_2$(g). Although several very acidic dihydrogen complexes have been reported,[10,18,27,44−47] only two others

can be prepared by use of H$_2$(g). One is an unstable iridium dihydrogen complex which can protonate the tetraphenylborate anion in THF.[22] The other is [Ru(H$_2$)-(CNH)(dppe)$_2$]$^{2+}$, which is generated from a ruthenium triflate complex in a fashion similar to **2**.[48]

Experimental Section

General Procedures. A PAR model 273 potentiostat was used for cyclic voltammetry studies. The electrochemical cell contained a Pt working electrode, a W secondary electrode, and a Ag-wire reference electrode. The samples were dissolved in CH$_2$Cl$_2$ containing 0.2 M n-Bu$_4$NPF$_6$ as the supporting electrolyte. The cyclic voltammograms were referenced to ferrocene, which was added to the solutions after the CV were recorded.

General Procedures for Cp Complexes. All manipulations were conducted under an atmosphere of purified nitrogen using Schlenk, high-vacuum, and/or glovebox techniques. Dry oxygen-free solvents were purified by vacuum distillation from sodium/benzophenone (diethyl ether, petroleum ether, and hexane) or P$_2$O$_5$ (CH$_2$Cl$_2$). A small amount of tetraglyme was added to hydrocarbon solvents to solubilize the ketyl. Deuterated solvents used in NMR experiments were dried by vacuum transfer of solvent onto activated molecular sieves and then degassed. Triflic acid was purified by vacuum distillation (70 Torr) prior to use. Deuterated triflic acid was purchased and used as received from Sigma-Aldrich. Elemental analyses were performed by Desert Analytics. Infrared spectra were recorded on a Perkin-Elmer 1600 FTIR instrument as Nujol mulls, unless otherwise noted. NMR spectra were obtained with a JEOL GSX-400 instrument unless stated otherwise. ^{31}P NMR spectra were referenced to an 85% H$_3$PO$_4$ external standard. ^{19}F NMR were referenced to a CF$_3$CO$_2$Et external standard (−75.32 ppm vs CFCl$_3$, with upfield shifts taken to be negative). T_1 experiments were made using the inversion recovery method. CpRu(dfepe)H and dfepe were prepared as described previously.[23,49,50]

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General Procedures for Cp* Complexes. All manipulations were performed under an Ar or H_2 atmosphere by use of Schlenk techniques. The prepurified gases were purchased from BOC Gases and were used as received. All solvents were distilled under Ar before use. Ethanol was dried over and distilled from magnesium ethoxide. Toluene and ether were dried over and distilled from sodium benzophenone ketyl. Dichloromethane was dried over and distilled from CaH_2. NMR solvents were dried over Linde type 4 Å molecular sieves and degassed prior to use. $Cp*RuCl_2$ was prepared according to literature methods.[51] The ligand depe was purchased and used as received from Organometallics, Inc. Fast atom bombardment mass spectra were obtained using a VG 70-250S mass spectrometer using Xe flux. The matrix used for the FAB-MS was *m*-nitrobenzyl alcohol (NBA). Microanalysis was performed by Guelph Chemical Laboratories Ltd. NMR spectra were recorded on Varian Gemini 300 at 300 MHz for ^{1}H and 120.5 MHz for ^{31}P or a Varian Unity for T_1 measurements.

CpRu(dfepe)OTf (3). A 50 mL round-bottom flask was charged with 405 mg (0.553 mmol) of CpRu(dfepe)H (**1**) and 20 mL of CH_2Cl_2 and cooled to -78 °C; 425 mg (2.83 mmol) of CF_3SO_3H was then added by syringe, and the mixture was allowed to warm to ambient temperature with stirring, with periodic removal of evolved hydrogen. After 3 days, the volatiles were removed and the orange oily residue was triturated in 20 mL of diethyl ether to produce 289 mg (61%) of yellow crystalline product. Anal. Calcd for $C_{16}H_9O_3F_{23}P_2SRu$: C, 21.81; H, 1.03. Found: C, 21.71; H, 1.06. ^{1}H NMR (400 MHz, 20 °C, CD_2Cl_2): δ 5.47 (s, 5H; η^5-C_5H_5), 2.69 (m, 4H; PCH_2CH_2P). ^{31}P{^{1}H} NMR (161.7 MHz, 20 °C, CD_2Cl_2): δ 110.6 (m). ^{19}F NMR (376.05 MHz, 20 °C, CD_2Cl_2): δ -77.94 (s, 3F; CF_3SO_3), -78.21 (d, $^3J_{FP}$ = 30 Hz, 12F; PCF_2CF_3), -102.8 to -108.5 (m, 8F; overlapping PCF_2CF_3 ABX multiplets).

CpRu(dfepe)H Protonation Studies. Mixtures of [CpRu(dfepe)(H)$_2$]$^+$ (**2a**) and [CpRu(dfepe)(η^2-H$_2$)]$^+$ (**2b**) were prepared as follows: A flame-dried 5 mm NMR tube was charged with CpRu(dfepe)H and cooled to -195 °C, and ca. 0.5 mL CD_2Cl_2 was added via vacuum transfer. The total solution volume was determined, and the appropriate amount of HOTf was added by syringe under nitrogen.

HD Studies of 2a and 2b. Under argon, 20 mg (0.027 mmol) of CpRu(dfepe)H was dissolved in approximately 0.8 mL of CD_2Cl_2, and 26 mg (0.17 mmol) of deuterated triflic acid was added. ^{1}H NMR spectra were recorded on a Varian Gemini 300 at 300 MHz. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 5.80 (s, 5H; η^5-C_5H_5), 2.7 (m, 4H; PCH_2CH_2P), -9.0 to -8.5 (m, RuH_2, RuHD, Ru(η^2-H$_2$), Ru(η^2-HD)). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 119.5 (m).

H$_2$ Heterolysis Studies. A typical experiment was as follows: A 5 mm NMR tube fitted with a Teflon valve (Chemglass) was flame dried and charged with 5 mg of **1** and CD_2Cl_2 via vacuum transfer at -78 °C. At this temperature 500 Torr of H_2 (UHP grade) was admitted, and the tube was sealed. The NMR tube was warmed in an isothermal 50 °C bath, and the extent of reaction was monitored at regular intervals by ^{1}H NMR.

Cp*Ru(depe)Cl. A method similar to the preparation of CpRu(dippe)Cl (dippe = 1,2-bis(diisopropylphosphino)ethane)[19] was followed, involving the thermolysis of $Cp*Ru(PPh_3)_2Cl$ in the presence of depe, resulting in an orange residue. ^{31}P{^{1}H} NMR (benzene-d_6, 20 °C): δ 69.2 (s).

Cp*Ru(dfepe)Cl (4). In an N_2-filled glovebox, Zn (0.234 g, 3.57 mmol) was added to a solution containing $Cp*RuCl_2$ (0.227 g, 0.740 mmol) and dfepe (0.628 g, 1.11 mmol) in 30 mL of toluene. The red brown solution was stirred for approximately 16 h. The solution was filtered to remove the zinc; the filtrate was bright orange. A dark yellow residue resulted upon

evaporation of the solvent under vacuum. Purification of the complex involved the slow diffusion of approximately 10 mL of ethanol into a saturated solution of approximately 0.50 g of crude $Cp*Ru(dfepe)Cl$ in 5 mL of dichloromethane, yielding 0.45 g of orange crystals (72%). The product is stable in air. Anal. Calcd for $C_{20}H_{19}ClF_{20}P_2Ru$: C, 28.67; H, 2.28. Found: C, 29.00; H, 2.28. ^{1}H NMR (benzene-d_6, 20 °C): δ 2.4$-$2.8 (m, 4H; PCH_2CH_2P), 1.82 (s, 15H; η^5-$C_5(CH_3)_5$). ^{31}P{^{1}H} NMR (benzene-d_6, 20 °C): δ 108.1 (m). FAB-MS: 838 (84.4% M$^+$), 803 (90.3% M$^+$ $-$ Cl), 272 (100% M$^+$ $-$ $(C_2F_5)_2PCH_2CH_2P$-$(C_2F_5)_2$).

Cp*Ru(dfepe)H (5). Under a hydrogen atmosphere, PPh_3 (0.040 g, 0.15 mmol) and **4** (0.10 g, 0.12 mmol) were stirred in 5 mL of CH_2Cl_2 to produce an orange solution. The entire mixture was cooled to -78 °C, and $AgBF_4$ (0.030 g, 0.15 mmol) was added. The solution was stirred for 15 min and then sealed under 1 atm of H_2 and left to slowly warm to ambient temperature (approximately 15 h). A yellow solution and a white solid were obtained. The solid, AgCl, was filtered, and the solution was evaporated to dryness. The addition of 3 mL of ether caused the precipitation of a white solid ([$HPPh_3$]BF_4). The solution was filtered and evaporated to dryness. Crystals were obtained by dissolving **5** in benzene and slowly diffusing in MeOH, yielding 0.08 g (83%). Anal. Calcd for $C_{20}H_{20}F_{20}P_2Ru$: C, 29.90; H, 2.51. Found: C, 29.30; H, 2.94. ^{1}H NMR (CD_2Cl_2, 20 °C): δ 2.3$-$2.7 (m, 4H; PCH_2CH_2P), 1.94 (s, 15H; η^5-$C_5(CH_3)_5$), -14.0 (t, $^2J_{HP}$ = 36.8 Hz, 1H; RuH). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 110.9 (m).

[Cp*Ru(dfepe)(H)$_2$]BF$_4$ (6). All glassware was flamed dried under vacuum. Under H_2, **4** (0.10 g, 0.12 mmol) and 3.0 mL of dichloromethane (freshly dried and distilled) were stirred at room temperature to give an orange solution. To this solution was added $AgBF_4$ (0.16 g, 0.88 mmol), which produced a dark yellow-green solution. The reaction mixture was immediately cooled to -78 °C. This mixture was allowed to stir for 1 h before sealing under 1 atm of H_2 and allowing to slowly warm to ambient temperature (ca. 15 h). The solvent was evaporated, giving a red-brown residue. Deuterated dichloromethane was added, and the solution was filtered into an NMR tube for analysis. Loss of H^+ to adventitious bases occurred during every crystallization attempt. ^{1}H NMR (CD_2Cl_2, 400 MHz, 20 °C): δ -8.90 (t, $^2J_{HP}$ = 34.4 Hz, Ru(H)$_2$). T_1 (s) (CD_2Cl_2): 1.91 ± 0.05 (20 °C), 1.39 ± 0.02 (0 °C), 1.12 ± 0.02 (-20 °C), 0.88 ± 0.03 (-40 °C), 0.59 ± 0.03 (-60 °C), 0.66 ± 0.07 (-70 °C).

[Cp*Ru(dfepe)(H)$_2$](OTf). Under a hydrogen atmosphere, a Schlenk flask was charged with **4** (0.0533 g, 0.064 mmol). Freshly distilled CH_2Cl_2 (5 mL) was added, and the orange solution was stirred. The flask was cooled to -78 °C, AgOTf (0.016 g, 0.062 mmol) was quickly added, and the reaction mixture was allowed to stir for 1 h. After this time the flask was sealed off from H_2 and allowed to slowly warm to ambient temperature with stirring for an additional 16 h. During this time the solution became yellow and a white solid formed. The precipitate was filtered off, and the solution was evaporated. NMR spectra of the yellow powder obtained showed a mixture of the monohydride and dihydride. Adding excess HOTf (ca. 5 equiv) to this mixture in CD_2Cl_2 under H_2 gave [Cp*Ru(dfepe)-(H)$_2$](OTf). ^{1}H NMR (CD_2Cl_2, 300 MHz, 20 °C): δ -8.80 (t, $^2J_{HP}$ = 34.3 Hz, Ru(H)$_2$). ^{31}P{^{1}H} NMR (CD_2Cl_2, 20 °C): δ 103.5 (m).

Crystal Structure of CpRu(dfepe)(OTf) (3). X-ray data were collected on a Siemens P3 automated diffractometer system. The radiation used was Mo Kα monochromatized by a highly ordered graphite crystal. The parameters used during the data collection are summarized in Table 1. All computations used the SHELXTL/IRIS (version 4.2) program library (Siemens Corp., Madison, WI). A suitable crystal of **3** was obtained from benzene solution. Monoclinic unit cell dimensions were derived from a least-squares fit of 33 random reflections ($20° < 2\theta < 30°$). Data were collected using the $2\theta/\theta$

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scan technique with a variable scan rate of 4.0–30.0 deg/min. Three standard reflections monitored after every 100 data collected showed no systematic variation; the R for averaging 184 redundant data was 8.71%. $P2_1/c$ symmetry deduced from a statistical analysis of all collected data was confirmed by successful refinement in this space group. Data were corrected for absorption using an empirical ellipsoidal model based on ψ-scans for 12 reflections with $10° < 2\theta < 35°$.

The structure of **3** was solved using the SHELXTL direct methods program; all nonhydrogen atoms were located on a series of difference Fourier maps. Hydrogen atom positions were added in ideal calculated positions with $d(C–H) = 0.96$ Å and with fixed isotropic thermal parameters set at 1.2–1.3 times the isotropic equivalent of the attached carbon atom, with a maximum value of $U = 0.10$. All non-hydrogen atoms were refined anisotropically. Full-matrix least-squares refinement gave an R value of 3.84% ($R_w = 4.55\%$) for 4455 data with $I > 2\sigma(I)$. The final difference Fourier map showed a maximum residual peak of 1.17 e/Å^3 associated with the ruthenium atom with no other residual electron density greater than 1.0 e/Å^3.

Crystal Structures of 4 and 5. A summary of selected crystallographic data is given in Table 1. The following details are for compound **4**; parameters for **5**, where different, are denoted in parentheses. Data were collected on an Enraf-Nonius CAD4 (Siemens P4) diffractometer using Mo Kα radiation, $\lambda = 0.710\ 73$ Å. The intensities of three standard reflections measured every 120 min (97 reflections) showed 10% (less than 3%) decay, and a linear correction was applied. The data were corrected for Lorentz and polarization effects and for absorption; min. and max. transmission coefficients were 0.5432 and 0.6438 (0.5390, 0.5720).[52,53]

The structures were solved and refined using the SHELXTL\PC[52] package. All non-hydrogen atoms were refined with anisotropic thermal parameters to minimize $\sum w(F_o - F_c)$, where $w = 1/\sigma^2(F) + gF^2$. Hydrogen atoms were included in calculated positions and treated as riding atoms. The position of the hydride atom in **5** was determined from a difference electron density map and was refined with an isotropic thermal parameter.

Supporting Information Available: Summaries of crystal data for complexes **3**, **4**, and **5**, including atomic positional parameters, bond distances and bond angles, thermal displacement parameters, and hydrogen coordinates (27 pages). Ordering information is given on any current masthead.

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