Wide Range of pK_a Values of Coordinated Dihydrogen. Synthesis and Properties of Some η^2-Dihydrogen and Dihydride Complexes of Ruthenium

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Abstract: The new ruthenium hydride complexes CpRuH(L) (L = $PR_2CH_2CH_2PR_2$, R = *p*-$CF_3C_6H_4$ (dtfpe) or R = *p*-$MeOC_6H_4$ (dape)) were prepared by reaction of NaOMe with CpRuCl(L), which were obtained by treating $CpRuCl(PPh_3)_2$ with L. Similarly, Cp*RuH(L) (L = dppm, $(PMePh_2)_2$) were prepared from the reaction of NaOMe with Cp*RuCl(L) obtained from the reaction of Cp^*RuCl_2 with L in the presence of Zn. Protonation of CpRuH(L) (L = dtfpe, dape) and Cp*RuH(dppm) with $HBF_4 \cdot Et_2O$ produces mixtures of $[CpRu(H)_2(L)]^+$ and $[CpRu(\eta^2\text{-}H_2)(L)]^+$, and $[Cp^*Ru(H)_2(dppm)]^+$ and $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]^+$. The p$K_a$ values of the dihydrogen/dihydride complexes $[CpRuH_2(L)]^+$ (L = dtfpe, dppm, dppe, $(PPh_3)_2$, dppp, dape) and $[Cp^*RuH_2(L)]^+$ (L = dppm, $(PMePh_2)_2$) are determined by studying acid/base equilibria by ^1H and ^{31}P NMR spectroscopy in both CH_2Cl_2 and THF. The electrochemical properties of the monohydrido complexes CpRuH(L) and Cp*RuH(L) are reported. Peak potentials for oxidation of these monohydrides and pK_a values of the cationic complexes are linearly related for all the complexes with a dihydrogen form: $pK_a(Ru(H_2)^+) = -10.7E_{pa}(RuH^+/RuH) + 13.0$. As expected η^2-H_2 acidity decreases as the parent hydride becomes easier to oxidize. The related complexes with just a dihydride form, $[CpRu(H)_2(L)]^+$ (L = $(PPh_3)_2$, dppp) and $[Cp^*Ru(H)_2(PMePh_2)_2]^+$, give a similar trend. Acidity constants have been determined for both tautomers when they observed; the pK_a of the η^2-H_2 form is ~0.3 pK_a unit less (more acidic) than that of the $(H)_2$ form for the complexes with L = dtfpe, dppe, and dape but is 0.4 unit greater for $[Cp^*RuH_2(dppm)]^+$. The acidities of the two tautomers are similar because their concentrations are similar and they have the same monohydrido conjugate base. Other trends in pK_a, $^1J(HD)$, and $\delta Ru(H_2)$ values of dihydrogen complexes and ratio of dihydride to dihydrogen tautomers and the peak potentials for oxidation of the monohydrido complexes are presented. These correlations are shown to be of value in explaining/predicting the propensity of dihydrogen to undergo heterolytic cleavage. Extremes in pK_a values of such cyclopentadienylruthenium(II) complexes are expected for $[Cp^*RuH_2(dmpe)]^+$ (pK_a ~ 12) and $[CpRuH_2(CO)_2]^+$ (pK_a ~ −6).

Introduction

The heterolytic cleavage of dihydrogen by metal ions and coordination complexes is a very important chemical reaction. For example, dihydrogen is believed to be cleaved at Zn^{2+} sites of the zinc oxide/copper catalyst during the synthesis of methanol from synthesis gas to give zinc hydride and hydroxide.[1] Similarly, the recovery of nickel from its ore involves a dihydrogen-splitting step. In fact, most catalytic hydrogenation reactions could involve dihydrogen intermediates that protonate adjacent alkyls in a "σ bond metathesis"[2,3] or heterolytic cleavage reaction.[4,5] The action of hydrogenase might involve the deprotonation of a dihydrogen complex of Ni.[6] A method that allows the rationalization and prediction of acidity of dihydrogen complexes would be very valuable in understanding/predicting the mechanism of catalytic hydrogenation reactions.

There are several reports that the dihydrogen ligand readily undergoes heterolytic cleavage. Examples of complexes (followed by the base and solvent used) include the following: $[CpRu(\eta^2\text{-}H_2)(dmpe)]^+$ (dmpe = $PMe_2CH_2CH_2PMe_2$) by NEt_3 in CH_3CN,[7] $[IrH(\eta^2\text{-}H_2)(bq)(L)_2]^+$ (bq = 7,8-benzoquinolinate, L = PPh_3, PCy_3) by BuLi (in ether),[8] $[MH(\eta^2\text{-}H_2)(dppe)_2]^+$ (M = Ru, Fe, dppe = $PPh_2CH_2CH_2PPh_2$) by OH^- in alcohol,[9] $[FeH(\eta^2\text{-}H_2)(dmpe)_2]^+$ by OEt^- in ethanol,[10] $[Cp^*Re(CO)(NO)(\eta^2\text{-}H_2)]^+$ by ether,[11] $[Re(\eta^2\text{-}H_2)(H)_6(PCy_3)_2]^+$ by NEt_3 in CD_2Cl_2,[12] and $[Fe(\eta^2\text{-}H_2)(H)(P(OEt)_3)_4]^+$ by NEt_3 in CD_2Cl_2.[13,14] Two hydrogenation catalyst precursors are $[Os(\eta^2\text{-}H_2)(H)_3(PMe_2Ph)_3]^+$, deprotonated by NEt_3 in CD_2Cl_2,[15] and $Ru(\eta^2\text{-}H_2)(H)_2(PPh_3)_3$,[16] deprotonated by $C_6H_{11}O^-$ in THF.[17,18] The η^2-dihydrogen ligand is known to be deprotonated in preference to the terminal hydride in the complex $[IrH(\eta^2\text{-}H_2)(bq)(L)_2]^+$.[8] The dihydrogen tautomer is thought to have the greater kinetic acidity in the mixture of complexes $[CpRu(\eta^2\text{-}H_2)(dmpe)]^+$ and $[CpRu(H)_2(dmpe)]^+$.[19] The complex $[Os(\eta^2\text{-}H_2)(NH_3)_5]^{2+}$ is not deprotonated by NaOMe in MeOH and so its pK_a must be greater than that of MeOH (~15).[20] We recently described a simple method for the ranking of the acidity of a range of η^2-dihydrogen and dihydride compounds by NMR spectroscopy in CD_2Cl_2.[21] The pK_a values for this series of ruthenium dihydrido complexes have been determined by use of $HPCy_3^+$ as a standard.

The objective of this work is the synthesis of isostructural dihydrogen complexes of the type $[CpRu(\eta^2\text{-}H_2)(diphosphine)]^+$, where the diphosphine has extremes in electronic properties in order to maximize changes in acidity while minimizing changes in steric features. Complexes with ligands $(p\text{-}RC_6H_4)_2PCH_2CH_2P(p\text{-}RC_6H_4)_2$ (R = MeO (dape), R = H

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(dppe), R = CF_3 (dtfpe)) are excellent candidates. The use of the pentamethylcyclopentadienyl ligand (Cp*) to further alter electronics is also investigated here briefly. This is the first systematic study of ligand effects on η^2-H_2 acidity. Dihydrogen complexes $[CpRu(\eta^2\text{-}H_2)(dppe)]^+$ and $[CpRu(\eta^2\text{-}H_2)(dppm)]^+$ as well as the dihydride $[CpRu(H)_2(dppp)]^+$ are already known from work by Conroy-Lewis and Simpson.[22] The compound $[CpRu(\eta^2\text{-}H_2)(dppe)]^+$ is in equilibrium with the dihydrido form in a ratio of 1:2. Chinn and Heinekey reported that the protonation of CpRuH(dmpe) produced a mixture of $[CpRu(\eta^2\text{-}H_2)(dmpe)]BF_4$ and $[CpRu(H)_2(dmpe)]BF_4$ in a ratio of 6:1.[7,19] The pK_a of this dihydrogen complex is reported to be 17.6 in CH_3CN.

Another objective is the measurement of the pK_a values of these cationic dihydrogen complexes and the correlation of this property with the electrochemical potentials ($E_{1/2}$) of the corresponding monohydrido complexes. This leads to a better understanding of the factors governing the acidity of molecular dihydrogen complexes. In principle, there should be a link between pK_a and $E_{1/2}$ based on the work of Breslow and Balasubramanian,[23] Bordwell et al.,[24] and Tilset and Parker[25,26] and there should also be a relationship between structure and $E_{1/2}$ based on the work of Lever[27] or ν(CO) and $E_{1/2}$ data of carbonyl complexes based on the work of Morris et al.[28] Thus, there is a possibility that the pK_a of a dihydrogen ligand can be predicted solely on the basis of the structure of the complex.

Experimental Section

Unless otherwise noted, all manipulations were done in an Ar or H_2 atmosphere by use of Schlenk techniques. Solids were handled in a Vacuum Atmosphere drybox under N_2. All solvents were dried over appropriate reagents and distilled under N_2 before use. Reagent-grade chemicals were used as purchased from Aldrich Chemical Co., Inc. unless otherwise stated. Phosphines ligands were purchased from Strem Chemical Co. or Digital Speciality Chemicals Ltd. $CpRuCl(PPh_3)_2$,[29] Cp^*RuCl_2,[30] dtfpe,[31] dape,[31] CpRuH(dppe),[32] CpRuH(dppm),[32] $CpRuH(PPh_3)_2$,[32] CpRuH(dppp),[32] $[CpRu(\eta^2\text{-}H_2)(dppm)]BF_4$,[22] $[CpRuH_2(dppe)]BF_4$,[22] $[CpRu(H)_2(dppp)]BF_4$,[22] and $[CpRu(H)_2(PPh_3)_2]BF_4$[33] were prepared according to literature methods.

NMR spectra were obtained on a Varian XL 400, operating at 400.00 MHz for ^1H and 161.98 MHz for ^{31}P, or on a Varian XL 200, operating at 200.00 MHz for ^1H and 80.98 MHz for ^{31}P. Chemical shifts refer to room-temperature condition unless specified otherwise. All ^{31}P NMR were proton decoupled. ^{31}P chemical shifts were measured relative to ~1% $P(OMe)_3$ in C_6D_6 sealed in coaxial capillaries and are reported relative to H_3PO_4 by use of $\delta(P(OMe)_3) = 140.4$ ppm. Integration of the ^{31}P resonances was carried out on spectra that were acquired with gated decoupling and 10-s delay times between acquisition pulse sequences; use of 15-s delay times gave identical integrations. ^1H chemical shifts were measured relative to partially deuterated solvent peaks, but are reported relative to tetramethylsilane.

Microanalyses were performed by the Canadian Microanalytical Service, Ltd. A PAR Model 273 potentiostat was used for cyclic voltammetry studies. The electrochemical cell contained a Pt working electrode, W secondary electrode, and Ag wire reference electrode in a Luggin capillary. The cyclic voltammograms were collected in THF containing 0.2 M n-Bu_4NPF_6 as supporting electrolyte. Reported potentials are referenced to ferrocene, which was added to these solutions.

CpRuCl(dtfpe). A mixture of dtfpe (1.0 g, 1.49 mmol) and $CpRuCl(PPh_3)_2$ (1.0, 1.38 mmol) in 50 mL of benzene was refluxed for 12 h to give an orange solution. The solvent was removed completely, and the residue was washed with hexane/Et_2O (6:1) to give a yellow precipitate. The precipitate was collected by filtration, washed with hexane, and dried under vacuum overnight. Yield: 1.1 g, 91%. $^{31}P\{^1H\}$ NMR (C_6H_6/C_6D_6): δ 80.3 (s). ^1H NMR (C_6D_6): δ 1.78 (m, 2 H, CH_2), 2.33 (m, 2 H, CH_2), 4.36 (s, Cp), 6.7–7.8 (m, Ph).

CpRuH(dtfpe). A mixture of CpRuCl(dtfpe) (0.60 g, 0.69 mmol) and NaOMe (0.2 g, 3.7 mmol) in 20 mL of benzene and 10 mL of MeOH was refluxed for 5 h to give a bright yellow solution. The solvents were removed completely, and the residue was extracted with 30 mL of hexane to give a yellow solution. The solvent was removed completely to give a flakelike bright yellow solid. Yield: 0.35 g, 61%. The compound can be recrystallized from MeOH at −76 °C. $^{31}P\{^1H\}$ NMR (C_6H_6/C_6D_6): δ 92.6 (s). ^1H NMR (C_6D_6): δ −13.47 (t, J(PH) = 34.4 Hz, RuH), 1.6–1.8 (m, CH_2), 4.62 (s, Cp), 7.1–7.6 (m, Ph). Anal. Calcd for $C_{35}H_{26}F_{12}P_2Ru$: C, 50.19; H, 3.12. Found: C, 49.62; H, 3.14.

$[CpRuH_2(dtfpe)]BF_4$. To a solution of CpRuH(dtfpe) (0.20 g, 0.24 mmol) in 30 mL of Et_2O was added 0.1 mL of $HBF_4\cdot Et_2O$. The reaction mixture was stirred for 30 min to give a white solid. The solid was collected by filtration, washed with Et_2O, and dried under vacuum. Yield: 0.14 g, 63%. The compound could be recrystallized by slow diffusion of Et_2O into a CH_2Cl_2 solution. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 80.5 (s, $[CpRu(\eta^2\text{-}H_2)(dtfpe)]^+$), 69.3 (s, $[CpRu(H)_2(dtfpe)]^+$). ^1H NMR (CD_2Cl_2): δ −8.76 (br, $Ru(\eta^2\text{-}H_2)$), −8.62 (t, J(PH) = 28.8 Hz, RuH_2), 1.5–3.2 (m, CH_2), 4.92 (s, $CpRu(\eta^2\text{-}H_2)$), 5.58 (s, $CpRuH_2$), 7.6–8.1 (m, Ph), $CpRu(\eta^2\text{-}H_2)/CpRuH_2$ = 1:1.6. Anal. Calcd for $C_{35}H_{27}BF_{16}P_2Ru$: C, 45.43; H, 2.94. Found: C, 45.02; H, 2.97.

$[CpRuHD(dtfpe)]BF_4$. The compound was prepared similarly except that DBF_4 was used instead of $HBF_4\cdot Et_2O$. The DBF_4 was prepared in situ by mixing $HBF_4\cdot Et_2O$ and D_2O in a ratio of 1:3 in volume. ^1H NMR (CD_2Cl_2): δ −8.80 (1:1:1 t, ^1J(HD) = 25.3 Hz, Ru(HD)), −8.67 (t, J(PH) = 28.8 Hz, RuHD).

CpRuCl(dape). A mixture of dape (0.70 g, 1.35 mmol) and $CpRuCl(PPh_3)_2$ (0.93 g, 1.28 mmol) in 50 mL of benzene was refluxed overnight to give a orange solution. The solvent was removed completely, and the residue was washed with hexane to give a yellow precipitate. The precipitate was collected by filtration, washed with hexane, and dried under vacuum. Yield: 0.90 g, 98%. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 76.5 (s). ^1H NMR (C_6D_6): δ 2.2–2.6 (m, CH_2), 3.78 (s, 2 CH_3), 3.83 (s, 2 CH_3), 4.50 (s, Cp), 6.8–7.1 (m, 12 H, Ph), 7.86 (m, 4 H, Ph).

CpRuH(dape). A mixture of CpRuCl(dape) (0.50 g, 0.69 mmol) and NaOMe (0.30 g, 5.6 mmol) in 20 mL of benzene and 10 mL of MeOH was refluxed for 5 h to give a yellow solution and some precipitate. The solvent was removed completely, and the residue was extracted with 40 mL of benzene. The solvent of the extract was removed again; addition of MeOH to the residue produced a light yellow solid. The solid was collected by filtration, washed with MeOH, and dried under vacuum overnight. Yield: 0.38 g, 80%. The compound was recrystallized by diffusion of MeOH into a benzene solution. $^{31}P\{^1H\}$ NMR (C_6H_6/C_6D_6): δ 88.9 (s). ^1H NMR (C_6D_6): δ −13.25 (t, J(PH) = 34.5 Hz, 1 H, RuH), 1.9–2.2 (m, 4 H, 2 CH_2), 3.26 (s, 2 CH_3), 3.29 (s, 2 CH_3), 4.92 (s, 5 H, Cp), 6.78 (m, 8 H, Ph), 7.55 (m, 4 H, Ph), 7.95 (m, 4 H, Ph). Anal. Calcd for $C_{36}H_{42}P_2O_5Ru$ (CpRuH(dape)·MeOH): C, 60.24; H, 5.89. Found: C, 60.24; H, 5.64.

$[CpRuH_2(dape)]BF_4$. The procedure for $[CpRuH_2(dtfpe)]BF_4$ was followed exactly. Yield, 71%. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 76.2 (s, $[CpRu(\eta^2\text{-}H_2)(dape)]^+$), 64.6 (s, $[CpRu(H)_2(dape)]^+$). ^1H NMR (CD_2Cl_2): δ −9.26 (br, $Ru(\eta^2\text{-}H_2)$), −8.73 (t, J(PH) = 28.9 Hz, RuH_2), 2.2–2.7 (m, CH_2), 3.85 (s, Me), 4.82 (s, $CpRu(\eta^2\text{-}H_2)$), 5.42 (s, $CpRuH_2$), 6.8–7.6 (m, Ph), $Ru(\eta^2\text{-}H_2)/RuH_2$ = 1:2.6. Anal. Calcd for $C_{35}H_{39}BF_4P_2O_4\cdot CH_3OH$: C, 53.67; H, 5.38. Found: C, 53.33; H, 5.04.

$[CpRuHD(dape)]BF_4$. The compound was prepared similarly except that DBF_4 was used instead of $HBF_4\cdot Et_2O$. The DBF_4 was prepared as above. ^1H NMR (CD_3COCD_3): δ −9.24 (1:1:1 t, ^1J(HD) = 24.3 Hz, Ru(HD)), −8.69 (t, J(PH) = 28.4 Hz, RuHD).

Cp*RuH(dppm). A mixture of Cp^*RuCl_2 (0.30 g, 0.98 mmol), dppm (0.45 g, 1.17 mmol), and Zn (0.30 g, 4.6 mmol) in 30 mL of benzene was stirred overnight to give a dark orange solution. To the solution was added 20 mL of MeOH and NaOMe (0.20 g, 3.7 mmol). The resulting mixture was refluxed for 6 h to give a yellow solution. The solvent was removed completely and the residue was extracted with benzene. The solvent of the extract was removed again. Addition of MeOH to the residue produced a yellow solid, which was collected by filtration, washed with MeOH, and dried under vacuum overnight. Yield: 0.32 g, 53%. Crystalline solid could be obtained by slow diffusion of MeOH into a saturated benzene solution. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 17.5 (s). ^1H NMR (C_6D_6): δ −10.63 (td, J(PH) = 32.0 Hz, ^4J(HH) = 3.5 Hz, RuH), 2.06 (t, J(PH) = 1.6 Hz, Cp*), 3.74 (m, CH_2), 4.64 (m, containing the

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^4J(HH) coupling of 3.5 Hz, CH_2), 7.02–7.8 (m, Ph). Anal. Calcd for $C_{35}H_{38}P_2Ru$: C, 67.62; H, 6.16. Found: C, 67.51; H, 6.25.

[Cp*RuH$_2$(dppm)]BF$_4$. The procedure for [CpRuH$_2$(dtfpe)]BF$_4$ was followed exactly. Yield: 70%. A crystalline solid was obtained by slow diffusion of Et_2O into a saturated dichloromethane solution. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 23.4 (s, [Cp*Ru(**H**)$_2$(dppm)]$^+$), 4.9 (s, [Cp*Ru(η^2-H$_2$)(dppm)]$^+$). ^1H NMR (CD_2Cl_2, 290 K, 200 MHz): δ −6.80 (br, Ru(η^2-H$_2$), T_1 = 49.8 ± 3 ms), −6.09 (t, J(PH) = 28.8 Hz, RuH$_2$, T_1 = 109 ± 9 ms), 1.70 (s, Cp*Ru(η^2-H$_2$)), 1.97 (s, Cp*RuH$_2$), 4.07–5.29 (m, CH_2), 7.38–7.55 (m, Ph). Ru(η^2-H$_2$)/RuH$_2$ = 2:1. Anal. Calcd for $C_{35}H_{39}BF_4P_2Ru$: C, 59.25; H, 5.54. Found: C, 59.03; H, 5.53.

[Cp*RuHD(dppm)]BF$_4$. The procedure for [CpRuHD(dtfpe)]BF$_4$ was followed exactly. ^1H NMR (CD_2Cl_2): δ −6.81 (1:1:1 t, ^1J(HD) = 20.9 Hz, Ru(HD)), −6.02 (t, J(PH) = 28.2 Hz, RuHD).

Cp*RuH(PMePh$_2$)$_2$. A mixture of Cp*RuCl$_2$ (0.30 g, 0.98 mmol), Zn (0.30 g, 4.6 mmol), and PMePh$_2$ (2 mL of 1.0 M solution in benzene, 2.0 mmol) in 20 mL of benzene was stirred overnight to give a deep orange solution. To this solution was then added 20 mL of MeOH and 0.20 g (3.7 mmol) of NaOMe. The resulting mixture was refluxed for 4 h. The solvents were then removed completely and the residue was extracted with benzene. The solvent of the extract was removed again. Addition of MeOH to the residue produced a yellow solid, which was collected by filtration, washed with MeOH, and dried under vacuum. Yield: 0.42 g, 67%. The compound can be recrystallized by slow diffusion of MeOH into a saturated benzene solution. $^{31}P\{^1H\}$ NMR (C_6H_6/C_6D_6): δ 46.3 (s). ^1H NMR (C_6D_6): δ −12.47 (t, J(PH) = 35.3 H, RuH), 1.67 (m, PMe), 1.83 (s, Cp*), 7.1–8.1 (m, Ph). Anal. Calcd for $C_{36}H_{42}P_2Ru$: C, 67.81; H, 6.64. Found: C, 67.50; H, 6.64.

[Cp*Ru(H)$_2$(PMePh$_2$)$_2$]BF$_4$. To a solution of Cp*RuH(PMePh$_2$)$_2$ (0.20 g, 0.31 mmol) in 20 mL of Et_2O was dropped HBF_4·Et_2O until the yellow color disappeared to leave a white suspension. After the mixture was stirred for an additional 30 min the white solid was collected by filtration, washed with Et_2O, and dried under vacuum. Yield: 0.21 g, 93%. $^{31}P\{^1H\}$ NMR (acetone/C_6D_6): δ 41.5 (s). ^1H NMR (acetone-d_6): δ −8.13 (t, J(PH) = 28.2 Hz, RuH$_2$), 1.43 (m, PMe), 1.53 (s, Cp*), 7.4–7.7 (m, Ph).

[HPCy$_3$]BPh$_4$. A solution of P(C$_6$H$_{11}$)$_3$ (0.50 g, 1.8 mmol) in 20 mL of Et_2O was titrated with HBF_4·Et_2O to give a white precipitate. The solid was collected by filtration, washed with Et_2O, and then redissolved in 15 mL of MeOH. Addition of $NaBPh_4$ (1.2 g, 3.6 mmol) to the MeOH solution gave the white product, which was collected by filtration, washed with MeOH, and dried in vacuo. Yield: 0.81 g, 75%. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 29.0. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 28.7.

[HP(*p*-tolyl)$_3$]BF$_4$. A solution of P(*p*-tolyl)$_3$ (0.30 g, 0.99 mmol) in 10 mL of Et_2O was titrated with HBF_4·Et_2O to give a white powder. The product was collected by filtration, washed with Et_2O, and dried under vacuum. Yield: 0.31 g, 75%. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 3.3. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ −7.9.

[HP(*t*-Bu)$_3$]BF$_4$. This was prepared in the same fashion as [HP(*p*-tolyl)$_3$]BF$_4$. Yield: 81%. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 48.7.

[HP(*t*-Bu)$_3$]BPh$_4$. This was prepared in the same fashion as [HPCy$_3$]BPh$_4$. Yield: 71%. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 56.6.

Determination of Equilibrium Constants. In a typical experiment, appropriate amounts of a neutral compound and an ionic complex were loaded into a NMR tube; then CD_2Cl_2 or THF was added. After a suitable period, an NMR spectrum was recorded. The equilibrium between the hydride complexes is reached very quickly, usually in less than 30 min. The K_{eq} values obtained 30 min or 4 h after mixing the reactants did not differ appreciably. By measuring the intensity of the hydride resonances (in ^1H NMR experiments) or the ^{31}P resonances, one can calculate the relative concentration of the hydride complexes or free and protonated phosphines in solution and therefore the equilibrium constants. Some ^{31}P NMR chemical shifts of free phosphines used are as follows. (THF): δ 62.6 (P(*t*-Bu)$_3$); 9.9 (PCy$_3$); −8.1 (P(*p*-tolyl)$_3$). (CH_2Cl_2): δ −8.9 (P(*p*-tolyl)$_3$).

Results

Preparation of Ruthenium Hydride Complexes. The new cyclopentadienylruthenium complexes [CpRuH$_2$(L)]$^+$ (L = dape, dtfpe) are prepared in the sequence

$$CpRuCl(PPh_3)_2 + L \rightarrow CpRuCl(L) + 2PPh_3 \quad (1)$$

$$CpRuCl(L) + NaOMe \rightarrow CpRuH(L) + NaCl + \text{"}OCH_2\text{"} \quad (2)$$

$$CpRuH(L) + HBF_4 \rightarrow [CpRuH_2(L)]BF_4 \quad (3)$$

Substitution of PPh_3 with diphosphine dape and dtfpe occurred smoothly in refluxing benzene to produce a yellow compound, presumably CpRuCl(L), via eq 1. A similar procedure has been previously employed for the preparation of CpRuCl(dppe) and CpRuCl(dppm).[32] Treatment of the yellow compounds CpRuCl(L) (L = dtfpe, dape) with NaOMe in refluxing MeOH/benzene produced the monohydrido complexes CpRuH(L) according to eq 2. The compound CpRuH(dape) could be easily precipitated with MeOH as a yellow powder; however, the hydride CpRuH(dtfpe) is extremely soluble in organic solvents such as hexane, MeOH, and Et_2O. Thus, it could only be crystallized from cold MeOH in low yield as bright yellow microcrystals.

Protonation of a solution of CpRuH(dape) with HBF_4·Et_2O in Et_2O gave a white solid (eq 3). The ^1H NMR and $^{31}P\{^1H\}$ NMR data showed that this solid dissolves to give a 2.6:1 mixture of the dihydrido complex [CpRu(H)$_2$(dape)]$^+$ and the dihydrogen complex [CpRu(η^2-H$_2$)(dape)]$^+$. The high-field ^1H NMR spectrum gave a triplet at −8.73 ppm (J(PH) = 28.9 Hz) for [CpRu(H)$_2$(dape)]$^+$ and a broad peak at −9.26 ppm for [CpRu(η^2-H$_2$)(dape)]$^+$. Treatment of CpRuH(dape) with HBF_4 in D_2O gave a mixture of isotopomers [CpRu(η^2-HD)(dape)]$^+$ and [CpRuHD(dape)]$^+$. The former isotopomer has a coupling ^1J(HD) of 24.3 Hz whereas no ^1J(HD) was resolved for the latter. Treatment of CpRuH(dtfpe) with HBF_4 under the similar condition produced a 1.6:1 mixture of [CpRu(H)$_2$(dtfpe)]$^+$ and [CpRu(η^2-H$_2$)(dtfpe)]$^+$. In CD_2Cl_2, the hydride resonance for [CpRu(H)$_2$(dtfpe)]$^+$ is a triplet (J(PH) = 28.7 Hz) at −8.61 ppm while the dihydrogen complex [CpRu(η^2-H$_2$)(dtfpe)]$^+$ gives a broad peak at −8.76 ppm, which overlapped with the right line of the triplet belonging to [CpRu(H)$_2$(dtfpe)]$^+$ (in a 200-MHz spectrum). The isotopomer of [CpRu(η^2-HD)(dtfpe)]$^+$ has a ^1J(HD) value of 25.3 Hz.

Treatment of Cp*RuCl$_2$ with ca. 1 equiv of dppm in benzene in the presence of excess Zn produced a dark orange solution. The orange solution can also be obtained by the reaction of excess dppm with Cp*RuCl$_2$ in a mixed solvent of CH_2Cl_2/MeOH. However, a longer reaction time is required. The dark orange solution presumably contains Cp*RuCl(dppm). A similar procedure has been employed previously for preparation of other Cp*Ru complexes such as Cp*RuCl(L$_2$) (L$_2$ = (PMe$_3$)$_2$,[30] dppe[34]) and Cp*RuCl(L)[35] (L = PCy$_3$, P(*i*-Pr)$_3$, P(*t*-Bu)$_3$). Treatment of Cp*RuCl(dppm) with NaOMe produced Cp*RuH(dppm) as in eq 2.

The hydride complex Cp*RuH(dppm) is an air-sensitive yellow compound. In the ^1H NMR spectrum, the hydride resonance is observed at −10.63 ppm as a triplet (J(PH) = 32.0 Hz) of doublets ^4J(HH) = 3.5 Hz). The last value is unusually large for such a long-range coupling. It arises from a coupling to one of the methylene protons of the dppm ligand. The Cp* resonance was observed at 2.06 ppm (t, ^3J(PH) = 1.6 Hz).

Protonation of Cp*RuH(dppm) with HBF_4·Et_2O in Et_2O produced a mixture of [Cp*Ru(H)$_2$(dppm)]$^+$ and [Cp*Ru(η^2-H$_2$)(dppm)]$^+$ in a ratio of ca. 1:2. In the ^1H NMR spectrum, the dihydride resonance was observed at −6.09 ppm (t, J(PH) = 28.8 Hz). The dihydrogen resonance was observed at −6.80 ppm as a broad peak. T_1 values at 200 MHz, 290 K, for the dihydride and dihydrogen signals were measured to be 109 and 50 ms in CD_2Cl_2, respectively. Intramolecular site exchange at a rate of ca. 10 Hz could explain why these values are so similar. The dihydride nuclei should have T_1 values many times greater than those of the dihydrogen nuclei. Complete averaging of T_1 values is observed at 313 K, 200 MHz, where T_1 times for both resonances are 86 ms. The isotopomers [Cp*Ru(η^2-HD)(dppm)]$^+$ and [Cp*Ru(H)(D)(dppm)]$^+$ were prepared by reaction of Cp*RuH(dppm) with HBF_4·Et_2O in D_2O. The η^2-HD isotopomer [Cp*Ru(η^2-HD)(dppm)]$^+$ displayed ^1J(HD) = 20.9 Hz.

Physical properties of the new ruthenium hydride and some similar complexes are collected in Table I.

Electrochemistry. Table II lists the electrochemical peak potentials of the monohydrido ruthenium complexes as measured

(34) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161–1164.
(35) Arliguie, T.; Border, C.; Chaudret, B.; Devillers, J.; Poilblanc, R. *Organometallics* **1989**, *8*, 1308–1314.

Table I. Selected Physical Data for the Cationic Ruthenium Complexes and Their Related Monohydride Complexes (RuH)[a]

RuH_2^+	δRuH,[b] ppm	δRuH$_2$,[c] ppm	δRu(H$_2$),[c] ppm	H$_2$/(H$_2$),[c] K_1	J(HD),[c] Hz	pK_a(RuH$_2^+$) CH$_2$Cl$_2$ (H)$_2$	CH$_2$Cl$_2$ (H$_2$)	THF (H)$_2$	THF (H$_2$)	E_{pa}(RuH), V
[CpRuH$_2$(dtfpe)]$^+$	−13.47	−8.62	−8.76	1.6	25.3[d]	4.4	4.3	4.9	4.6	0.17
[CpRuH$_2$(dppe)]$^+$	−13.26[e]	−8.60[f]	−9.02[f]	2[f]	24.9[f]	7.3	7.0	7.5	7.2	−0.09
[CpRu(H$_2$)(dppm)]$^+$	−11.00[e]		−6.89	<10^{-3}	21.9		7.1		7.5	−0.04
[CpRu(H)$_2$(PPh$_3$)$_2$]$^+$	−11.13[e]	−7.44[g]		>10^3		8.3		8.0		−0.20
[CpRu(H)$_2$(dppp)]$^+$	−12.84	−8.62[f]		>10^3		8.4		8.6		−0.22
[CpRuH$_2$(dape)]$^+$	−13.25	−8.73	−9.26	2.6	24.3[d]	8.5	8.1	9.0	8.6	−0.22
[Cp*RuH$_2$(dppm)]$^+$	−10.63	−6.09[f]	−6.80[f]	0.5	20.9			8.8	9.2	−0.25
[CpRuH$_2$(dmpe)]$^+$		−9.83[h]	−10.07[h]	0.17[h]	22[h]				9.8[i]	−0.29[j]
[Cp*RuH$_2$(PMePh$_2$)$_2$]$^+$	−12.47	−8.13[d]		>10^3				12.1		−0.49

[a] The complexes are listed in order of increasing pK_a value (or decreasing anodic peak potential, E_{pa}, vs Fc/Fc$^+$; see Table II). [b] In C_6D_6. [c] In CD_2Cl_2. [d] In acetone-d_6. [e] From ref 29. [f] From ref 22. [g] From ref 33. [h] From ref 7. [i] Converted from pK_a value in CH_3CN.[7] [j] Calculated from Lever's electrochemical parameter E_L(dmpe) = 0.28 V.[27]

Table II. Peak Potentials As Determined by Cyclic Voltammetry[a] and Predicted ($\sum E_L$) by Lever's Method[b]

compound	$E_{pa}(1)$[c] d^6 → d^5	$E_{pa}(2)$[c] vs Fc/Fc$^+$	E_{pc}[c]	$E_{pa}(1)$[d] vs NHE	$\sum E_L$[b,d]
CpRuH(dtfpe)	0.17			0.77	0.72
CpRuH(dppm)	−0.04	0.04	0.24	0.56	0.64
CpRuH(dppe)	−0.09	0.49	0.32	0.51	0.50
CpRuH(dape)	−0.22	0.30	0.14	0.38	0.44
CpRuH(dmpe)	−0.29[b]			0.31	0.34
Cp*RuH(dppm)	−0.25	0.22	0.10	0.35	0.39
CpRuH(PPh$_3$)$_2$	−0.20	0.43			
CpRuH(dppp)	−0.22	0.29, 0.55	0.39		
Cp*RuH(PMePh$_2$)$_2$	−0.49	0.06	−0.29		

[a] Voltammograms were collected by using THF solutions containing 0.2 M Bu_4NPF_4 as the supporting electrolyte. E_{pa}, anodic peak potentials; E_{pc}, cathodic peak potentials in volts. [b] Calculated from Lever's electrochemical parameters E_L: Cp$^-$ 0.08, H$^-$ −0.30, dtfpe 0.47, dppm 0.43, dppe 0.36, dape 0.33, dmpe 0.28, Cp^{*-} −0.17 V.[27] [c] Versus Fc/Fc$^+$. [d] Versus NHE.

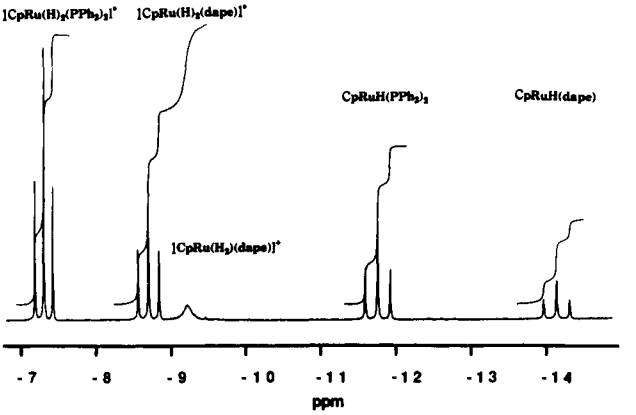


Figure 1. ^{1}H NMR spectrum (200 MHz) in the hydride region for the mixture of CpRuH(dape) and [CpRu(H)$_2$(PPh$_3$)$_2$]BF$_4$ in CD_2Cl_2 (K_{eq} = 1.1, entry 8, Table III).

by cyclic voltammetry at scan rates of 0.25 V s^{-1} in THF containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. The cyclic voltammograms for the hydride complexes display an irreversible oxidation wave, $E_{pa}(1)$, the value of which is dependent on the nature of the complex; there is also a more positive oxidation wave, $E_{pa}(2)$. An exception to this pattern is CpRuH(dtfpe), which exhibits only one irreversible wave at E_{pa} = 0.17 V vs Fc/Fc$^+$. The first wave probably corresponds to the oxidation of CpRuH(L) to [CpRuH(L)]$^+$. The more positive wave is possibly due to the Ru(III)/Ru(IV) couple. It is not due to ligand released upon oxidation of the complex because the free phosphines (e.g., PPh$_3$, dppm) do not oxidize in the voltage range within which the complexes were oxidized. Despite the lack of reversibility in the electrochemistry of the complexes CpRuH(L), the E_{pa} values follow a sensible order of increasing electron richness at the ruthenium center: dtfpe < dppm < dppe < PPh$_3$ < dppp ≃ dape < dmpe.

This ordering is maintained quantitatively if the scan rate is changed. The E_{pa} values increased by ~0.02 V for each complex when a scan rate of 0.5 V s^{-1} was employed and decreased by 0.02 V with a scan rate of 50 m V s^{-1}. The difference between E_{pa} values of two complexes is independent of the scan rate. Thus, a mixture of Cp*RuH(dppm) and CpRuH(dtfpe) gave a constant difference of 0.42 V between oxidation waves independent of the scan rate. It is this difference that greatly influences the slope of eq 22 (see below).

Acidity Measurements. We have recently reported a simple method for the ranking of η^2-dihydrogen and dihydrido compounds.[21] The method involves the determination by ^{1}H NMR spectroscopy of the equilibrium constant K_{eq} for a mixture of neutral monohydrides and cationic dihydrogen or dihydrido complexes (eq 4). Although CH_3CN is the preferred solvent for

$$MH + M'H_2^+ \rightleftharpoons MH_2^+ + M'H \quad (4)$$

hydride pK_a determination,[36] it displaces H_2 from most dihydrogen complexes, including the ones described in this work. Thus, we choose CH_2Cl_2 and THF as the measurement medium. Both of them are good solvents for neutral and ionic hydride complexes but have poor coordination ability. However, CH_2Cl_2 reacts with hydrides with $E°(MH^+/MH)$ < ca. −0.25 V vs Fc/Fc (see below). To minimize specific ion-pairing effects in these low dielectric solvents, weakly coordinating counterions are used (e.g., BF_4^-, BPh_4^-).

The order of the acidity of the dihydrogen and dihydrido complexes is determined by comparing the magnitude of the equilibrium constants, K_{eq}, of the reactions between a monohydrido complex CpRuH(L) or Cp*RuH(L), L = diphosphines, with [CpRu(H)$_2$(PPh$_3$)$_2$]$^+$ (eq 5). As a check, the reverse reaction

$$CpRuH(L) + [CpRu(H)_2(PPh_3)_2]^+ \overset{K_{eq}}{\rightleftharpoons} [CpRuH_2(L)]^+ + CpRuH(PPh_3)_2 \quad (5)$$

can also be studied since the equilibrium can be approached from either side. Both ^{1}H and ^{31}P{^{1}H} NMR spectroscopy can be used for measuring the equilibrium constants. The ^{31}P NMR spectra must be acquired under conditions where peak integration is meaningful (gated decoupled with correct time delays). Typical ^{1}H and ^{31}P{^{1}H} NMR spectra for an equilibrium mixture are shown in Figures 1 and 2, respectively.

Analysis of the equilibria involving mixtures of tautomers (e.g., eq 6) is more complex. In this case the fraction of tautomers must

$$CpRuH(dppe) + [CpRu(\eta^2\text{-}H_2)(dppm)]^+ \rightleftharpoons 0.34[CpRu(H_2)(dppe)]^+ + 0.66[CpRu(H)_2(dppe)]^+ + CpRuH(dppm) \quad (6)$$

be taken into consideration and K_{eq} = 0.88 in CH_2Cl_2 is calculated as in eq 7. This is a more rigorous treatment than that of our preliminary note about this work, where the sum of the concen-

(36) Weberg, R. T.; Norton, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 1105–1108, and references therein.

$$K_{eq} = [CpRu(H_2)(dppe)^+]^{0.34}[CpRu(H)_2(dppe)^+]^{0.66}[CpRuH(dppm)]/[CpRuH(dppe)][CpRu(H_2)(dppm)^+] \quad (7)$$

trations of the two tautomers was used to calculate a combined equilibrium constant of 1.71 for this reaction of the dppe complex.[21] The equilibrium constants, K_{eq}, are collected in Table III.

The measured equilibrium constants obtained by ^1H or $^{31}P\{^1H\}$ NMR spectroscopy are internally consistent.[21] Thus, similar K_{eq} values are obtained when the equilibrium is approached from either the right or left side of the reaction. For example, for eq 8

$$CpRuH(dppm) + [CpRu(H)_2(PPh_3)_2]^+ \rightleftarrows CpRuH(PPh_3)_2 + [CpRu(H)_2(dppm)]^+ \quad (8)$$

conducted in THF, an equilibrium constant of 0.30 is obtained by ^{31}P signal integration when approached from the left and 0.34 when approached from the right. Similarly, the same equilibrium constant of 12.5 is obtained if Cp*RuH(dppm) and $[CpRu(H)_2(PPh_3)_2]^+$ are mixed or if $CpRuH(PPh_3)_2$ and $[Cp^*RuH_2(dppm)]^+$ are mixed. The K_{eq} for eq 6 in THF is related to those of entries 3 and 4 of Table III, i.e., $K_{eq}(6) = K_{entry\ 4}/K_{entry\ 3} = 0.23/0.32 = 0.72$. This is within the error of the experimentally determined value of 0.62 (entry 5). Similarly, K_{eq} for eq 9 is

$$Cp^*RuH(dppm) + HPCy_3^+ \rightleftarrows [Cp^*RuH_2(dppm)]^+ + PCy_3 \quad (9)$$

related to those of entries 6 and 9: $K_{eq}(9) = K_{entry\ 6}K_{entry\ 9} = 0.018 \times 12.5 = 0.23$, which is close to the experimentally determined value of 0.27 (entry 10).

To obtain the solvent effect on the equilibrium constant, equilibria in both CD_2Cl_2 (by ^1H NMR, except $[CpRuH_2(dtfpe)]^+$) and THF (by ^{31}P NMR) were studied when this was feasible. For the reaction of Cp*RuH(dppm) and $[CpRu(H)_2(PPh_3)_2]^+$, we were unable to obtain K_{eq} in CD_2Cl_2 when the equilibrium was approached from either the right or left side since Cp*RuH(dppm) reacts with CH_2Cl_2 fairly quickly. As listed in Table III, all the equilibrium constants for the reactions where $[CpRu(H)_2(PPh_3)_2]^+$ is one of the reactants are consistently larger in THF than in CD_2Cl_2.

The $pK_a(RuH_2^+)$ values of the acidic dihydrido complexes can be estimated from the equilibrium constants for the reactions between a protonated base, BH^+, of known pK_a and the corresponding monohydrido complex (eq 10). We find that bulky

$$RuH + BH^+ \overset{K_{eq}}{\rightleftharpoons} RuH_2^+ + B \quad (10)$$

$$pK_a(RuH_2^+) = pK_a(BH^+) - pK_{eq} \quad (11)$$

phosphines are very useful bases for this purpose. Protonated phosphines can have pK_a values that range from 1.0 ($P(p\text{-}ClC_6H_4)_3$) to 11.4 ($P(t\text{-}Bu)_3$).[37,38] As long as bases of similar structure are used, then the ordering of acidities should remain the same in either THF or (by extrapolation) aqueous solution. Both ^1H and ^{31}P NMR spectroscopy can be used. When ^{31}P NMR is employed, one can observe all the reactants and products for a reaction; thus, the exact amount initially mixed does not have to be known, and side reactions, if there are any, are readily detected. One disadvantage of using phosphines as bases is that they might react with the metal complexes (either replacing dihydrogen or ancillary neutral ligands); the use of bulky phosphines usually overcomes this problem.

Even better than free phosphines as base B are hydride complexes of known pK_a that contain phosphines since these show no side reactions. By measurement of the equilibrium constant for eq 12 the aqueous pK_a value for $[CpRu(H)_2(PPh_3)_2]^+$ was esti-

$$CpRuH(PPh_3)_2 + [HPCy_3]^+ \rightleftarrows [CpRu(H)_2(PPh_3)_2]^+ + PCy_3 \quad (12)$$

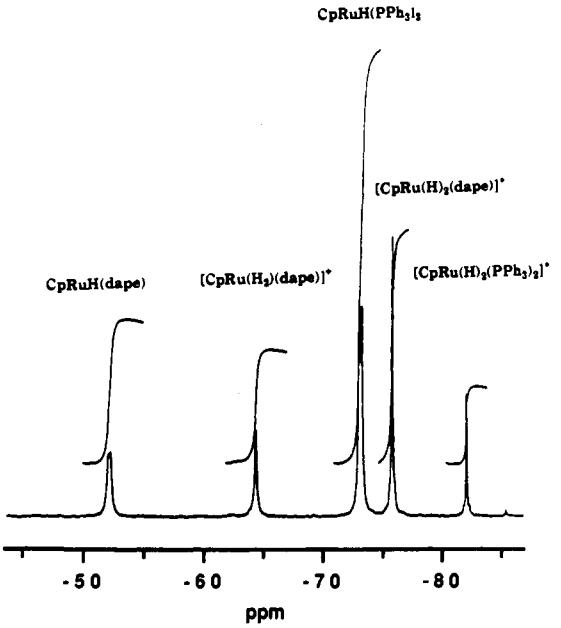
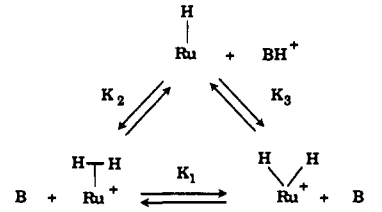


Figure 2. Gated decoupled $^{31}P\{^1H\}$ NMR spectrum (81 MHz) for the mixture of CpRuH(dape) and $[CpRu(H)_2(PPh_3)_2]BF_4$ in THF (K_{eq} = 6.3, entry 8, Table III). Chemical shifts were measured relative to $P(OMe)_3$ (at 140.4 ppm vs 85% H_3PO_4). There is residual $^2J(PH)$ coupling in the monohydride resonances.

Scheme I



mated as 8.3 from measurements in CD_2Cl_2 and as 7.96 from measurements in THF based on the pK_a of $[HPCy_3]^+$ of 9.7 (determined in CH_3NO_2 but extrapolated to the aqueous scale).[37] The pK_a values for the dihydride/dihydrogen complexes of dppm, dppe, dppp, and dape could then be calculated from the pK_a value for $[CpRu(H)_2(PPh_3)_2]^+$ and the equilibrium constants for the reactions of this PPh_3 complex with the corresponding monohydrido complexes as listed in Tables III and IV.

Calculation of the Thermodynamic Acidity of the Tautomeric Forms. The equilibria required to separate the contributions of the $Ru(H_2)^+$ and $Ru(H)_2^+$ tautomers to the overall acidity are shown in Scheme I. The following equations are utilized to calculate $pK_a(Ru(H_2)^+)$ and $pK_a(Ru(H)_2^+)$:

$$pK_a(Ru(H_2)^+) = pK_a(BH^+) - pK_2 \quad (13)$$

$$pK_a(Ru(H)_2^+) = pK_a(BH^+) - pK_3 \quad (14)$$

The values for K_1 (Table I), K_2, and K_3 (Table IV) are calculated from appropriate integrals of peaks in the NMR spectra. Representative values of $pK_a(Ru(H_2)^+)$ and $pK_a(Ru(H)_2^+)$ determined from one or two sets of equilibria are given in Table IV and the best values are listed in Table I. These are related by the ratio of their two concentrations (K_1) as indicated by eq 15. Errors

$$pK_1 = pK_a(Ru(H_2)^+) - pK_a(Ru(H)_2^+) \quad (15)$$

in the measurement of K_2 and K_3 result in pK_a differences that only roughly match the pK_1 values. For example, in four separate determinations for $[CpRuH_2(dppe)]^+$ (entries 4 and 5, Table IV), the pK_a difference of eq 15 averages to −0.23 unit whereas pK_1 is −0.3 (from Table I).

The $pK_a(RuH_2^+)$ values for the tautomers of $[CpRuH_2(dtfpe)]^+$, however, could not be obtained by the reaction with $CpRuH(PPh_3)_2$ in either CD_2Cl_2 or THF, since they are much

(37) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985.
(38) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681–686.

Table III. pK_a Values for the Cationic Ruthenium Complexes with $[HPCy_3]^+$ as a Standard

				CH_2Cl_2[a]		THF[b]	
no.	RuH	$Ru'H_2^+$	RuH_2^+	K_{eq}	$pK_a(RuH_2^+)$	K_{eq}	$pK_a(RuH_2^+)$
1	CpRuH(dtfpe)	$[CpRuH_2(PPh_3)_2]^+$	$[CpRuH_2(dtfpe)]^+$	$<10^{-4}$	c	c	c
2	CpRuH(dtfpe)	$HP(p\text{-tolyl})_3^+$	$[CpRuH_2(dtfpe)]^+$	3.6[b]	d	8.7	d
3	CpRuH(dppm)	$[CpRuH_2(PPh_3)_2]^+$	$[CpRu(H_2)(dppm)]^+$	0.068	7.1	0.32	7.5
4	CpRuH(dppe)	$[CpRuH_2(PPh_3)_2]^+$	$[CpRuH_2(dppe)]^+$	0.075	d	0.23	d
5	CpRuH(dppe)	$[CpRu(H_2)(dppm)]^+$	$[CpRuH_2(dppe)]^+$	0.88	d	0.62	d
6	$CpRuH(PPh_3)_2$	$HPCy_3^+$	$[CpRu(H)_2(PPh_3)_2]^+$	0.038	8.3	0.018	8.0
7	CpRuH(dppp)	$[CpRuH_2(PPh_3)_2]^+$	$[CpRu(H)_2(dppp)]^+$	1.34	8.4	4.6	8.6
8	CpRuH(dape)	$[CpRuH_2(PPh_3)_2]^+$	$[CpRuH_2(dape)]^+$	1.1	d	6.3	d
9	Cp*RuH(dppm)	$[CpRuH_2(PPh_3)_2]^+$	$[Cp^*RuH_2(dppm)]^+$	c	c	12.5	d
10	Cp*RuH(dppm)	$HPCy_3^+$	$[Cp^*RuH_2(dppm)]^+$	c	c	0.27	d
11	$Cp^*RuH(PMePh_2)_2$	$HP(t\text{-Bu})_3^+$	$[Cp^*Ru(H)_2(PMePh_2)_2]^+$	c	c	5.8	12.1

[a] Obtained by ^1H NMR unless otherwise stated. [b] Obtained by $^{31}P\{^1H\}$ NMR unless otherwise stated. [c] Unable to obtain (see text). [d] pK_a values of each tautomer are listed in Table IV.

Table IV. pK_a Values for the Two Tautomers of the Cationic Ruthenium Complexes Calculated by Use of Eqs 13 and 14[a]

		CH_2Cl_2[b]				THF[c]			
no.	RuH_2^+	K_2	$pK_a(Ru(H_2)^+)$	K_3	$pK_a(Ru(H)_2^+)$	K_2	$pK_a(Ru(H_2)^+)$	K_3	$pK_a(Ru(H)_2^+)$
2	$[CpRuH_2(dtfpe)]^+$	2.8[c]	4.3	3.9[b]	4.4	5.4	4.6	11.1	4.9
4	$[CpRuH_2(dppe)]^+$	0.051	7.0	0.10	7.3	0.15	7.2	0.30	7.5
5	$[CpRuH_2(dppe)]^+$	0.63	6.9	1.08	7.1	0.46	7.1	0.75	7.3
8	$[CpRuH_2(dape)]^+$	0.61	8.1	1.51	8.5	4.2	8.6	7.8	9.0
9	$[Cp^*RuH_2(dppm)]^+$	d	d	d	d	16.5	9.2	5.5	8.7
10	$[Cp^*RuH_2(dppm)]^+$	d	d	d	d	0.34	9.2	0.16	8.9

[a] The entry numbers refer to the equilibria in Table III. [b] Obtained by ^1H NMR unless otherwise stated. [c] Obtained by $^{31}P\{^1H\}$ NMR unless otherwise stated. [d] Unable to obtain (see text).

more acidic than $[CpRu(H)_2(PPh_3)_2]^+$. The pK_a values for $[CpRuH_2(dtfpe)]^+$ must also be smaller than $[CpRu(\eta^2\text{-}H_2)(dppm)]^+$ since no reaction occurred when CpRuH(dtfpe) was mixed with $[CpRu(\eta^2\text{-}H_2)(dppm)]^+$ (aqueous pK_a 7.1 as measured in CD_2Cl_2, pK_a 7.5 in THF). Fortunately, we were able to obtain the equilibrium constant for eq 16 in both CH_2Cl_2 ($x = 0.44$, K_{eq}

$$CpRuH(dtfpe) + [HP(p\text{-tolyl})_3]^+ \rightleftharpoons x[CpRu(H_2)(dtfpe)]^+ + (1-x)[CpRu(H)_2(dtfpe)]^+ + P(p\text{-tolyl})_3 \quad (16)$$

$= 3.6$) and THF ($x = 0.33$, $K_{eq} = 8.7$). Thus, the aqueous $pK_a(Ru(H_2)^+)$ value for $[CpRu(H_2)(dtfpe)]^+$ is estimated to be 4.3 as determined in CH_2Cl_2 and 4.6 as determined in THF based on the aqueous pK_a value of 3.85 for $[HP(p\text{-tolyl})_3]^+$ (Table IV). For a mixture of $[HP(p\text{-tolyl})_3]^+$ and $P(p\text{-tolyl})_3$ in THF, the intermolecular proton transfer is fast and so only one ^{31}P NMR signal is observed; the same is also true for $[HPPh_3]^+/PPh_3$. The chemical shift is the weighted average of the chemical shifts of the two components and thus from it the ratio of $[HP(p\text{-tolyl})_3]^+$ to $P(p\text{-tolyl})_3$ can be calculated. However, the chemical shifts of the two components are very similar so that there is a large error in the equilibrium constant value and a large error in the pK_a values (±0.3). However, both species in CH_2Cl_2 are observed as separated broad peaks in the ^{31}P NMR spectrum so that integrals give a reliable value for the pK_a of the dihydrogen tautomer of 4.3 ± 0.1. Considering that the pK_a values in THF are 0.3 ± 0.1 unit higher than those determined in CH_2Cl_2 (see Table I), the value of 4.6 for the complex in THF is reasonable. A slow substitution reaction that does not influence the pK_a determination gives a complex that is presumed to be $[CpRu(P(p\text{-tolyl})_3)(dtfpe)]^+$. In contrast, little or no side reactions were observed between the other ruthenium hydride complexes. The $pK_a(Ru(H_2)^+)$ value for $[CpRuH_2(dmpe)]^+$ was obtained by taking the value in CH_3CN of 17.6[7] and converting it to the aqueous scale.[21]

From the pK_a values listed in Table I, the relative acidity of the dihydrogen complexes can be ranked as $[CpRu(H_2)(dtfpe)]^+ > [CpRu(H_2)(dppe)]^+ \sim [CpRu(H_2)(dppm)]^+ > [CpRu(H_2)(dape)]^+ > [Cp^*Ru(H_2)(dppm)]^+$, the same order as the electrochemical potentials of the first oxidation wave apart from the dppe complex.

Discussion

All of the complexes $[CpRuH_2(diphosphine)]^+$ exist as a mixture of η^2-dihydrogen and dihydride forms apart from the dppm complex, which is 100% dihydrogen, and the dppp complex, which is 100% dihydride as reported by Conroy-Lewis and Simpson.[22] The dihydrogen form is thought to have a typical "three-legged piano stool" structure with the $\eta^2\text{-}H_2$ ligand occupying one of the legs.[7,22] An X-ray crystal structure determination of the complex $[Cp^*RuH_2(dppm)]BF_4$ suggests that it is completely in this dihydrogen form in the solid state, judging from the phosphorus positions relative to the Cp* ring. However, the H atoms were not located.[39] The dihydrido complexes in solution are all thought to be "square-based piano stools" with pseudo-trans hydride ligands, and this results in a triplet pattern in the hydride region of the ^1H NMR spectrum.[19] The X-ray crystal structure of $[CpRu(H)_2(PPh_3)_2]PF_6$ and several diphosphine analogues verifies this structure in the solid state.[40]

When steric properties are held constant, as in the para-substituted diphosphine series, then the ratio of concentrations of complexes $[CpRu(H)_2L]^+/[CpRu(\eta^2\text{-}H_2)L]^+$ increases as the diphosphine becomes more electron donating (dtfpe < dppe < dape, see Table I). Higher electron density on the ruthenium should favor the dihydride form, and this is observed. Backbonding to the dihydrogen ligand should also increase (or the dihydride character of the dihydrogen ligand should increase) so that the H–H bond should lengthen and the $^1J(H,D)$ coupling constant should drop, as is also the case. Even the chemical shift of the dihydrogen nuclei is sensitive to this electronic change: there is a significant shift upfield going from dtfpe to dppe to dape. There is little change, by comparison, in the chemical shifts of the dihydrido complexes, $[CpRu(H)_2L]^+$, and monohydrido complexes, CpRuHL. As the H_2 ligand becomes less like free dihydrogen (with $\delta = +4.6$ ppm[41]) the chemical shift becomes more negative. These trends have also been established for the dihydrogen complexes $[M(\eta^2\text{-}H_2)(H)(diphosphine)_2]^+$.[42,43]

The separation of steric and electronic influences in the other complexes listed in Table I is more difficult. Certainly electro-

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chemistry provides a sensible ordering of electronic effects (see below). In the *trans*-dihydrido complexes, the large ligands can stay further apart than in the η^2-dihydrogen form. The ligands that crowd the coordination sphere (Cp*, PPh_3, dppp) do give complexes with much higher ratios of dihydride to dihydrogen forms (Table I) than comparable complexes with smaller ligands (dppm, dmpe). Apparently even the dppm ligand with its small "bite angle" can span the trans positions of a square-based piano stool, since the compound $[Cp^*RuH_2(dppm)]^+$ does have a dihydride form. As already noted, the less electron rich Cp complex is exclusively in the isomeric form $[CpRu(\eta^2\text{-}H_2)(dppm)]^+$.[22]

The existence of two tautomeric forms for these complexes makes analysis of their acid/base chemistry more complex. Further study is required to determine relative kinetics acidities. The two forms interconvert with half-lives in the order of seconds at 290 K, judging from how rapidly equilibria between dihydrogen and dihydride tautomers are achieved and how rapidly the T_1 times of the hydrogen nuclei ($H_2/\eta^2\text{-}H_2$) average. For the dmpe complex there is evidence that the $\eta^2\text{-}H_2$ form is deprotonated more rapidly than the dihydride.[7,19] The microscopic reverse reaction is the protonation of a hydride complex to give the dihydrogen ligand and this appears to take place at the hydride hydrogen.[2,8,19,22,42,44] We show that the cationic dihydrides studied here have thermodynamic acidities similar to their dihydrogen tautomers and that both can function as Brønsted acids.

Acidity constants have been determined for both tautomers (Tables I and IV). The pK_a of the $\eta^2\text{-}H_2$ form, $pK_a(Ru(H_2)^+)$, is 0.3 ± 0.2 pK_a unit less than that of the $(H)_2$ form for the complexes with L = dtfpe, dppe, and dape. For $[Cp^*RuH_2(dppm)]^+$, which has a ratio of dihydride to dihydrogen forms of 0.5, the pK_a of the dihydride form is 0.4 unit less in this case. The thermodynamic acidity of the two tautomers must be similar because they are in equilibrium with the same monohydrido conjugate base and they have similar concentrations.

Correlation between the Acidity of Dihydrogen/Dihydrido Complexes and the Electrochemical Oxidation Potential of the Deprotonated Monohydrido Complexes. The pK_a values of the M–H bond of some carbonyl metal hydride complexes[25] have recently been related by use of thermodynamic cycles to the dissociation free energy of the metal hydride bond, $\Delta G_{BDE}(MH)$, and to electrochemical potentials for the oxidation of the deprotonated species ($E°(M/M^-)$):

$$\Delta G_{BDE}(MH) = 1.37\ pK_a(MH) + 23.1E°(M/M^-) + 53.6 \quad (17)$$

where the constant 53.6 (recently changed from the original value of 45.6)[45] applies to pK_a and $E°$ values (vs NHE) measured in CH_3CN. This was based on earlier work on the acidity of C–H, O–H, or N–H bonds of organic compounds.[24]

Since the complexes under consideration have a bishydrido formulation, eq 17 can be modified as follows:

$$\Delta G_{BDE}(M(H)_2^+) = 1.37pK_a(M(H)_2^+) + 23.1E°(MH^+/MH) + C \quad (18)$$

where the constant C depends on the solvent system and $E°(MH^+/MH) = E_{1/2}(MH^+ + e^- \rightleftarrows MH)$ refers to the half-wave potential for the oxidation of the deprotonated, neutral, monohydrido species. Note that the signs of $E°$ are those of standard *reduction potentials* corresponding to the $d^5 \rightleftarrows d^6$ couple in our case. According to eq 18, as complexes are made more electron rich by using more electron donating coligands, $E°$ will be more negative and the pK_a will increase. Equation 18 predicts that a series of cationic bishydrido complexes, $[M(H)_2L_n]^+$, where M is changed, should show an increase in pK_a down the group as the metal–hydride bond energy, $\Delta G_{BDE}(M(H)_2^+)$, increases[25] as long as $E°$ remains constant. This prediction is currently under investigation.

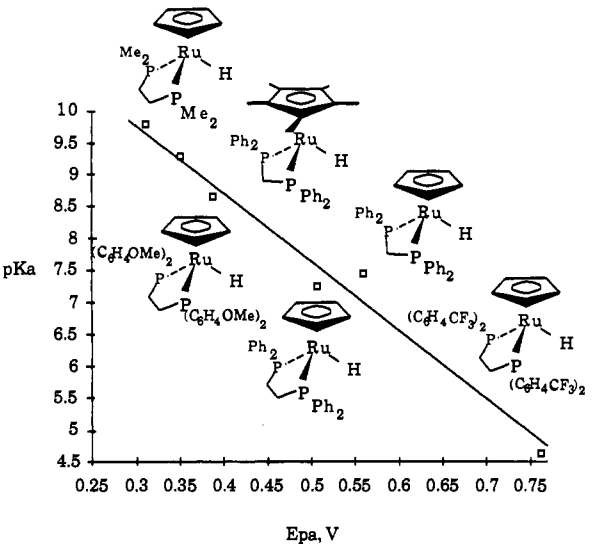

Figure 3. Plot of $pK_a(Ru(H_2)^+)$ values for the ruthenium complexes that have an $\eta^2\text{-}H_2$ tautomer vs the anodic peak potential, E_{pa} (vs NHE), for the corresponding monohydrido ruthenium complexes (structure shown). The normal hydrogen electrode is assumed to be −0.6 V from Fc/Fc^+.

Neither a change in phosphine nor permethylation of the cyclopentadienyl ring is expected to change the Ru–H bond energy, $\Delta G_{BDE}(Ru(H)_2^+)$, significantly in the complexes $[CpRu(H)_2L]^+$, according to the work of Tilset and Parker. Thus, eq 18 simplifies further:

$$pK_a(MH_2^+) = -16.9E°(MH^+/MH) + C' \quad (19)$$

A plot of the $pK_a(Ru(H)_2^+)$ values for the dihydride complexes in THF vs the anodic peak potential, E_{pa}, of the corresponding monohydrido complexes gives a least-squares line with a correlation coefficient of −0.99:

$$pK_a(Ru(H)_2^+) = -10.5E°(MH^+/MH) + 12.8 \quad (20)$$

Perhaps the assumption of the constancy of the metal–hydride bond energy is not valid here because the slope of eq 20 is less than the one expected. $\Delta G_{BDE}(Ru(H)_2^+)$ may be changing systematically in eq 18 to give the linear relationship of eq 20.

The irreversibility of the electrochemistry might also explain the difference in slope. If the cation-radical monohydride formed in the first oxidation rapidly loses H^+, then it is possible that the difference between the true E_{ox} value and the measured E_{pa} value varies systematically with pK_a. Such chemistry has been uncovered for some carbonylcyclopentadienylmetal hydrides that are less electron rich than the Ru complexes under study.[26] However, the characteristic broad wave for the reduction of H^+ in THF at Pt is not observed in our system. Thus, rapid loss of proton from the initially oxidized product may not be the explanation.

The expression for dihydrogen complexes, eq 21 (where C and $E°(MH^+/MH)$ were defined above), only differs from that of

$$\Delta G_{BDE}(M(\eta^2\text{-}H_2)^+) = 1.37\ pK_a(M(\eta^2\text{-}H_2)^+) + 23.1E°(MH^+/MH) + C \quad (21)$$

the dihydride in the bond dissociation energy involved, $\Delta G_{BDE}(M(\eta^2\text{-}H_2)^+)$, which is the energy required to take a hydrogen atom from the $\eta^2\text{-}H_2$ ligand. The problem with eq 21 is that the term $\Delta G_{BDE}(M(\eta^2\text{-}H_2^+))$ is not readily determined experimentally.

A plot of the $pK_a(Ru(H_2)^+)$ values for the $\eta^2\text{-}H_2$ complexes in THF vs the anodic peak potential, E_{pa}, of the corresponding monohydrido complexes is shown in Figure 3. As expected, the pK_a values for the dihydrogen complexes continuously decrease as the E_{pa} for the corresponding monohydrido complexes increase. The linear regression (eq 22) of these data has a correlation

$$pK_a(Ru(\eta^2\text{-}H_2)) = -10.7E°(MH^+/MH) + 13.0 \quad (22)$$

coefficient of −0.99. The slope is less than the theoretical value of −16.9 and is similar to that of eq 20. There is a maximum error

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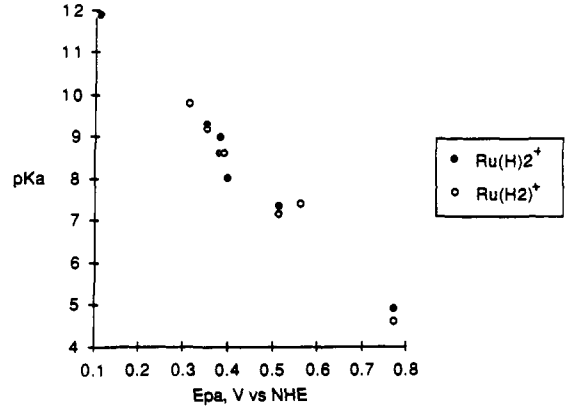

Figure 4. Plot of $pK_a(Ru(H_2)^+)$ (open circles) and $pK_a(Ru(H)_2^+)$ (closed circles) for the cationic ruthenium complexes in THF vs peak potential (vs NHE) for oxidation of the corresponding monohydrido ruthenium complexes.

of 1.0 in the slope (−10.7 ± 1.0) because of the uncertainty in the pK_a value of the dtfpe complex (see above).

Again it is not clear why the slope of a plot of eq 22 is so low. It could be that the $\Delta G_{BDE}(M(\eta^2\text{-}H_2)^+)$ term of eq 21 is changing continuously or that there is a problem in the transfer of the pK_a values of the protonated phosphine ligands between solvents.

Figure 4 is a plot of the $pK_a(Ru(H)_2^+)$ and $pK_a(Ru(H_2)^+)$ data for THF solutions taken from Table I. The slope of a least-squares line through all the points is −10.6 (correlation coefficient −0.99). Therefore, when the contributions to the acidity of the dihydrogen and dihydride forms are factored out, the two forms give the same pK_a vs E_{pa} equations. A change in electron density at the metal, as reflected by the E_{pa} value, results in similar changes to the acidity of the dihydride and dihydrogen forms.

Explaining and Predicting the Acidity of Other Dihydrogen Complexes. Now that a link has been established between the acidity of coordinated dihydrogen and the electrochemical potential, at least for cyclopentadienylruthenium(II) complexes (eq 22), can it be used to predict the acidity of other dihydrogen complexes where the electrochemistry has not yet been done? Lever has proposed a method involving additive ligand parameters, E_L, for predicting electrochemical potentials for the $d^5 \rightleftarrows d^6$ couples for several transition metals.[27] He cautioned that covalently bonded ligands like hydride and cyclopentadienyl may lead to "noninnocent behavior".

In the case of Ru(II), parameters for the six ligands are simply added to obtain $E_{1/2}(ox)$. Lever provided parameters for dppm, dppe, PPh_3, dppp, dmpe, and hydride (see Table II). The value for hydride is −0.3, but this may change from complex to complex due to noninnocent behavior (changes in acidic/hydridic character). No parameters are provided by Lever for the Cp and Cp* ligands. However, it is known that complexes containing the Cp* ligand are 0.25 ± 0.10 V easier to oxidize than isostructural ones containing the Cp ligand.[25,26,28,46-48] If hydride is taken as −0.3, then the most consistent values for Cp* and Cp for these complexes are −0.17 and 0.08 V, respectively (these are the total contribution of the ligand to the complex; they are not divided by three coordination sites). These values work well for the potential of oxidation of all "half-sandwich" complexes of Fe(II) and Ru(II), but they do not work for the ferrocene and ruthenocene complexes because of the large difference in solvation of the two structural types. Values of E_L for dape and dtfpe can be obtained by plotting electrochemical data for complexes $M(N_2)_2(diphosphine)_2$, M = Mo, W,[49] and $ReCl(N_2)(diphosphine)_2$[31] vs E_L where they are known; such plots yield E_L values for dape and dtfpe of 0.33 and 0.47 V, respectively. Table II shows that the sum of ligand parameters agrees with the observed peak potential E_{pa} for each of these complexes within the errors of the method.

Table V. Predicted $E_{1/2}(ox)$ and pK_a Values[a]

	L′ = H⁻	L′ = H_2	
	$E_{1/2}(ox) = \sum E_L$, V[b]	pK_a(calc)	pK_a(obs)
$[RuCp^*(CO)_2(L')]^+$	1.5	−3	<0
$[RuCp^*(dmpe)(L')]^+$	0.1	12	unknown
$[RuCp(CO)_2(L')]^+$	1.8	−6	unknown
$[RuCp(CO)(PMe_3)(L')]^+$	1.1	1	unknown
$[RuCp(CO)(CNPh)(L')]^+$	1.2	0	unknown
$[RuCp(dmpe)(L')]^+$	0.3	10	10
$[RuH(L')(dppe)_2]^+$	0.8	4	>10
$[Ru(H)_2(L')(PPh_3)_3]$	0.3	10	~16

[a] $E_{1/2}(ox)$ value is for the hydride with L′ = H⁻, which when protonated gives the dihydrogen complex with L′ = H_2. The pK_a of this dihydrogen complex, pK_a(calc), is calculated by use of eq 22. E_L values: Cp^{*-} −0.17, CO 0.99, H⁻ −0.30, dmpe 0.28, Cp^- 0.08, PMe_3 0.33, CNPh 0.41. [b] Versus NHE.

The complex $[Cp^*Ru(H_2)(CO)_2]^+$ has been reported to have a pK_a value of less than zero,[11] but the electrochemical properties of $Cp^*Ru(H)(CO)_2$ are unknown to date. The Lever method predicts $E_{1/2}(ox)$ to be 1.5 V (Table V). Then eq 22 does indeed predict a pK_a of −3 for the dihydrogen complex. Electrochemical potentials can also be predicted from infrared data of carbonyl complexes.[28] The Cotton–Kraihanzel CO force constant for $Cp^*Ru(H)(CO)_2$ is calculated from its ν(CO) frequencies[50] to be 15.5 mdyn Å^{-1}. The predicted $E_{1/2}(ox)$ of 1.3 ± 0.2 V agrees with the value predicted by the Lever method (Table V). Stable dihydrogen complexes $[CpRu(H_2)(L)(CO)]^+$, L = PR_3[7] and CNR,[51] are also known. Their predicted properties are also listed in Table V. In principle, members of this series could be synthesized with dihydrogen ligands with pK_a values ranging from 12, predicted for $[Cp^*Ru(dmpe)(H_2)]^+$, to −6, predicted for $[CpRu(CO)_2(H_2)]^+$ (Table V). Thus it appears that the correct combination of ligands will produce a transition-metal complex that can coordinate dihydrogen and makes it as acidic as sulfuric acid!

The method does not work for polyhydride complexes. According to the Lever method, $RuH_2(dppe)_2$ would have an $E_{1/2}(ox)$ of 0.84 (Table V). The predicted pK_a for $[RuH(H_2)(dppe)_2]^+$ is much too low. In actual fact, the E_{pa} for the dihydride is measured to be 0.6 V vs NHE, thus providing a pK_a of 7, which is still too low. Similarly, the predicted pK_a for $Ru(H)_2(H_2)(PPh_3)_3$ is too low, assuming the predicted $E_{1/2}(ox)$ value is correct. Since this dihydrogen complex is deprotonated by and is in equilibrium with the alkoxide of cyclohexanol,[17] its pK_a must be near to that of cyclohexanol (16).

The pK_a values of such complexes, which are outside of the pK_a range of protonated phosphines (>12), can be reached by use of metal complexes with increasingly electron donating ligands. In a subsequent paper it will be demonstrated that the series of dihydrides $[Ru(H)_2(C_5Me_5)(PR_3)_2]^+$, PR_3 = PPh_3, $PMePh_2$, PMe_2Ph, and PMe_3, extends the range out above pK_a 12 where some of the pK_a values of our diphosphine complexes $[M(H_2)(H)(diphosphine)_2]^+$ are expected.

Conclusions. In the isosteric series of complexes $[CpRuH_2L]^+$, where L is a para-substituted tertiary diphosphine ligand, decreasing the electron density on the metal favors the formation of the η^2-dihydrogen tautomer over that of the dihydride. It also causes an increase in the H–H interaction in the dihydrogen tautomer, as indicated by the increase in ^1J(H,D) and the marked change in chemical shift of the H_2 and in the lability of the dihydrogen ligand (qualitative observation). Decreasing the electron density increases the acidity of the complexes. In fact, the pK_a of the cationic dihydrogen complexes and electrochemical

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peak potentials for oxidation of the corresponding neutral monohydrides are linearly related by eq 22. It is not clear yet why the slope of the pK_a vs E_{pa} plots is −10.7 and not the −16.9 value predicted by theory.

When the contributions to the acidity of the dihydrogen and dihydride forms are factored out, the two forms give approximately the same pK_a vs E_{pa} equations (Figure 4). Thus, the dihydrogen ligand does not appear to have an acid/base chemistry distinct from that of dihydrides in this case. The thermodynamic acidity of the two tautomers just depends on relative amounts of the two forms. When the dihydride form is more abundant, as in the complexes $[CpRuH_2(L)]^+$, L = dppm, dppe, and dape, the dihydrogen form is more acidic, as reported previously.[21] However, for the more electron rich complexes $[CpRuH_2(dmpe)]^+$ and $[Cp^*RuH_2(dppm)]^+$, the dihydride form has a greater thermodynamic acidity. The kinetics of protonation/deprotonation of the dihydrogen and dihydride forms of the complexes remains to be determined so that any differences in the kinetic acidity can be detected.

Equation 22 can be used to predict that cyclopentadienylruthenium(II) dihydrogen complexes can have a wide range of pK_a values—from −6 to 12. This explains how dihydrogen gas (with $pK_a \sim 35$[52]) can be converted into a strong acid when it is coordinated to transition-metal ion. New chemical reactions of acidic dihydrogen complexes will be reported shortly.

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EXAFS Studies of Ni^{II}, Ni^{I}, and Ni^{I}–CO Tetraazamacrocycles and the Crystal Structure of (5,7,7,12,14,14-Hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene)nickel(I) Perchlorate

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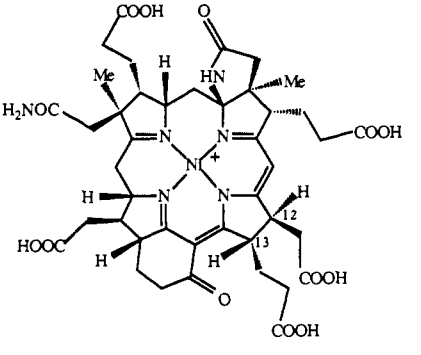
Abstract: Nickel(II) complexes of tetraazamacrocycles undergo one-electron reduction to produce either a nickel(I) complex or a nickel(II) anion radical. Both reduced species react with CO. The nature of the parent Ni(II) complexes, the reduced species, and the Ni^{I}–CO complexes were studied in CH_3CN by means of EXAFS and UV–vis spectroscopy to characterize structural differences as a function of oxidation state and axial ligation of the metal in solution. The EXAFS results reveal that the reduction of Ni(II) to Ni(I) results not only in an expansion of the macrocycle core (0.1 Å change in Ni–N bond distance) but also a distortion. On the other hand, the Ni(II) to Ni(II) anion radical reduction leaves the geometry around the nickel atom unchanged. The anion radical of Ni(II) tetraene$^+$ (NiL_3^+, L_3 = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene) dimerizes in solution forming diamagnetic adducts. The monomer–dimer equilibrium constant was determined to be $K_1 = (5.5 \pm 1.0) \times 10^4$ M^{-1} from the electronic spectra. EXAFS data on CO adducts of $Ni^{I}L_1$, $-L_2$, and $-L_3$ (L_1 = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, L_2 = 5,7,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,14-diene) clearly indicate that these are five-coordinate complexes with a short Ni–C bond. Both $Ni-N_{imine}$ and $Ni-N_{amine}$ distances in the CO adducts of the Ni(I) complexes increase quite dramatically compared to those in the parent Ni(II) and Ni(I) complexes. The structure of the title nickel(I) complex has been determined from single-crystal X-ray diffraction data collected by using Mo Kα radiation. Crystallographic data are as follows: space group $P2/n$ with $a = 15.717$ (6) Å, $b = 8.196$ (2) Å, $c = 16.049$ (6) Å, $\beta = 100.67$ (3)°, $V = 2031$ (2) Å^3, $Z = 4$. The two square-planar nickel atoms in the asymmetric unit are situated on crystallographic inversion centers. The $Ni-N_{imine}$ distances are 1.988 (7) and 1.979 (7) Å and $Ni-N_{amine}$ distances are 2.063 (6) and 2.068 (6) Å, which are in good agreement with the EXAFS data.

Introduction

Factor 430 (**1**) is a nickel(II) hydrocorphin and the prosthetic group of methyl coenzyme M reductase. It catalyzes the reductive cleavage of *S*-methyl coenzyme M to coenzyme M and methane in the final step of the reduction of carbon dioxide to methane in methanogenic bacteria.[2] The structure of the pentamethyl ester derivative (F430M) has been determined by a combination of biosynthetic and NMR spectroscopic methods.[3]



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Although the detailed function of F430 is not known, an ESR signal detected[4] in suspensions of whole cells of *Methanobacterium thermoautotrophicum* was attributed to the active site and in-

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