Synthesis and the Kinetic and Thermodynamic Acidity of η^2-Dihydrogen and Dihydride Complexes of the Type $[Ru(C_5Me_5)H_2L_2]^+$. X-ray Crystal Structure Determination of the Complex $[Ru(C_5Me_5)(\eta^2\text{-}H_2)(PPh_2CH_2PPh_2)]BF_4$

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A series of $Cp^*RuH(L_2)$ complexes were readily prepared by the reaction of NaOMe (excess) with $Cp^*RuCl(L_2)$ (L_2 = dppm, dppp, $(PPh_3)_2$, $(PMePh_2)_2$, $(PMe_2Ph)_2$, $(PMe_3)_2$). The chloro starting materials were prepared in situ by the reactions of Cp^*RuCl_2 with L_2 in the presence of Zn. Protonation of complexes $Cp^*RuH(L_2)$ gives dihydride complexes $[Cp^*Ru(H)_2(L_2)]^+$ or a mixture of dihydride complexes $[Cp^*Ru(H)_2(L_2)]^+$ and η^2-dihydrogen complexes $[Cp^*Ru(\eta^2\text{-}H_2)(L_2)]^+$, depending on the phosphines around the ruthenium center. Protonation of $Cp^*RuH(dppp)$ or $CpRuH(L_2)$ at −60 °C gives initially as the exclusive product the dihydrogen complexes $[Cp^*Ru(\eta^2\text{-}H_2)(dppp)]^+$ or $[CpRu(\eta^2\text{-}H_2)(L_2)]^+$ when $L_2 = R_2PCH_2CH_2PR_2$ and R = C_6H_5, *p*-C_6H_4OMe, *p*-$C_6H_4CF_3$. When the reactant is $Cp^*RuH(dppm)$, then both $[Cp^*Ru(H)_2(dppm)]^+$ and $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]^+$ are produced. Concurrent reactions at −60 °C involving protonation at the metal center and at the hydride might occur in this case. The two tautomers of $[Cp^*RuH_2(dppm)]^+$ start to interconvert at temperatures above −40 °C. Protonation of $Cp^*RuH(PMePh_2)_2$ at −60 °C gives the dihydride $[Cp^*Ru(H)_2(PMePh_2)_2]^+$ as the only product detectable by NMR spectroscopy. The dihydrogen complexes are thought to have slowly rotating dihydrogen ligands with an H–H distance of 1.1 Å on the basis of T_1 and $^1J(H,D)$ measurements. Acid–base equilibria for the complexes $[Cp^*RuH_2L_2]^+$ indicate that they have a pK_a range from 8.8 to 16.3. An increase in the basicity of phosphine, L, results in a large decrease in the acidity of the complexes $[CpRu(H)_2L_2]^+$ and $[Cp^*Ru(H)_2L_2]^+$. The Ru–H bond energy varies by 5 kcal mol^{-1}, depending on L, as indicated by a thermodynamic cycle utilizing electrochemical potentials of the monohydride complexes. A single-crystal X-ray diffraction study of $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$ shows that it crystallizes in the space group $P2_1$ with cell parameters a = 10.853 (2) Å, b = 15.125 (6) Å, c = 10.992 (2) Å, β = 113.48 (2)°, Z = 2, V = 1655 (2) Å^3, R = 0.046, and R_w = 0.049.

Introduction

A topic of current interest is the comparison of the acidic properties of η^2-dihydrogen complexes and hydride complexes.[1-4] Equilibrium constants for reactions (eq 1) be-

$$MHL_n + HPR_3^+ \rightleftarrows [MH_2L_n]^+ + PR_3 \qquad (1)$$

tween hydride complexes and protonated bulky phosphines of known pK_a are readily measured by NMR methods, and these provide the pK_a values of dihydride or dihydrogen complexes. However, this approach cannot be used to obtain the pK_a values of hydride complexes with pK_a values significantly larger than 11.4, the pK_a value of the least acidic protonated phosphine, $HP(t\text{-}Bu)_3^+$. In addition, side reactions sometimes occur such as substitution of ligands on the hydride complex by the phosphine which is the conjugate base in eq 1.

Hydride complexes with known pK_a values can also be used as reference standards to determine the pK_a values of other hydride complexes (eq 2). By using protonated

$$M'HL'_n + [MH_2L_n]^+ \rightleftarrows [M'H_2L'_n]^+ + MHL_n \qquad (2)$$

phosphines or acidic hydride complexes with known pK_a values as standards, the pK_a values (from 4.6 to 12.1) of a series of ruthenium dihydrogen/dihydride complexes were determined.[1,2] In fact it is advantageous to use acidic hydride complexes as standards compared with protonated bulky phosphines. Side reactions are less common when substitution-inert hydride complexes are used. More importantly, hydride complexes provide a much larger range of pK_a values than protonated phosphines. Norton's research group[3] and our own[1,2] have demonstrated that hydride complexes are available with a wide range of pK_a values because hydride acidity is dramatically influenced by the coligands. Electron-donating coligands decrease the acidity of the metal hydride complex.

There is evidence that η^2-dihydrogen has a greater kinetic acidity than a tautomeric dihydride form. The dihydrogen tautomer $[CpRu(\eta^2\text{-}H_2)(dmpe)]^+$ (dmpe = bis(dimethylphosphino)ethane) is deprotonated more rapidly than the dihydride tautomer $[CpRu(H)_2(dmpe)]^+$, and the pK_a of the dihydrogen tautomer is 17.6 on the CH_3CN acidity scale.[4] For every one of the complexes of the type $CpRuH(L)(L')$ examined as well as for the complexes Cp^*RuHL_2 (L_2 = dmdppe ($PPh_2CH_2CH_2PMe_2$), $(PPh_3)_2$, $(CO)(PCy_3)$), the kinetic product resulting from their protonation is the dihydrogen complex.[4] The η^2-dihydrogen ligand is known to be deprotonated in preference to the terminal hydride in the complex $[IrH(\eta^2\text{-}H_2)(bq)(L)_2]^+$ (bq = 7,8-benzoquinolinate; L = PPh_3, PCy_3), by deuterium labeling studies.[5] Selective removal of a dihydrogen proton is suspected in the deprotonation of $[RuH(\eta^2\text{-}H_2)(dppe)_2]^+$ at low temperature.[6]

The wide range of thermodynamic acidities of η^2-dihydrogen is becoming apparent. The complexes $[Cp^*Re(CO)(NO)(\eta^2\text{-}H_2)]^+$ and $[Cp^*Ru(CO)_2(\eta^2\text{-}H_2)]^+$ are

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remarkably acidic with pK_a values (aqueous scale) less than zero.[7] Some complexes $[CpRu(L_2)(\eta^2\text{-}H_2)]^+$, where L_2 is a bidentate phosphine ligand, have pK_a values ranging from 4 to 9, depending on the ligand,[1] whereas the series $[M(H)(\eta^2\text{-}H_2)(L_2)_2]^+$ (M = Fe, Ru, Os; L_2 = dppe ($PPh_2CH_2CH_2PPh_2$), depe ($((CH_3CH_2)_2PCH_2CH_2P(CH_2CH_3)_2$), dtfpe ($(p\text{-}CF_3C_6H_4)_2PCH_2CH_2P(p\text{-}CF_3C_6H_4)_2$), dape ($(p\text{-}MeOC_6H_4)_2PCH_2CH_2P(p\text{-}MeOC_6H_4)_2$)) has values ranging from 8 to greater than 16.[2,6,8] The pK_a value of $[FeH(H_2)(dmpe)_2]^+$ is thought to be near 15.9.[9]

The present study had two goals: first, to understand the effects of coligands on the properties of η^2-dihydrogen or dihydride complexes, and second, to synthesize hydride complexes with pK_a values comparable to those of the η^2-dihydrogen complexes of the type $[MH(\eta^2\text{-}H_2)(L_2)_2]^+$ (M = Fe, Ru, Os; L_2 = dppe, dape, depe).[6,10,11] To this end we have synthesized and characterized some electron-rich Cp*Ru hydride complexes Cp*RuH(L_2) and $[Cp^*RuH_2(L_2)]^+$, where L_2 is a bidentate phosphine or two monodentate phosphines. The pK_a values of the complexes $[Cp^*RuH_2(L_2)]^+$ in THF are also reported here. In a subsequent paper, we will show how they can be used in reactions such as that of eq 2 to estimate the pK_a values of η^2-dihydrogen complexes of the type $[MH(\eta^2\text{-}H_2)(L_2)_2]^+$.[11]

Experimental Section

Unless otherwise noted, all manipulations were done under an Ar or H_2 atmosphere by use of Schlenk techniques. Solids were handled in a Vacuum Atmospheres 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. unless otherwise stated. Phosphine ligands were purchased from Strem Chemical Co. or Digital Specialty Chemicals Ltd. Cp^*RuCl_2,[12] Cp*RuH(dppm),[1] $[Cp^*RuH_2(dppm)]BF_4$,[1] Cp*RuH($PMePh_2$)$_2$,[1] $[Cp^*RuH_2(PMePh_2)_2]BF_4$,[1] and $[HP(t\text{-}Bu)_3]^+$[1] were prepared as described previously.

NMR spectra were obtained on a Varian XL 400 spectrometer, operating at 400.00 MHz for ^1H and 161.98 MHz for ^{31}P, or on a Varian XL 200 instrument, operating at 200.00 MHz for ^1H and 80.98 MHz for ^{31}P. Chemical shifts refer to room-temperature conditions unless specified otherwise. All ^{31}P NMR spectra 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. T_1 measurements were made using the inversion recovery method.

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, a W secondary electrode, and a Ag-wire reference electrode in a Luggin-Haber capillary probe. The cyclic voltammograms were measured on solutions of the complexes in THF containing 0.2 M $n\text{-}Bu_4NPF_6$ as supporting electrolyte. Reported potentials are referenced to ferrocene, which was added to these solutions.

Cp*RuH(PPh_3)$_2$. A mixture of 0.40 g of Cp^*RuCl_2 (1.30 mmol), 0.80 g of PPh_3 (3.1 mmol), and 0.40 g of Zn (6.1 mmol) in 20 mL of benzene was stirred at room temperature overnight to give a dark orange solution. To this solution was added 20 mL of MeOH and 0.30 g of NaOMe (5.6 mmol). The resulting mixture was refluxed for 5 h to give a yellow solution. The solvents were then completely evaporated under vacuum, and the residue was extracted with benzene. The benzene 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 0.55 g, 56%. This compound has been reported, but without preparative details.[13] $^{31}P\{^1H\}$ NMR (C_6D_6): δ 70.3 (s). ^1H NMR (C_6D_6): δ −11.90 (t, J(PH) = 33.6 Hz, Ru–H), 1.46 (s, Cp*), 6.9–7.7 (m, Ph).

$[Cp^*RuH_2(PPh_3)_2]BF_4$. A stirred solution of 0.20 g of Cp*RuH(PPh_3)$_2$ (0.26 mmol) in 30 mL of Et_2O was titrated with $HBF_4\cdot Et_2O$ until the precipitation of a white solid was complete. After the reaction mixture was stirred for an additional 30 min, the white solid was collected by filtration, washed with Et_2O, and dried under vacuum: yield 0.18 g, 82%. A slightly different preparation of this compound has been recently reported.[4] $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 63.6 (s). ^1H NMR (CD_2Cl_2): δ −7.34 (t, J(PH) = 26.5 Hz, Ru–H), 1.33 (s, Cp*), 7.3–7.5 (m, Ph).

$[Cp^*RuH_2(PMe_2Ph)_2]BPh_4$. A mixture of Cp^*RuCl_2 (0.30 g, 0.98 mmol), Zn (0.30 g, 4.6 mmol), and PMe_2Ph (2 mL of a 1.0 M solution in benzene, 2.0 mmol) in 20 mL of benzene was stirred overnight to give a deep orange solution. To the reaction mixture was then added 0.20 g of NaOMe (3.7 mmol) and 20 mL of EtOH. The resulting mixture was refluxed for 5 h. The solvents were removed completely. The residue was then extracted with benzene. The benzene was removed again to give an oily orange-yellow residue. The predominant species in this oil, which is detectable by ^{31}P and ^1H NMR spectroscopy, is Cp*RuH(PMe_2Ph)$_2$. The residue was redissolved in ca. 20 mL of Et_2O. Titration of the ether solution with $HBF_4\cdot Et_2O$ gave a white precipitate, which turned into a sticky mass when excess $HBF_4\cdot Et_2O$ was added. The ether solvent was removed completely under vacuum. The residue was redissolved in ca. 30 mL of MeOH. To the MeOH was added 0.40 g of $NaBPh_4$ (1.2 mmol) to give a white precipitate. The precipitate was collected by filtration, washed with MeOH, and dried under vacuum: yield 0.52 g, 64%. $^{31}P\{^1H\}$ NMR (CH_2Cl_2/C_6D_6): δ 25.4. ^1H NMR (acetone-d_6): δ −9.29 (t, J(PH) = 30.1 Hz, Ru–H), 1.62 (s, Cp*), 1.83 (m, P–Me), 6.7–7.8 (m, Ph). Anal. Calcd for $C_{50}H_{59}BP_2Ru$: C, 72.02; H, 7.13. Found: C, 71.23; H, 7.09. We were not successful at getting a good elemental analysis for this complex, even though the spectra indicated complete purity of the product.

Cp*RuH(PMe_2Ph)$_2$. A mixture of 0.30 g of $[Cp^*RuH_2(PMe_2Ph)_2]BPh_4$ (0.36 mmol) and 0.10 g of NaO(t-Bu) (1.04 mmol) in 20 mL of THF was stirred overnight at room temperature. The solvent was removed completely. The residue was extracted with 15 mL of benzene. The benzene was removed again to give a yellow solid, which was dried under vacuum: yield 0.09 g, 54%. $^{31}P\{^1H\}$ NMR (THF/C_6D_6): δ 26.4. ^1H NMR (C_6D_6): δ −13.21 (t, J(PH) = 36.8 Hz, Ru–H), 1.31 (m, P–Me), 1.41 (m, P–Me), 1.76 (s, Cp*), 7.13 (m, 8 H, m- + p-Ph), 7.70 (m, 4 H, o-Ph). This very soluble complex could not be recrystallized, but the spectra suggest that it is pure.

$[Cp^*RuH_2(PMe_3)_2]BPh_4$. A mixture of Cp^*RuCl_2 (0.30 g, 0.98 mmol), Zn (0.30 g, 4.6 mmol), and PMe_3 (2.0 mL of a 1.0 M solution in THF, 2.0 mmol) in 20 mL of benzene was stirred at room temperature overnight. The solvent was removed completely, and to the residue was added 0.10 g of NaOMe (1.9 mmol), 0.10 g of $NaBH_4$ (2.9 mmol), and 30 mL of THF. The resulting mixture was refluxed overnight to give a yellow solution. The THF was removed completely, and the residue was extracted with Et_2O. To the Et_2O solution was then added $HBF_4\cdot Et_2O$ to give some oily material. The Et_2O was removed completely, and the residue was redissolved in MeOH. Addition of 0.30 g of $NaBPh_4$ (8.7 mmol) produced a white solid, which was collected by filtration, washed with MeOH, and dried under vacuum: yield 0.35 g, 50%. Crystalline solid can be obtained by slow diffusion of MeOH into a saturated CH_2Cl_2 solution. $^{31}P\{^1H\}$ NMR (ace-

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tone-d_6): δ 14.4 (s). ^{1}H NMR (acetone-d_6): δ −10.03 (t, J(PH) = 32.4 Hz, Ru–H), 1.54 (m, P–Me), 1.90 (s, Cp*), 6.6–7.2 (m, Ph). Anal. Calcd for $C_{40}H_{55}BP_2Ru$·MeOH: C, 66.39; H, 8.02. Found: C, 66.60; H, 7.71.

Cp*RuH(dppp). A mixture of 0.60 g of Cp*$RuCl_2$ (2 mmol), 0.30 g of Zn (4.6 mmol), and 0.88 g of dppp (2.1 mmol) in 20 mL of benzene and 20 mL of MeOH was stirred at room temperature overnight to give an orange solution. To this solution was then added 0.30 g of NaOMe (5.6 mmol). The resulting mixture was refluxed for 5 h to give a yellow solution. The solvents were removed completely, and the residue was extracted with benzene. The benzene was removed again. Addition of MeOH produced a yellow powder, which was collected by filtration, washed with MeOH, and dried under vacuum: yield 0.80 g, 61%. Crystalline solid could be obtained by slow diffusion of MeOH into a saturated benzene solution. ^{31}P{^{1}H} NMR (C_6D_6): δ 53.6 (s). ^{1}H NMR (C_6D_6) δ −13.00 (t, J(PH) = 35.1 Hz, Ru–H), 1.60 (s, Cp*), 1.90 (m, CH_2), 2.5 (m, CH_2), 7.0–7.7 (m, Ph). Anal. Calcd for $C_{37}H_{42}P_2Ru$·MeOH: C, 67.00; H, 6.80. Found: C, 67.04; H, 6.42.

[Cp*RuH_2(dppp)]BF_4. A solution of Cp*RuH(dppp) (0.30 g, 0.46 mmol) in 30 mL of Et_2O was titrated with HBF_4·Et_2O to give a white solid. The solid was then collected by filtration, washed with Et_2O, and dried under vacuum to give a light pink solid: yield 0.31 g, 91%. A crystalline solid was obtained by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution. ^{31}P{^{1}H} NMR (THF/C_6D_6): δ 28.4 (s, [Cp*Ru(η^2-H_2)(dppp)]$^+$), 56.2 (s, [Cp*RuH_2(dppp)]$^+$). ^{1}H NMR (CD_2Cl_2): δ −8.67 (t, J(PH) = 29.0 Hz, RuH_2), −8.80 (br, Ru(η^2-H_2)), 1.36 (s, Cp*RuH_2), 1.48 (s, Cp*Ru(η^2-H_2)), 2.0–2.7 (m, CH_2), 7.2–7.7 (m, Ph). Anal. Calcd for $C_{37}H_{43}BF_4P_2Ru$: C, 60.25; H, 5.88. Found: C, 59.89; H, 6.09.

[Cp*RuHD(dppp)]BF_4. The compound was prepared similarly except that DBF_4 was used instead of HBF_4·Et_2O. The DBF_4 was prepared in situ by mixing HBF_4·Et_2O and D_2O in a ratio of 1:3 (v/v). ^{1}H NMR (CD_2Cl_2): δ −8.86 (t, ^1J(HD) = 23.3 Hz, Ru(HD)), −8.68 (t, J(PH) = 29.2 Hz, Ru(H)(D)).

Protonation Reactions at Low Temperature. A 5-mm NMR tube was charged with ca. 10 mg of a hydride complex and ca. 0.8 mL of an appropriate deuterated solvent (CD_2Cl_2 for CpRuH(L_2), L_2 = dtfpe, dppe, dape; acetone-d_6 for Cp*RuH(L_2), L_2 = dppm, dppp, $(PMePh_2)_2$). The sample was then cooled with N_2(l). A small drop of HBF_4·Et_2O was added to the wall at the top of the tube, which was then capped. The ^{1}H NMR probe was cooled to −60 °C. The NMR tube was removed from the N_2(l), shaken so that the acid could mix with the solvent, and then inserted into the spinner and lowered into the probe. The shims were adjusted, and then ^{1}H NMR spectra were collected.

Deprotonation Reactions at Low Temperature. A slight excess of alkoxide (NaOEt or NaOMe) and the cationic complex ([CpRuH_2(L_2)]BF_4, L_2 = dtfpe, dppe, dape) were loaded into a 5-mm NMR tube. The tube was then cooled with N_2(l), and solvent was added (CD_2Cl_2 when L_2 = dtfpe, dppe; acetone-d_6 when L_2 = dape). The NMR tube was removed from the N_2(l), shaken to mix the reactants, and then inserted into the spinner and lowered into the probe, which was cooled to −60 °C. The shims were adjusted, and then ^{1}H NMR spectra were collected.

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 THF or acetone was added. After a suitable period, an NMR spectrum was recorded. The equilibrium is confirmed by monitoring the reaction with NMR spectroscopy or by approaching the equilibrium from different sides of the reaction. By measuring the intensity of the hydride resonances (in ^{1}H NMR experiments) or the ^{31}P resonances, one can calculate the relative concentrations of the hydride complexes or free and protonated P(t-Bu)$_3$ in solution and therefore the equilibrium constants. The ^{31}P NMR chemical shifts for the protonated and free phosphine have been reported previously.[1]

Crystallographic Analysis of [Cp*Ru(η^2-H_2)(dppm)]BF_4. Suitable yellow crystals were obtained by slow diffusion of Et_2O into a saturated CH_2Cl_2 solution.

Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer at room temperature, using graphite-monochromated Mo K$\bar{\alpha}$ radiation (λ = 0.710 73 Å). The $\omega/2\theta$ scan technique was applied with scan speeds varying from 1.3 to 5.5°/min. The intensities of three standard reflections measured every 2 h showed no decay. An empirical absorption correction was applied[14] (minimum and maximum corrections 0.626 and 1.326).

Table I. Crystallographic Details for [Cp*RuH_2(dppm)]BF_4

empirical formula	$C_{35}H_{39}BF_4P_2Ru$
M_r	709.6
cryst size, mm	0.23 × 0.23 × 0.20
cryst class	monoclinic
space group	$P2_1$
a, Å	10.853 (2)
b, Å	15.125 (6)
c, Å	10.992 (2)
β, deg	113.48 (2)
V, Å^3	1655 (2)
Z	2
D_{calcd}, g cm^{-3}	1.42
μ(Mo Kα), cm^{-1}	6.03
F(000)	728
ω scan width, deg	0.8 + 0.35 tan θ
range θ collected (hkl), deg	1–27 (h, −1 to 13; k, 0 to 19, l, −14 to 14)
total no. of rflns	4307
no. of indep rflns	3490
R_{merge}	0.035
no. of obsd data [$I > 3\sigma(I)$]	2723
weighting g	0.005
R	0.046
R_w	0.049
goodness of fit	0.81
largest Δ/σ	0.024
no. of params refined	415
max density in ΔF map, e Å^{-3}	0.92

The Ru atom was located by the Patterson method, and the positions of other non-hydrogen atoms were determined from Fourier and difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically by full-matrix least squares to minimize $\sum w(F_o - F_c)^2$, where $w^{-1} = \sigma^2(F) + gF^2$. The BF_4^- anion was disordered over two orientations of equal occupancy having B(1) and F(1) in common but having the other F atoms related to each other by 60° rotations about the B(1)–F(1) bond. Hydrogen atoms were positioned on geometric grounds (C–H = 0.95 Å), and an overall hydrogen atom thermal parameter for phenyl and methylene hydrogens was refined to a value of 0.079 (1) Å^2; the methyl hydrogen thermal parameters had fixed values of 0.12 Å^2. Parallel refinements which were carried out (using 3117 observed reflections, including Friedel pairs) to determine the enantiomorph gave R_w = 0.0504 and 0.0511. Final cycles of refinement were performed with averaged data and used the enantiomorph with the lowest R_w. Although the top five peaks in the final difference Fourier (0.92–0.47 e Å^{-3}) were located in the vicinity of the Ru atom, the dihydrogen ligand could not be located and was not included in the calculations. Crystal data, data collection, and least-squares parameters are listed in Table I. All calculations were performed using SDP,[15] SHELX76,[16] and SHELXS86[17] on a PDP11/23 and an Apollo computer. Final atomic coordinates and selected bond lengths and angles are presented in Tables II and III, respectively.

Results and Discussion

Preparation and Characterization of the New Ruthenium Hydride Complexes. We required a general synthetic route for Cp*Ru complexes of the type Cp*RuH(L_2) or [Cp*RuH_2(L_2)]$^+$, where L is a phosphine. When we started the work, Cp*RuH(PMe_3)$_2$ was known. It had been prepared by the reactions of Cp*RuCl(PMe_3)$_2$

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Table II. Positional and Thermal Parameters for [Cp*Ru(η^2-H_2)(dppm)]BF_4

atom	x	y	z	U_{eq}, Å^2
Ru	−0.08478 (5)	0.0	0.13227 (5)	0.04266 (23)
C(1)	−0.1382 (7)	−0.1173 (5)	0.0016 (5)	0.0792 (10)
C(2)	−0.2605 (6)	−0.0816 (5)	0.0055 (5)	0.0594 (10)
C(3)	−0.2516 (5)	−0.0851 (5)	0.1340 (6)	0.0664 (9)
C(4)	−0.1222 (7)	−0.1270 (5)	0.2136 (5)	0.0672 (10)
C(5)	−0.0594 (6)	−0.1457 (5)	0.1301 (7)	0.0906 (10)
C(6)	−0.12466 (9)	−0.13299 (6)	−0.12673 (15)	0.2232 (10)
C(7)	−0.37835 (14)	−0.05187 (6)	−0.11447 (14)	0.0901 (10)
C(8)	−0.35915 (14)	−0.06467 (6)	0.18140 (10)	0.1351 (10)
C(9)	−0.08335 (9)	−0.15112 (6)	0.35570 (16)	0.2061 (10)
C(10)	0.06293 (15)	−0.20121 (8)	0.16004 (9)	0.1615 (10)
C(11)	0.1045 (5)	0.1295 (5)	0.3457 (6)	0.0468 (9)
P(1)	−0.07812 (17)	0.11260 (15)	0.27517 (17)	0.0404 (7)
C(11P)	−0.1534 (6)	0.2186 (5)	0.2083 (6)	0.0469 (9)
C(12)	−0.1131 (7)	0.2942 (6)	0.2814 (7)	0.0672 (10)
C(13)	−0.1736 (7)	0.3756 (6)	0.2331 (7)	0.0803 (10)
C(14)	−0.2732 (7)	0.3809 (6)	0.1129 (7)	0.0753 (10)
C(15)	−0.3156 (7)	0.3068 (6)	0.0385 (7)	0.0755 (10)
C(16)	−0.2581 (6)	0.2261 (6)	0.0842 (7)	0.0540 (9)
C(21)	−0.1298 (6)	0.1016 (5)	0.4143 (6)	0.0533 (9)
C(22)	−0.2610 (7)	0.1177 (7)	0.3904 (7)	0.0874 (10)
C(23)	−0.3075 (7)	0.1094 (7)	0.4907 (7)	0.0954 (10)
C(24)	−0.2192 (7)	0.0822 (7)	0.6144 (7)	0.1032 (10)
C(25)	−0.0916 (7)	0.0670 (8)	0.6375 (7)	0.1004 (10)
C(26)	−0.0441 (7)	0.0754 (6)	0.5366 (7)	0.0825 (10)
P(2)	0.13463 (17)	0.04490 (15)	0.24099 (17)	0.0388 (6)
C(31)	0.2231 (6)	0.1016 (5)	0.1540 (6)	0.0430 (9)
C(32)	0.3307 (6)	0.1565 (6)	0.2240 (6)	0.0554 (9)
C(33)	0.3973 (6)	0.1992 (6)	0.1583 (7)	0.0654 (9)
C(34)	0.3594 (7)	0.1876 (6)	0.0237 (7)	0.0759 (9)
C(35)	0.2548 (7)	0.1325 (6)	−0.0466 (7)	0.0809 (10)
C(36)	0.1866 (6)	0.0891 (6)	0.0183 (6)	0.0573 (9)
C(1)	0.2613 (6)	−0.0301 (5)	0.3453 (5)	0.0450 (9)
C(42)	0.2642 (6)	−0.0563 (6)	0.4690 (6)	0.0654 (9)
C(43)	0.3558 (7)	−0.1169 (7)	0.5436 (7)	0.0813 (10)
C(44)	0.4443 (7)	−0.1549 (6)	0.5002 (7)	0.0845 (10)
C(45)	0.4416 (7)	−0.1308 (7)	0.3777 (8)	0.1100 (10)
C(46)	0.3529 (7)	−0.0676 (6)	0.3057 (7)	0.0818 (9)
B(1)	−0.4018 (7)	−0.3448 (7)	0.3167 (7)	0.0673 (10)
F(1)	−0.3128 (7)	−0.4047 (6)	0.3124 (6)	0.1491 (9)
F(2)	−0.5200 (9)	−0.3496 (8)	0.2185 (8)	0.1141 (10)
F(3)	−0.4169 (8)	−0.3482 (8)	0.4276 (7)	0.1414 (10)
F(4)	−0.3520 (9)	−0.2708 (8)	0.2898 (9)	0.2634 (10)
F(2*)	−0.4580 (9)	−0.2952 (8)	0.2189 (8)	0.1485 (10)
F(3*)	−0.3372 (9)	−0.2873 (9)	0.4199 (9)	0.2081 (10)
F(4*)	−0.4909 (9)	−0.3857 (9)	0.3438 (9)	0.3282 (10)

Table III. Selected Bond Distances (Å) and Bond Angles (deg) in [Cp*Ru(η^2-H_2)(dppm)]BF_4

Bond Lengths (Å)

Ru-C(1)	2.210 (7)	Ru-C(2)	2.232 (6)	Ru-C(3)	2.227 (7)
Ru-C(4)	2.223 (7)	Ru-C(5)	2.222 (7)	Ru-P(1)	2.298 (2)
Ru-P(2)	2.301 (2)	C(1)-C(2)	1.449 (10)	C(1)-C(5)	1.396 (9)
C(2)-C(3)	1.378 (8)	C(3)-C(4)	1.470 (9)	C(4)-C(5)	1.373 (10)

Bond Angles (deg)

P(1)-Ru-P(2)	71.46 (7)	P(1)-C(11)-P(2)	94.0 (3)
Ru-P(1)-C(11)	97.28 (24)	Ru-P(2)-C(11)	97.20 (22)
P(1)-Ru-C(1)	165.41 (20)	P(1)-Ru-C(2)	128.51 (18)
P(1)-Ru-C(3)	103.10 (18)	P(1)-Ru-C(4)	109.05 (17)
P(1)-Ru-C(5)	140.53 (20)	P(2)-Ru-C(1)	121.60 (20)
P(2)-Ru-C(2)	159.63 (8)	P(2)-Ru-C(3)	147.44 (17)
P(2)-Ru-C(4)	111.31 (17)	P(2)-Ru-C(5)	101.04 (19)
C(1)-C(2)-C(3)	109.0 (5)	C(2)-C(3)-C(4)	106.7 (5)
C(3)-C(4)-C(5)	107.6 (5)	C(4)-C(5)-C(11)	110.2 (6)
C(5)-C(1)-C(2)	106.5 (5)		

with RMgX (R = *t*-Bu, *i*-Pr).[12] The preparations of Cp*RuH(L_2) and [Cp*$RuH_2(L_2)$]$^+$ (L_2 = $(PPh_3)_2$, $(CH_3)_2PCH_2CH_2PPh_2$, (CO)(PCy_3)) were reported by Chinn and Heinekey during the course of this work.[4] The procedures we employed to synthesize the Cp*Ru hydride complexes are shown in the sequence

$$Cp^*RuCl_2 + Zn + 2L \rightarrow Cp^*RuCl(L_2) \quad (3)$$

$$Cp^*RuCl(L_2) + NaOMe \rightarrow Cp^*RuH(L_2) \quad (4)$$

$$Cp^*RuH(L_2) + HBF_4 \rightarrow [Cp^*RuH_2(L_2)]BF_4 \quad (5)$$

Table IV. Selected NMR Data for the Cp*Ru Hydride Complexes[a]

complex	^{1}H NMR δ(Ru-H)	^{1}H NMR J(PH), Hz	^{1}H NMR δ(Cp*)	^{31}P NMR δ(P)
Cp*RuH(dppm)	−10.63	32.0	2.06	17.5[d]
Cp*RuH(dppp)	−13.00	35.1	1.60	53.6
Cp*RuH$(PPh_3)_2$	−11.90	33.6	1.46	70.3
Cp*RuH$(PMePh_2)_2$	−12.47	35.3	1.83	46.3
Cp*RuH$(PMe_2Ph)_2$	−13.21	36.8	1.76	26.4
[Cp*Ru$(H)_2$(dppm)]BF_4	−6.09[b]	28.8	1.97	4.9[d]
[Cp*Ru(η^2-H_2)(dppm)]BF_4	−6.80[b]		1.70	23.4[d]
[Cp*Ru$(H)_2$(dppp)]BF_4	−8.67[b]	29.0	1.36	54.2[d]
[Cp*Ru(η^2-H_2)(dppp)]BF_4	−8.80[b]		1.48	38.4[d]
[Cp*Ru$(H)_2(PPh_3)_2$]BF_4	−7.34[b]	26.5	1.33	63.6[b]
[Cp*Ru$(H)_2(PMePh_2)_2$]BF_4	−8.13[b]	28.2	1.53	41.5[c]
[Cp*Ru$(H)_2(PMe_2Ph)_2$]BPh_4	−9.29[c]	30.1	1.62	25.4[b]
[Cp*Ru$(H)_2(PMe_3)_2$]BPh_4	−10.03[b]	32.4	1.90	14.4[c]

[a] Solvent is benzene-d_6 unless otherwise stated. [b] In dichloromethane-d_2. [c] In acetone-d_6. [d] In THF.

Treatment of Cp*$RuCl_2$ with ca. 1 equiv of dppm or dppp or 2 equiv of monophosphines such as PPh_3, $PMePh_2$, PMe_2Ph, and PMe_3 in benzene in the presence of Zn produced an orange to dark orange solution. The dark orange solution presumably contains the Ru(II) complexes Cp*RuCl(L_2). The complexes Cp*RuCl(L_2) (L_2 = $(PMe_3)_2$,[12] $(PPh_3)_2$,[4] dppe[18]) and Cp*RuCl(L)[19] (L = PCy_3, P(*i*-Pr)$_3$) have been prepared by the reactions of Cp*$RuCl_2$ with an excess of the appropriate phosphine in EtOH. The Ru(II) complex Cp*RuCl(P(*t*-Bu)$_3$) is also obtained in a single step involving the reduction of a mixture of Cp*$RuCl_2$ and P(*t*-Bu)$_3$ with Zn.[19]

Monohydride Complexes. The hydride complexes Cp*RuH(L_2) (L_2 = dppm, dppp, $(PPh_3)_2$, $(PMePh_2)_2$, $(PMe_2Ph)_2$) were easily prepared by refluxing a mixture of NaOMe (excess) and Cp*RuCl(L_2) in a mixed solvent of MeOH/benzene (ca. 1:1 in volume). Similar procedures have been employed previously in the preparation of CpRuH(L_2) (e.g. L_2 = dppe, dppm, $(PPh_3)_2$)[20] and Cp*RuH(L_2) (L_2 = $(PPh_3)_2$, dmdppe).[4] The hydride complexes Cp*RuH(L_2) (L_2 = dppm, dppp, $(PPh_3)_2$, $(PMePh_2)_2$) could be readily isolated as yellow solids upon precipitation by addition of MeOH. However, it is more difficult to crystallize Cp*RuH$(PMe_2Ph)_2$ owing to its high solubility in common organic solvents. The dihydride complex [Cp*$RuH_2(PMe_2Ph)_2$]BPh_4 can be easily purified and isolated (see below). Therefore, the pure complex Cp*RuH$(PMe_2Ph)_2$ was obtained by deprotonating the dihydride with NaO(*t*-Bu) and then separating the neutral complex from the salt by extraction into benzene. The previously known complex Cp*RuH$(PMe_3)_2$ could be synthesized by the reaction of NaOMe (excess) with Cp*RuCl$(PMe_3)_2$ in THF. An uncharacterized mixture resulted if the reaction medium contained MeOH, presumably owing to the reaction of MeOH with the basic hydride of Cp*RuH$(PMe_3)_2$ (see below).

The complexes Cp*RuH(L_2) were isolated as air-sensitive yellow solids and were readily characterized by their ^{1}H and ^{31}P{^{1}H} NMR spectroscopic data (see Table IV) and elemental analysis. The ^{1}H NMR spectra of the monohydride complexes show the methyl resonance of the Cp* ligand as a singlet at around 1.6 ppm and the hydride resonance as a sharp triplet due to coupling to the two equivalent phosphorus atoms. An exception to the hydride pattern is the triplet of doublets of Cp*RuH(dppm) caused

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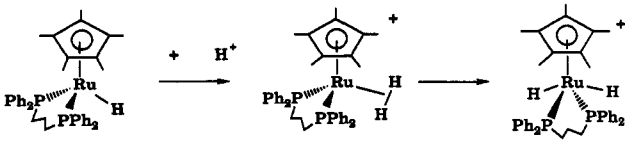
Scheme I. Consecutive Reactions in the Protonation of Cp*RuH(dppp)



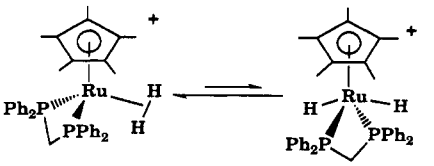
by additional coupling to a dppm methylene proton.[1] The ^{31}P NMR spectra of the monohydrido complexes show a singlet for the phosphorus signals.

Protonation Reactions. Protonation of the monohydride complexes $Cp^*RuH(L_2)$ with $HBF_4 \cdot Et_2O$ in Et_2O produced the corresponding dihydride complexes $[Cp^*RuH_2(L_2)]BF_4$ (L_2 = dppm, dppp, $(PPh_3)_2$, $(PMePh_2)_2$, $(PMe_2Ph)_2$, $(PMe_3)_2$), according to eq 5. Depending on the nature of the complex, the composition of the final protonation products at room temperature may be exclusively the dihydride form $[Cp^*Ru(H)_2(L_2)]^+$ or a mixture of the dihydride tautomer $[Cp^*Ru(H)_2(L_2)]^+$ and the η^2-dihydrogen tautomer $[Cp^*Ru(\eta^2\text{-}H_2)(L_2)]^+$. ^1H and $^{31}P\{^1H\}$ NMR spectra indicate that the thermodynamic products are all in the dihydride form when L_2 is dppp, PPh_3, $PMePh_2$, PMe_2Ph, or PMe_3. When L_2 is dppm, the final protonation product is a mixture of complexes $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$ and $[Cp^*Ru(H)_2(dppm)]BF_4$ in a ratio of 2:1. Conroy-Lewis and Simpson[21] have reported that the protonation of CpRuH(dppm) gives exclusively $[CpRu(\eta^2\text{-}H_2)(dppm)]^+$. Thus, an increase in the electron density around the ruthenium center on going from the Cp to the Cp* ligand favors the formation of the dihydride form over that of the η^2-dihydrogen form.

The initial protonation products may be quite different from the final thermodynamic product, as suggested by the following NMR experiments. Chinn and Heinekey[4] reported that reaction of $Cp^*RuH(PPh_3)_2$ with an excess (1.1–1.5 equiv) of 85% $HBF_4 \cdot Et_2O$ at −78 °C in dichloromethane resulted in complete conversion to the complex $[Cp^*Ru(\eta^2\text{-}H_2)(PPh_3)_2]BF_4$, which isomerized into the dihydride complex $[Cp^*Ru(H)_2(PPh_3)_2]BF_4$ upon warming to room temperature. Protonation of Cp*RuH(dmdppe) under similar conditions appeared to give a similar sequence of reactions. According to Chinn and Heinekey, the initial kinetic product of protonation is always the dihydrogen complex, at least for complexes of the type $Cp^*RuH(L_2)$ or $CpRuH(L_2)$.[4]

The kinetic product of the reaction of Cp*RuH(dppp) with HBF_4 is a η^2-dihydrogen complex, at least at low temperatures. If the hydride Cp*RuH(dppp) is protonated at −60 °C with $HBF_4 \cdot Et_2O$, the η^2-dihydrogen complex $[Cp^*Ru(\eta^2\text{-}H_2)(dppp)]BF_4$ is the only product according to ^1H and ^{31}P NMR spectra. However, if the product, $[Cp^*RuH_2(dppp)]BF_4$, is formed by rapid reaction and precipitation from ether at room temperature, then the ^1H or ^{31}P NMR spectra obtained immediately after dissolving the isolated solid reveal the presence of both the η^2-dihydrogen complex $[Cp^*Ru(\eta^2\text{-}H_2)(dppp)]BF_4$ and the dihydride complex $[Cp^*Ru(H)_2(dppp)]BF_4$. When it stands, $[Cp^*Ru(\eta^2\text{-}H_2)(dppp)]BF_4$ gradually isomerizes into the dihydride tautomer $[Cp^*Ru(H)_2(dppp)]BF_4$ (Scheme I). Kinetic experiments to learn about the isomerization process were conducted at room temperature by following the rate of the disappearance of the phosphorus resonance of the dihydrogen complex $[Cp^*Ru(\eta^2\text{-}H_2)(dppp)]BF_4$ by ^{31}P NMR spectroscopy with time. These indicate that the isomerization is a first-order process with a rate constant of ca. 2.4×10^{-2} min^{-1} and a half-life of ca. 29 min at 20 °C. The T_1 values of the η^2-H_2 and hydride nuclei (see below) of the two isomers do not average at room temperature, as expected, by this slow, irreversible isomerization.

Scheme II. Interconversion of $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$ and $[Cp^*Ru(H)_2(dppm)]BF_4$ When the Temperature Is above 230 K



Protonation of the complexes $Cp^*RuH(L_2)$ (L = $PMePh_2$, PMe_2Ph, PMe_3) probably also gives the η^2-dihydrogen complexes initially. However, the rate of isomerization is too rapid to allow observation of the η^2-dihydrogen intermediate at room temperature. In an attempt to observe the dihydrogen intermediate, protonation of the monohydride $Cp^*RuH(PMePh_2)_2$ in acetone-d_6 at −60 °C with $HBF_4 \cdot Et_2O$ was monitored by ^1H NMR spectroscopy. The NMR spectrum in the hydride region only displays the triplet corresponding to the hydride signal of the dihydride complex $[Cp^*Ru(H)_2(PMePh_2)_2]BF_4$. This experiment suggests that the rate of isomerization is too fast to allow the detection of the dihydrogen intermediate even at −60 °C. Nevertheless, the possibility that the initial product is the dihydride complex $[Cp^*Ru(H)_2(PMePh_2)_2]BF_4$ cannot be excluded.

Interconversion of the η^2-dihydrogen complex $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$ and the hydride complex $[Cp^*Ru(H)_2(dppm)]BF_4$ must be fast at 20 °C (Scheme II). Thus, the relative intensities of the signals for $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$ and $[Cp^*Ru(H)_2(dppm)]BF_4$ do not change when spectra of the protonation products were collected immediately or several hours later after dissolving the isolated solid at room temperature. Intramolecular H atom site exchange would explain why the T_1 values for the dihydrogen and the dihydride signals are so similar at 296 K and 200 MHz. These values were 102 and 61 ms, respectively, with CD_2Cl_2 as the solvent (see Table V). Without exchange the values should have been about 2700 and 50 ms, respectively (see below). Complete averaging of the T_1 values is observed at 313 K, 200 MHz, where T_1 times for both dihydride and dihydrogen resonances are 86 ms in acetone-d_6. This is in contrast with the $[Cp^*RuH_2(dppp)]^+$ tautomers, where the T_1 values indicate that the two tautomers do not interconvert at an appreciable rate.

When the monohydride complex Cp*RuH(dppm) was protonated in acetone-d_6 at −60 °C, a mixture of the two tautomers was observed. Interconversion of the two tautomers of $[Cp^*RuH_2(dppm)]^+$ should be very slow under these conditions, and so it could be concluded that both the dihydride and η^2-dihydrogen forms are kinetic products of the reaction. However, the reactants in the NMR tube might have warmed up enough while they were being mixed to allow some interconversion, and so we are not confident of this conclusion.

Two groups[1,21] have reported that protonation of the cyclopentadienyl complexes $CpRuH(L_2)$ (L_2 = $R_2PCH_2CH_2PR_2$; R = Ph,[21] p-$CF_3C_6H_4$,[1] p-$MeOC_6H_4$[1]) gives a mixture of the η^2-dihydrogen complex $[CpRu(\eta^2\text{-}H_2)(L_2)]^+$ and the dihydride complex $[CpRu(H)_2(L_2)]^+$ at room temperature. We find that when the protonation of

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Table V. T_1 Values of the η^2-Dihydrogen and Hydride Ligands for the Cp*Ru Complexes

$[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]^+$ and $[Cp^*Ru(H)_2(dppm)]^+$ [a]

		T, K (200-MHz spectrometer)						
		313[b]	293	274	253	233	213	197
$T_1(Ru(\eta^2\text{-}H_2))$, ms	obs	86	61	34	30	21[c]	18[c]	13[c]
	calc[d]	79[e]	60[e]	30	21	15	10	9
$T_1(Ru(H)_2)$, s	obs	0.086	0.10	0.17	0.70	0.73	0.41[c]	0.23[c]
	calc[f]	3.64	2.71	1.97	1.32	0.85	0.53	0.38

		T, K (400-MHz spectrometer)					
		293	251	234	220	199	189
$T_1(Ru(\eta^2\text{-}H_2))$, ms	obs	50	23	20	18	20	24
	calc[d]	60[e]	24	20	18	20	24
$T_1(Ru(H)_2)$, s	obs	0.12	0.93	0.92	0.78	0.67	0.64
	calc[f]	2.62	1.31	0.97	0.78	0.64	0.66

$[Cp^*Ru(\eta^2\text{-}H_2)(dppp)]^+$ and $[Cp^*Ru(H)_2(dppp)]^+$ [a]

		T, K (400-MHz spectrometer)			
		296	273	253	233
$T_1(Ru(\eta^2\text{-}H_2))$, ms	obs	32	24	21	g
	calc[h]	32	25	21	21
$T_1(Ru(H)_2)$, s	obs	0.86	0.62	0.48	0.4[g]
	calc[i]	0.86	0.62	0.47	0.39

[a] Solvent is CD_2Cl_2 unless otherwise stated. [b] Acetone-d_6. [c] The values are not very reliable, owing to the overlap of the dihydrogen and the dihydride resonances. [d] $\tau_0 = 0.60$ ps, $E_a = 2.6$ kcal mol^{-1}, r(H–H) = 1.10 Å (no rotation of H_2).[26a] [e] Calculated assuming rapid averaging with dihydride T_1 $(3/(2/T_1(H_2) + 1/T_1(H)_2)$. [f] $\tau_0 = 0.26$ ps, $E_a = 2.7$ kcal mol^{-1}, r(H···H) = 2.0 Å. [g] The values are not reliable, owing to the overlap of the dihydrogen and dihydride resonances and the weak intensity of the dihydrogen resonance; by the time the T_1 experiment was performed at the indicated temperature, most of the $Ru(H_2)$ was converted to $Ru(H)_2$. [h] $\tau_0 = 0.86$ ps, $E_a = 2.7$ kcal mol^{-1}, r(H–H) = 1.10 Å (no rotation of H_2).[26a] [i] $\tau_0 = 0.54$ ps, $E_a = 2.7$ kcal mol^{-1}, T_1(min) = 0.38.

these Cp complexes is performed at −60 °C in CD_2Cl_2, the initial product is exclusively in the η^2-dihydrogen form $[CpRu(\eta^2\text{-}H_2)(L_2)]^+$.

Cationic Dihydride and η^2-Dihydrogen Complexes. The dihydride complexes $[Cp^*Ru(H)_2(L_2)]^+$ are readily characterized by elemental analysis and their NMR spectroscopic properties. The resonances of the pseudo-trans hydride ligands appear as a sharp triplet in the ^1H NMR spectra because of ^2J(HP) couplings to two equivalent cis phosphorus nuclei in a "square-based piano-stool" structure.[4] The X-ray crystal structures of $[CpRu(H)_2(PPh_3)_2]PF_6$ and several ditertiary phosphine analogues verify that this is the structure in the solid state.[22]

Dihydrogen complexes of the type $[(C_5R_5)Ru(\eta^2\text{-}H_2)L_2]^+$ are thought to have a three-legged piano-stool structure with the η^2-H_2 ligand occupying one of the legs.[4,21,23] However, no such complexes have been structurally characterized as yet. A single-crystal X-ray structure determination of $[Cp^*RuH_2(dppm)]BF_4$ reveals that it is completely in the η^2-dihydrogen form in the solid state, judging from the positions of the phosphorus atoms relative to the Cp* ring (see below).

The presence of the η^2-dihydrogen ligand in $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$ and $[Cp^*Ru(\eta^2\text{-}H_2)(dppp)]BF_4$ is confirmed by the observation of short relaxation times, T_1, for the broad η^2-H_2 resonances and large coupling constants, ^1J(HD), of the corresponding η^2-HD isotopomers. The isotopomers $[Cp^*Ru(\eta^2\text{-}HD)(dppm)]BF_4$ and $[Cp^*Ru(\eta^2\text{-}HD)(dppp)]BF_4$ were prepared by reaction of $Cp^*RuH(L_2)$ with HBF_4 in D_2O. They display 1:1:1 triplets with ^1J(HD) couplings of 20.9 and 23.3 Hz, respectively, in the ^1H NMR spectra. These large couplings provide the best evidence for the retention of the H–D bond.[24,25] However J(HD) couplings in the range 10–25 Hz might be caused by an elongated H–H bond (>0.9 Å) or by a rapid equilibrium between two tautomers: a large ^1J(HD) coupling for an η^2-HD complex averaging with a small ^2J(HD) coupling of a *cis*-(H)(D) tautomer.[10] The more likely explanation in this case is that the η^2-HD group has an unusually long H–D distance of 1.1 Å (see below) and hence a coupling smaller than that of typical η^2-HD complexes with couplings of >30 Hz and H–D distances of <0.9 Å.[24,25] It is interesting to note that although Cp*RuH(dppp) is more basic (electron rich) than Cp*RuH(dppm) (see below), the J(HD) value for the complex $[Cp^*Ru(\eta^2\text{-}HD)(dppp)]^+$ (23.3 Hz) is larger than that for $[Cp^*Ru(\eta^2\text{-}HD)(dppm)]^+$. One would expect that as the basicity at the ruthenium center is increased, the ^1J(HD) coupling constant should decrease. A change in the bite angle of the ligand L_2 must result in a change in orbital hybridization at ruthenium, a change in the relative strength of the H–H interaction in the complexes $[Cp^*Ru(\eta^2\text{-}H_2)(L_2)]^+$, and hence, a variation in the magnitude of the J(HD) value.

The relaxation times, T_1, of the dihydrogen and hydride nuclei of the tautomers of $[Cp^*RuH_2(dppm)]BF_4$ were determined by ^1H NMR spectroscopy over the temperature range 313–197 K (Table V). As noted above, averaging of T_1 values corresponding to the broad singlet of the dihydrogen resonance and the triplet of the dihydride resonance occurs above 230 K. In the slow-exchange region the T_1 value of the dihydrogen nuclei is much smaller than that of the dihydride; for example, respective values are 21 and 735 ms at 233 K, 200 MHz with CD_2Cl_2 as the solvent.

The T_1 values of the dihydrogen ligand pass through a minimum of 18 ms at 220 K, 400 MHz. Below 230 K, the T_1 values could not be determined accurately at 200 MHz owing to the overlap of the two resonances. This T_1(min) value corresponds to a dihydrogen bond distance of 0.87

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Å for $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$ if rapid spinning of the η^2-dihydrogen ligand is assumed and 1.10 Å if spinning of the ligand is slow with respect to the tumbling of the molecule.[26] The former distance is comparable with that calculated for the complex *trans*-$[RuH(\eta^2\text{-}H_2)(dppe)_2]^+$ (0.89 (2) Å); however, this complex has a coupling, $^1J(H,D)$, of 33 Hz, whereas the dppm complex under consideration has a much smaller coupling (20.9 Hz).[6,26a] Hence, we conclude that the η^2-H_2 ligand in the dppm complex is in the slow-rotation regime with an H–H distance of 1.10 Å. Support for this distance calculation comes from the X-ray crystallographic work of Litster et al.,[27] where an H–H distance of 1.01 (14) Å was reported for $[CpRu(H_2)dppm]^+$. The dihydrogen ligand is likely to be moving fast enough to average the magnetic environments of the H nuclei, since the dihydrogen in the analogous chiral complex $[Cp^*Ru(dmdppe)(H_2)]^+$ has magnetically equivalent nuclei.[4]

A model of $[Cp^*Ru(H_2)(dppm)]^+$ was constructed with reasonable positions for the H atoms, and then the method of Desrosiers et al.[26b] was applied to find out what percentage of the relaxation rate of the dihydrogen nuclei was due to nuclei on the Cp* and dppm ligands. The total contribution from ligand nuclei was found to be 4%, the remaining 96% being due to one dihydrogen proton relaxing the other by the dipolar mechanism. The T_1(min) value for the dihydrogen nuclei with these contributions removed is 18.6 ms (a little longer than the original value of 18 ms), and the dihydrogen H–H distance is calculated to be 1.10 Å as before. Thus, ligand contributions are negligible in this case.

Values calculated from the temperature-dependent T_1 equation[26] using the best-fit parameters listed in Table V satisfactorily match the observed data obtained at 400 MHz for the dihydride and dihydrogen complexes when there is no intramolecular exchange of H atoms (≤235 K). The τ_0 parameter reflects the moment of inertia of an isotropically tumbling molecule. The smaller value of τ_0 (0.26 ps) for the more symmetrical complex $[Cp^*Ru(H)_2(dppm)]^+$ suggests that it tumbles more rapidly in solution than $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]^+$ (τ_0 = 0.60 ps), a result that might be expected on the basis of the different geometries of the two complexes (see Scheme II). The fit to the 200-MHz data is not as good, but these data were obtained from measurements on overlapping resonances.

The dihydrogen resonance for $[Cp^*Ru(\eta^2\text{-}H_2)(dppp)]BF_4$ in CD_2Cl_2 was observed at −8.80 ppm as a broad peak in the ^1H NMR spectrum. The dihydride resonance for $[Cp^*Ru(H)_2(dppp)]BF_4$ occurs at −8.67 ppm as a triplet. The T_1 values at 400 MHz were measured over the temperature range of 296–233 K (see Table V). The T_1 value for the dihydrogen resonance is much smaller than that for the dihydride signal. For example, at 253 K, the T_1 values are 21 and 481 ms, respectively. The fact that the T_1 values are not averaged indicates that the two tautomers do not interconvert at an appreciable rate at 296 K or at lower temperatures. Below 233 K, the dihydrogen and the dihydride resonances overlap, and so the T_1 values are inaccurate. The T_1 values of 21 ms for the dihydrogen ligand at 253 K is comparable to the minimum T_1 value for the dppm complex, and so this complex is also expected to have an H–H distance of 1.1 Å in a slowly rotating dihydrogen ligand. The temperature dependence of the T_1 values is readily accounted for (Table V). The τ_0 parameters for the larger dppp complexes are greater than the corresponding τ_0 parameters for the smaller dppm complexes, as expected.

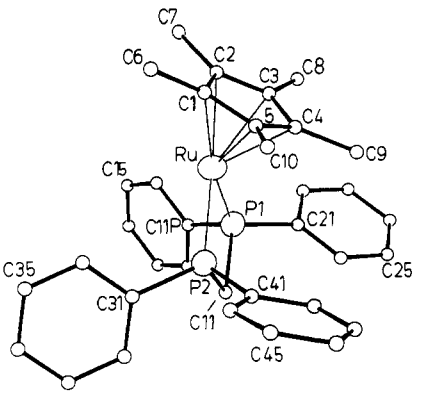

Figure 1. Molecular structure of $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$. The hydrogen atoms are omitted for clarity.

Description of the Structure of $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$. The molecular structure of $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$ is shown in Figure 1. Selected bond lengths and angles are presented in Table III. The dihydrogen ligand is not located. The overall geometry of the complex is very similar to that observed for three-legged piano-stool complexes of the type $(C_5R_5)MXL_2$ such as $CpRuCl(PPh_3)_2$,[28] CpFePh(dppm),[29] and $[CpRu(\eta^2\text{-}dppm)(\eta^1\text{-}dppm)]PF_6$.[30]

The Cp* ring is essentially planar with C–C bond lengths in the range 1.37 (1)–1.47 (1) Å, giving a mean value of 1.42 Å. The Ru–C distances range from 2.210 (7) to 2.232 (6) Å (mean 2.22 Å). The mean value is very close to that found in related ruthenium complexes: 2.22 Å in $Cp^*RuI(\eta^4\text{-butadiene})$,[31] 2.26 Å in $Cp^*RuH_3(PPh_3)$,[32] and 2.20 Å in $[Cp^*Ru(H_2O)(CO)_2]CF_3SO_3$.[33] Angles from the centroid of the ring to atoms P(1) and P(2) are 133.5 and 133.2°, respectively. These angles are expected for a three-legged piano-stool structure, with the other "leg" being the undetected H_2 below C(1) and C(2).

The two bond distances Ru–P(1) (2.298 (2) Å) and Ru–P(2) (2.301 (2) Å) are essentially equivalent. The Ru–P distances fall in the range of Ru–P distances found in the complex $[CpRu(\eta^2\text{-}dppm)(\eta^1\text{-}dppm)]PF_6$:[30] 2.295 (3), 2.325 (3), and 2.323 (2) Å. The P(1)–Ru–P(2) angle (71.46 (7)°) is comparable with the corresponding angles reported for other chelating dppm ligands in complexes such as CpFePh(dppm) (73.8 (1)°)[29] and $[CpRu(\eta^2\text{-}dppm)(\eta^1\text{-}dppm)]PF_6$ (70.0 (1)°).[30] The P(1)–Ru–P(2) angle, however, is significantly smaller than the P–Ru–P angles for complexes with larger chelate rings: for example, 82.9 (1)° in $CpRuCl(Ph_2PCHMeCH_2PPh_2)$[34] and 85.1 (1)° in $CpRu((E)\text{-}MeO_2CC{=}CHCO_2Me)(dppe)$.[35] It is also

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Table VI. Ligand Effect on the Acid–Base Properties of Cp*Ru and CpRu Hydride Complexes

compd	E_{pa}[a] vs Fc/Fc$^+$, V	E_{pa}[b] vs NHE, V	$\sum E_L$[c] vs NHE, V	compd, MH_2^+	pK_a(MH_2^+)[d]
CpRuH(dtfpe)[e]	0.17[e]	0.77	0.72	$[CpRuH_2(dtfpe)]^+$	4.6[e]
CpRuH(dppe)[e]	−0.09[e]	0.51	0.50	$[CpRuH_2(dppe)]^+$	7.5[e]
$CpRuH(PPh_3)_2$	−0.20[e]	0.40	0.56	$[CpRuH_2(PPh_3)_2]^+$	8.0[e]
CpRuH(dppp)	−0.22[e]	0.38	0.48	$[CpRuH_2(dppp)]^+$	8.6[e]
CpRuH(dape)	−0.22[e]	0.38	0.44	$[CpRuH_2(dape)]^+$	9.0[e]
Cp*RuH(dppm)	−0.25[e]	0.35	0.29	$[Cp^*RuH_2(dppm)]^+$	8.8[e]
Cp*RuH(dppp)	−0.44	0.16	0.13	$[Cp^*RuH_2(dppp)]^+$	10.4
$Cp^*RuH(PPh_3)_2$	−0.46	0.14	0.21	$[Cp^*RuH_2(PPh_3)_2]^+$	11.1
$Cp^*RuH(PMePh_2)_2$	−0.49	0.11	0.17	$[Cp^*RuH_2(PMePh_2)_2]^+$	12.2
$Cp^*RuH(PMe_2Ph)_2$	−0.57	0.03	0.09	$[Cp^*RuH_2(PMe_2Ph)_2]^+$	14.3
$Cp^*RuH(PMe_3)_2$	−0.62	−0.02	0.03	$[Cp^*RuH_2(PMe_3)_2]^+$	16.3

[a] Voltammograms were collected using THF solutions containing 0.2 M Bu_4NPF_6 as the supporting electrolyte. E_{pa} = anodic peak potentials. [b] Assume that $E_{1/2}(Fc/Fc^+)$ = 0.6 V vs NHE. [c] Calculated from Lever's electrochemical parameters E_L: Cp^-, 0.08; H, −0.30; dtfpe, 0.47; dppe, 0.36; dppm, 0.43; dape, 0.33; dppp, 0.35; PPh_3, 0.39; $PMePh_2$, 0.37; PMe_2Ph, 0.33; PMe_3, 0.30; Cp^{*-}, −0.27. [d] Obtained in THF. See Table VII in this work. [e] From ref 1.

Table VII. pK_a Values of the Cp*Ru Dihydride Complexes[a]

RuH	BH^+	RuH_2^+	K_{eq}	pK_a(BH^+)	pK_a(RuH_2^+)
Cp*RuH(dppp)	$[Cp^*Ru(H_2)(dppm)]^+$	$[Cp^*RuH_2(dppp)]^+$	15 ± 7	9.2	10.4 ± 0.5
$Cp^*RuH(PPh_3)_2$	$HP(t\text{-}Bu)_3^+$	$[Cp^*RuH_2(PPh_3)_2]^+$	0.3 ± 0.1[b]	11.4	11.1 ± 0.2
$Cp^*RuH(PMePh_2)_2$	$HP(t\text{-}Bu)_3^+$	$[Cp^*RuH_2(PMePh_2)_2]^+$	5.8 ± 3.9[b]	11.4	12.2 ± 0.4
$Cp^*RuH(PMe_2Ph)_2$	$[Cp^*RuH_2(PMePh_2)_2]^+$	$[Cp^*RuH_2(PMe_2Ph)_2]^+$	130 ± 50	12.2	14.3 ± 0.5
$Cp^*RuH(PMe_3)_2$	$[Cp^*RuH_2(PMe_2Ph)_2]^+$	$[Cp^*RuH_2(PMe_3)_2]^+$	116 ± 50	14.3	16.3 ± 0.7

[a] Obtained by ^1H NMR spectroscopy in THF-d_8 unless otherwise stated. [b] By ^{31}P NMR spectroscopy.

smaller than those for complexes with monodentate phosphines: for example, 93.7 (1)° in $CpRu(\eta^2\text{-}CH_2{=}CHCH{=}CH_2)(PMe_3)_2$,[36] 103.9 (4)° in $CpRuCl(PPh_3)_2$,[28] and 94.7 (2)° in $CpRuCl(PMe_3)_2$.[28] The P(1)–C(11)–P(2) angle (94.0 (3)°) is comparable with the 92.1 (4)° angle of the η^2-dppm ligand in the complex $[CpRu(\eta^2\text{-dppm})(\eta^1\text{-dppm})]PF_6$.[30]

Electrochemistry. Table VI lists the electrochemical peak potentials of some monohydridoruthenium complexes as measured by cyclic voltammetry at scan rates of 0.25 V s^{-1} in THF containing 0.2 M n-Bu_4NPF_6 as supporting electrolyte. Some of the data were taken from ref 1. The cyclic voltammograms for the Cp*Ru hydride complexes display an irreversible oxidative wave, the potential of which is dependent on the nature of the complex. This wave probably corresponds to the oxidation of $Cp^*RuH(L_2)$ to $[Cp^*RuH(L_2)]^+$. The irreversibility seems related to the presence of the hydride ligand. The oxidation wave is reversible for Cp*RuCl(dppm).[37] Despite the lack of reversibility, the E_{pa} values follow a sensible order of increasing electron richness at the ruthenium center: dppm < dppe < dppp ≈ PPh_3 < $PMePh_2$ < PMe_2Ph < PMe_3. The electron-donating properties of the phosphines increase in this order.[38]

Lever has recently 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.[39] In the case of Ru(II), parameters for the six ligands are simply added to obtain $E_{1/2}$(ox). Lever provided the parameters for dppm, dppe, dppp, PPh_3, $PMePh_2$, PMe_2Ph, PMe_3, and hydride. No parameters were provided for the Cp and Cp* ligands. If the E_L value for the hydride is taken as −0.3 V, then the most consistent E_L values for Cp and Cp* for the complexes studied here are 0.08 and −0.27 V, respectively (these are the total contribution of the Cp or Cp* ligand to the complex; they are not divided by 3 and hence are not the contribution per coordination site). We previously reported a less well substantiated value for Cp* of −0.17 V.[1] Table VI also shows that the sum of the ligand parameters agrees well with the observed peak potentials for each of these complexes.

Thermodynamic Acidity Measurements. Thermodynamic acidity of transition-metal hydrides plays an important role in many of their reactions.[3] Norton and his co-workers have determined the pK_a values of a number of transition-metal hydride complexes in acetonitrile.[40] We have recently started studying the acidic nature of η^2-dihydrogen and dihydride complexes.[1,2,41,42] The pK_a values of η^2-dihydrogen and dihydride complexes can be determined by NMR spectroscopic measurement of the equilibrium constant K_{eq} of the reaction of a neutral monohydride and a protonated base BH^+ of known pK_a (eq 6). The pK_a value of a dihydrogen complex or a dihydride

$$MH + BH^+ \overset{K_{eq}}{\rightleftharpoons} MH_2^+ + B \qquad (6)$$

complex could then be calculated from the equilibrium constant K_{eq} and $K_a(BH^+)$ as shown in eq 7. By using this

$$pK_a(MH_2^+) = pK_a(BH^+) + \log K_{eq} \qquad (7)$$

method, the pK_a values of a series of ruthenium hydride/dihydrogen complexes were determined in THF. The pK_a values are on an aqueous scale extrapolated from THF by use of protonated phosphines with known aqueous pK_a values as standards. We now extend the method to determine the pK_a values of the weakly acidic Cp*Ru dihydride complexes, which are useful for ranking the acidity properties of the dihydrogen complexes of the type *trans*-$[MH(\eta^2\text{-}H_2)(L_2)_2]^+$ (M = Fe, Ru, Os; L_2 = dppe, depe, dape, dtfpe).[6,8,10,42] The equilibria are summarized in Table VII.

The equilibrium constant for eq 8 was determined by ^1H NMR integration to be 15 in THF-d_8. The pK_a value

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$$Cp^*RuH(dppp) + [Cp^*Ru(\eta^2\text{-}H_2)(dppm)]^+ \rightleftarrows [Cp^*Ru(H)_2(dppp)]^+ + Cp^*RuH(dppm) \quad (8)$$

of $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]^+$ was estimated to be 9.2 using $HPCy_3^+$ (pK_a = 9.7) or $CpRu(H)_2(PPh_3)_2]^+$ (pK_a = 8.0) as standards in THF.[1] Therefore, the pK_a value of $[Cp^*Ru(H)_2(dppp)]BF_4$ is estimated to be 10.4 in THF.

The dihydride complexes $[Cp^*RuH_2L_2]^+$ (L = PPh_3, $PMePh_2$) must be much weaker acids than $[Cp^*RuH_2(dppm)]^+$ because (i) no reaction was observed by NMR experiments when $[Cp^*RuH_2L_2]^+$ and $Cp^*RuH(dppm)$ were mixed and (ii) reaction of $[Cp^*RuH_2(dppm)]^+$ and Cp^*RuHL_2 (L = PPh_3, $PMePh_2$) goes to completion in THF to form $Cp^*RuH(dppm)$ and $[Cp^*RuH_2L_2]^+$. The pK_a values for $[Cp^*RuH_2L_2]^+$ (L = PPh_3, $PMePh_2$) were estimated by determining the equilibrium constants of their reactions with $HP(t\text{-}Bu)_3^+$ in THF (eq 9). The

$$Cp^*RuHL_2 + HP(t\text{-}Bu)_3^+ \rightleftarrows [Cp^*RuH_2L_2]^+ + P(t\text{-}Bu)_3 \quad (9)$$

aqueous pK_a value of $HP(t\text{-}Bu)_3^+$ is reported to be 11.4.[43] There is no evidence for the coordination of $P(t\text{-}Bu)_3$ to ruthenium during the proton-transfer reactions of Cp^*RuHL_2 or $[Cp^*RuH_2L_2]^+$. The equilibrium constants for eq 9 were determined by ^{31}P NMR spectroscopy in THF to be 0.32 when L = PPh_3 and 5.8 when L = $PMePh_2$. Therefore, the pK_a values for $[Cp^*Ru(H)_2(PPh_3)_2]^+$ and $[Cp^*Ru(H)_2(PMePh_2)_2]^+$ were calculated to be 11.1 and 12.2, respectively. The pK_a values indeed verify that $[Cp^*RuH_2(dppm)]^+$ is a much stronger acid than $[Cp^*RuH_2L_2]^+$ (L = PPh_3, $PMePh_2$).

The pK_a value of $[Cp^*RuH_2(PMe_2Ph)_2]^+$ must be much higher than that of $HP(t\text{-}Bu)_3^+$, since no reaction occurred between $[Cp^*RuH_2(PMe_2Ph)_2]^+$ and $P(t\text{-}Bu)_3$, whereas the reaction of $Cp^*RuH(PMe_2Ph)_2$ and $HP(t\text{-}Bu)_3^+$ goes to completion to form $[Cp^*RuH_2(PMe_2Ph)_2]^+$ and $P(t\text{-}Bu)_3$ as indicated by ^{31}P NMR spectroscopy in THF. An equilibrium in THF was established between the monohydride and the dihydride pairs of the complexes containing $PMePh_2$ and PMe_2Ph ligands (eq 10). The pK_a

$$[Cp^*RuH_2(PMe_2Ph)_2]^+ + Cp^*RuH(PMePh_2)_2 \rightleftarrows Cp^*RuH(PMe_2Ph)_2 + [Cp^*RuH_2(PMePh_2)_2]^+ \quad (10)$$

value of $[Cp^*RuH_2(PMe_2Ph)_2]^+$ is estimated to be 14.3 ± 0.5 on the basis of the fact that K_{eq} for eq 10 is 0.0077 and that the pK_a value of $[Cp^*RuH_2(PMePh_2)_2]^+$ is 12.2 ± 0.4 (see above). The inverse of K_{eq} (for the reverse of eq 10) is reported in Table VII to be consistent with the format of this table. Attempts were made at determining the equilibrium constant for the reverse of eq 10, but since the reagents $[Cp^*RuH_2(PMePh_2)_2]^+$ and $Cp^*RuH(PMe_2Ph)_2$ were not mixed in equal amounts and since the extent of the reaction to the left was so large, one could not observe the signal for the limiting reagent.

The equilibrium constant of 0.0086 is obtained for the reaction of $[Cp^*RuH_2(PMe_3)_2]^+$ and $Cp^*RuH(PMe_2Ph)_2$ (eq 11) in THF as determined by ^1H NMR integration.

$$[Cp^*RuH_2(PMe_3)_2]^+ + Cp^*RuH(PMe_2Ph)_2 \rightleftarrows Cp^*RuH(PMe_3)_2 + [Cp^*RuH_2(PMe_2Ph)_2]^+ \quad (11)$$

Again we were unable to detect the concentration of the limiting agent if the equilibrium is approached from the right (i.e. mixing $Cp^*RuH(PMe_3)_2$ and $[Cp^*RuH_2(PMe_2Ph)_2]^+$). The pK_a value of $[Cp^*RuH_2(PMe_3)_2]^+$ is therefore calculated to be 16.3 ± 0.7, knowing that the equilibrium constant for eq 11 is 0.0086 and that $[Cp^*RuH_2(PMe_2Ph)_2]^+$ has a pK_a value of 14.3 ± 0.5. This explains why the hydride $Cp^*RuH(PMe_3)_2$ reacts with MeOH, which has a pK_a value of 15.2,[44] presumably to give the dihydride cation.

Kinetic Aspects of the Protonation and Deprotonation Reactions. One question about the acid–base properties of metal hydride complexes concerns the site of protonation and deprotonation reactions. The η^2-dihydrogen ligand is known to be deprotonated in preference to the terminal hydride, and a dihydrogen tautomer usually has greater kinetic acidity than a dihydride tautomer (see Introduction). This greater kinetic acidity can be attributed to the fact that there is little rearrangement of the coordination sphere of the metal when dihydrogen is deprotonated; the conversion of cationic dihydride complexes to neutral monohydride complexes results in a reduction in coordination number and thus a greater electronic rearrangement at the metal center and a slower rate of proton transfer. Similar arguments have been made for the relatively slow proton-transfer reactions of monohydrides.[3] Recently Chinn and Heinekey[4] reported that protonation of the hydride complexes Cp^*RuHL_2 (L_2 = $(PPh_3)_2$, $(CO)(PCy_3)$, dmdppe) or $CpRuHL_2$ (L_2 = $(CO)(PCy_3)$, $(CO)(PPh_3)$, $(CO)(PMe_2Ph)$, $(CO)(PMe_3)$, dmpe, dmdppe, (*R*)-(+)-$Ph_2PCH_2CH(CH_3)PPh_2$ ((*R*)-prophos), $(PPh_3)_2$) at low temperature gives exclusively the dihydrogen complexes $[Cp^*Ru(\eta^2\text{-}H_2)(L_2)]^+$ or $[CpRu(\eta^2\text{-}H_2)(L_2)]^+$, respectively. They therefore concluded that the kinetic product of protonation is always the dihydrogen complex, at least for these types of complexes.

We have reacted solutions of Cp^*RuHL_2 (L_2 = dppm, dppp, $(PMePh_2)_2$) and $CpRuHL_2$ (L_2 = dppe, dtfpe, dape) with HBF_4 at −60 °C and studied the products by ^1H NMR spectroscopy. At −60 °C, the initial protonation product is exclusively the dihydrogen complex $[CpRu(\eta^2\text{-}H_2)(L_2)]^+$ for all L_2 or $[Cp^*Ru(\eta^2\text{-}H_2)(L_2)]^+$ for L_2 = dppp only (Scheme I). However, protonation of $Cp^*RuH(dppm)$ at −60 °C in acetone-d_6 produced a mixture of the η^2-dihydrogen complex $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]^+$ and the dihydride complex $[Cp^*Ru(H)_2(dppm)]^+$ (Scheme II). The dihydrogen complex $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]^+$ might form initially and then isomerize to give the mixture at −60 °C. However, the T_1 studies described above suggest that this isomerization would be stopped as long as the temperature remained below −40 °C. It is possible that protonation at both the hydride and the Ru center took place to give the mixture of the two tautomers. Protonation of $Cp^*RuH(PMePh_2)_2$ at −60 °C in acetone-d_6 gives the dihydride complex $[Cp^*Ru(H)_2(PMePh_2)_2]^+$. The possibility of protonation at the ruthenium center directly cannot be discounted in this case as well.

When a solution containing a mixture of $[CpRu(\eta^2\text{-}H_2)L_2]^+$ and $[CpRu(H)_2L_2]^+$ (L_2 = dtfpe, dppe, dape) was treated with NaOEt or NaOMe at −60 °C in acetone-d_6 or dichloromethane-d_2 the η^2-dihydrogen tautomer was deprotonated rapidly and completely by the time a ^1H NMR spectrum was collected (Scheme III). However, it takes more than 30 min for the dihydride tautomer to be deprotonated completely under similar conditions. Thus, the dihydrogen tautomer for these cyclopentadienylruthenium complexes is kinetically more acidic than the corresponding dihydride tautomers.

Attempts to quantify the rate of proton-transfer reactions by line-shape analysis failed. When a mixture of $Cp^*RuH(dppm)$, $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]^+$, and $[Cp^*Ru$-

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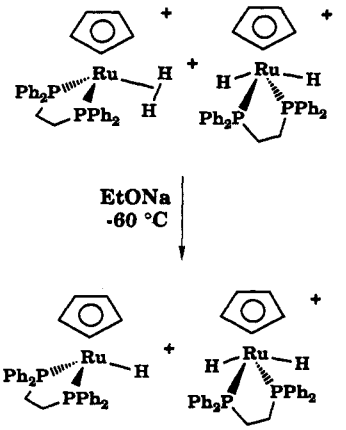
Scheme III. Selective Deprotonation and Hence Higher Kinetic Acidity of the η^2-Dihydrogen Tautomer of $[CpRuH_3(dppe)]^+$



$(H)_2(dppm)]^+$ in CD_3NO_2 is heated while being monitored by ^1H NMR spectroscopy, the hydride resonances of $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]^+$ and $[Cp^*Ru(H)_2(dppm)]^+$ become broad around 80 °C and eventually merge at 90 °C while the monohydride resonance is unchanged. Similarly, when a mixture of CpRuH(dppe), $[CpRu(\eta^2\text{-}H_2)(dppe)]^+$, and $[CpRu(H)_2(dppe)]^+$ in CD_3NO_2 is heated while being monitored by ^1H NMR spectroscopy, the hydride resonances for the dihydrogen and the dihydride tautomer merge first. Thus, the intermolecular proton self-exchange reaction is slow compared with the intramolecular interconversion of the two isomers, and we have not been able to obtain the absolute rate constants for the proton-transfer reaction yet.

Correlation between the Acidity of the Dihydride Complexes and the Electrochemical Potentials for the Oxidation of the Deprotonated Monohydrido Complexes. The pK_a values of some hydridocarbonylmetal complexes have recently been related[45] by use of thermodynamic cycles to the homolytic dissociation free energy of the metal hydride bond, $\Delta G_{BDE}(M\text{–}H)$, and to the electrochemical potentials for oxidation of the deprotonated species, $E°(M/M^-)$

$$\Delta G_{BDE}(MH) = 1.37[pK_a(MH)] + 23.1[E°(M/M^-)] + 53.6 \quad (12)$$

where the constant 53.6[46] applies to pK_a and $E°$ values (vs NHE) measured in CH_3CN.

The dihydride complexes under consideration have a dihydrido formulation. Thus, eq 12 can be modified as follows:

$$pK_a(MH_2^+) = -16.9[E°(MH^+/MH)] + 0.73[\Delta G_{BDE}(MH_2^+)] + C \quad (13)$$

where $E°(MH^+/MH)$ refers to the half-wave potential for the oxidation of the deprotonated neutral, monohydride species, $\Delta G_{BDE}(MH_2^+)$ is the energy required to remove a hydrogen atom from the dihydride, and the constant C depends on the solvent and electrochemical reference. According to eq 13, as complexes are made more basic by using more electron-donating coligands, $E°$ will be more negative, and the pK_a of the dihydride form will increase. This trend is clearly observed in Table VI, where data from the present work are combined with data from a previous study.[1]

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(46) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1990**, *112*, 2843.

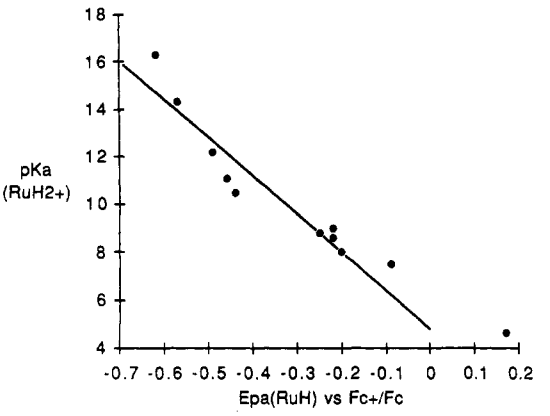

Figure 2. Plot of $pK_a(RuH_2)^+$ for the cationic ruthenium dihydride complexes in THF vs the peak potentials (vs Fc^+/Fc) for oxidation of the corresponding monohydridoruthenium complexes. The line is a plot of eq 14 when the Ru–H bond energy is 65 kcal mol^{-1}.

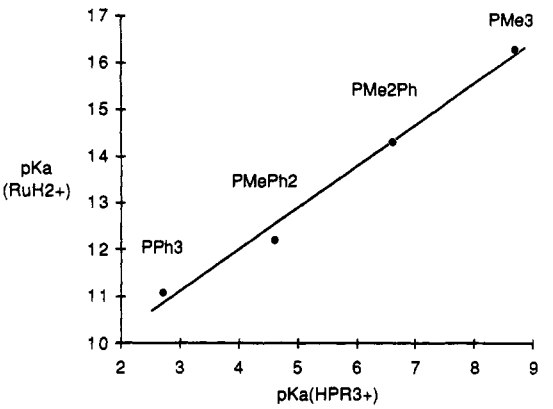

Figure 3. Plot of $pK_a(RuH_2)^+$ for the cationic dihydridobis(phosphine)ruthenium complexes in THF vs the pK_a value of the corresponding protonated phosphine.

A plot of $pK_a(RuH_2^+)$ values for the dihydride complexes in THF versus the anodic peak potential, E_{pa}, of the corresponding monohydride complexes (Figure 2) gives a curved line. An increase in the basicity of the metal center does result in a decrease in the acidity of the metal hydride complex, as expected, but the relationship is not a linear one. If the ΔG_{BDE} term of eq 13 remained constant at a reasonable Ru–H bond energy of 65 kcal mol^{-1}, then the straight line defined by eq 14 and shown in Figure 2 should

$$pK_a(RuH_2^+) = -16.9[E_{pa}(RuH)] + (0.73)(65) - 42.7 \quad (14)$$

have been observed (E_{pa} versus $FeCp_2^+/FeCp_2$). Deviations from the line can be explained by differences in the Ru–H bond energies between complexes. Complexes with points above the line have greater bond energies (up to 68 kcal mol^{-1}), and complexes below the line have lower energies (down to 63 kcal mol^{-1}). This analysis remains uncertain until more is learned about the kinetics of the irreversible oxidation of the monohydride complexes.

A plot of $pK_a(Ru(\eta^2\text{-}H_2))$ values for the η^2-H_2 complexes in THF versus the anodic peak potential, E_{pa}, of the corresponding monohydrido complexes gives a straight line with a slope of −10.7, which is less than the theoretical value of −16.9.[1] This deviation is also probably caused by the variation of bond energy, $\Delta G_{BDE}(M(\eta^2\text{-}H_2))$.

It is also interesting to know to what extent is the basicity of a phosphine transferred to the metal center. A plot of the pK_a values of $[Cp^*RuH_2(L_2)]^+$ complexes vs the pK_a values of the phosphine[47] gives a straight line with a

slope of 0.9. The pK_a values of the dihydride complexes and those of the free phosphines are related by eq 15. Thus, the basicity of the phosphine is efficiently transferred to the metal center.

$$pK_a(RuH_2^+) = 8.4 + 0.9[pK_a(HPR_3^+)] \quad (15)$$

Conclusion

The Cp^*RuHL_2 complexes can be readily prepared by the reaction of NaOMe (excess) with Cp^*RuClL_2, which can be prepared in situ by the reactions of Cp^*RuCl_2 with L_2 in the presence of Zn. Protonation of Cp*RuH(dppp) or $CpRuHL_2$ at low temperature gives exclusively the dihydrogen complexes $[Cp^*Ru(\eta^2\text{-}H_2)(dppp)]^+$ or $[CpRu(\eta^2\text{-}H_2)L_2]^+$ when L_2 = dppe, dape, dtfpe. This is consistent with the microscopic reverse of this reaction, where the η^2-dihydrogen form has a higher kinetic acidity than the dihydride form. However, protonation at the metal as well as the hydride might be concurrent processes for Cp*RuH(dppm) and $Cp^*RuH(PMePh_2)_2$. The most thermodynamically stable products for the electron-rich Cp* complexes are the *trans*-dihydrides in a square-based piano-stool geometry with monodentate phosphines or a bidentate phosphine with a large enough bite angle (i.e. dppp) to span trans sites without much strain. Bidentate ligands forming four- or five-membered rings with the metal allow both the *trans*-dihydride and η^2-dihydrogen tautomers to coexist. The $\eta^2\text{-}H_2$ ligand is thought to have hindered rotation on the Ru binding sites and have an H–H distance of approximately 1.1 Å. An increase in the basicity of the phosphine results in an increase in the basicity of the metal center and a decrease in the acidity of the resulting metal dihydride or dihydrogen complex. A range of pK_a values from 10 to 16 has been determined here, but the overlapping equilibrium method results in large uncertainties in the values greater than 11. The Ru–H bond energy of the *trans*-dihydride complexes appears to vary by about 5 kal mol^{-1} depending on the type of phosphine ligand in the complex.

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Registry No. Cp*RuH(dppm), 131296-11-2; Cp*RuH(dppp), 137436-50-1; $Cp^*RuH(PPh_3)_2$, 112861-28-6; $Cp^*RuH(PMePh_2)_2$, 108083-42-7; $Cp^*RuH(PMe_2Ph)_2$, 137436-51-2; $[Cp^*Ru(H)_2(dppm)]BF_4$, 137436-53-4; $[Cp^*Ru(\eta^2\text{-}H_2)(dppm)]BF_4$, 131296-13-4; $[Cp^*Ru(H)_2(dppp)]BF_4$, 137436-55-6; $[Cp^*Ru(\eta^2\text{-}H_2)(dppp)]BF_4$, 137436-57-8; $[Cp^*Ru(H)_2(PPh_3)_2]BF_4$, 121183-76-4; $[Cp^*Ru(H)_2(PMePh_2)_2]BF_4$, 131274-36-7; $[Cp^*Ru(H)_2(PMe_2Ph)_2]BPh_4$, 137436-59-0; $[Cp^*Ru(H)_2(PMe_3)_2]BPh_4$, 137436-61-4; $[Cp^*Ru(\eta^2\text{-}HD)(dppp)]BF_4$, 137436-63-6; Cp^*RuCl_2, 92390-47-1; $Cp^*RuH(PMe_3)_2$, 87640-53-7; $[Cp^*Ru(H_2)(dppm)]^+$, 131296-12-3; $[Cp^*Ru(H)_2(PMePh_2)_2]^+$, 131274-35-6; $[Cp^*Ru(H)_2(PMe_2Ph)_2]^+$, 137436-58-9; $[Cp^*Ru(H)_2(dppp)]^+$, 137436-54-5; $[Cp^*Ru(H)_2(PPh_3)_2]^+$, 121183-75-3; $[Cp^*Ru(H)_2(PMe_3)_2]^+$, 137436-60-3; $HP(t\text{-}Bu)_3^+$, 137436-49-8.

Supplementary Material Available: Listings of H atom coordinates and anisotropic thermal parameters (3 pages); a table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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Preparation and Reactions of (π-Allyl)palladium and -platinum Carbonate Complexes

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The tertiary-phosphine-coordinated Pd(0) complexes Pd(styrene)L_2 (L = PMe_3, PMe_2Ph, $PMePh_2$) react readily with allylic carbonates (methyl 2-methylallyl carbonate and allyl ethyl carbonate) in THF to afford cationic (π-allyl)palladium complexes having an alkyl carbonate anion $[(\pi\text{-allyl})PdL_2]^+[OCOOR]^-$ (allyl = 2-MeC_3H_4, R = Me, L = PMe_3 (**1a**), PMe_2Ph (**1c**), $PMePh_2$ (**1d**); allyl = C_3H_5, R = Et, L = PMe_3 (**1b**)). Complexes **1a–1d** are extremely moisture sensitive and readily react with water to give the corresponding hydrogen carbonate complexes $[(\pi\text{-allyl})PdL_2]^+[OCOOH]^-$. X-ray analysis of the hydrogen carbonate complex (**2a**) derived from **1a** has revealed that **2a** has a dimeric structure, in which two $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pd(PMe_3)_2]^+[OCOOH]^-$ units are associated with each other by hydrogen bonds between the hydrogen carbonate anions. Crystal data for **2a**: $C_{11}H_{26}O_3P_2Pd$, a = 12.055 (2) Å, b = 14.497 (2) Å, c = 9.602 (2) Å, β = 97.93 (1)°, monoclinic, $P2_1/a$, Z = 4. Treatment of **1a** with active hydrogen compounds including 2,4-pentanedione, dimethyl malonate, and cyclohexanone gives the allylation products, whereas **1a** reacts with CO to afford methyl 3-methyl-3-butenoate together with methyl 2-methylallyl ether. Preparation of related (π-allyl)platinum carbonate complexes $[(\eta^3\text{-}2\text{-}MeC_3H_4)Pt(PMe_3)_2]^+[OCOOR]^-$ (R = Me (**3**), H (**4**)) are reported.

Introduction

The palladium complex-catalyzed organic reactions using allylic carbonates have wide applications in organic synthesis.[1] In the presence of tertiary-phosphine-coordinated palladium catalysts, allylic carbonates serve as efficient allylating reagents for active hydrogen compounds without assistance of a base, whereas palladium-catalyzed carbonylation of allylic carbonates proceeds under very

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