8, 621-87-4; 9, 24731-07-5; TPP, 917-23-7; Fe(Pc), 132-16-1; Co(TPP), 28132-69-6; Co(salophen), 39836-45-8; $Pd(OAc)_2$, 33571-36-7; Co(salen), 14167-18-1; Mn(TPP), 31004-82-7; $H_2C{=}CH(CH_2)_7CH_3$, 872-05-9; $H_2C{=}CH(CH_2)_9CH_3$, 112-41-4; $PhOCH_2CH{=}CH_2$, 1746-13-0; salophen, 118-57-0; *o*-phenylenediamine, 95-54-5; salicylaldehyde, 90-02-8; hydroquinone, 123-31-9; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; 2-allylcyclohexanone, 94-66-6; 2-(ethoxycarbonyl)-2-allylcyclohexanone, 61771-75-3; 1-acetoxy-2-cyclohexene, 14447-34-8; cyclohexene, 110-83-8; 2-methoxy-3,6-dihydroxybenzoic acid, 118303-91-6.

Dihydrogen Complexes of Ruthenium. 2. Kinetic and Thermodynamic Considerations Affecting Product Distribution

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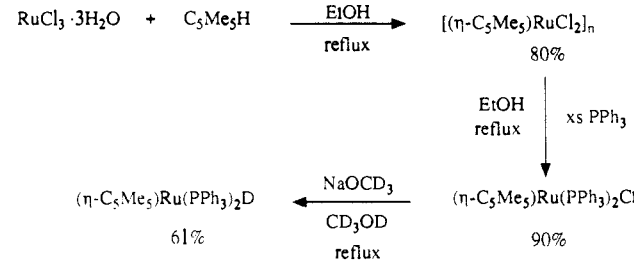
Abstract: Cationic ruthenium dihydrogen complexes of the form $[(\eta\text{-}C_5H_5)Ru(L)(L')(\eta^2\text{-}H_2)]BF_4$ (L = CO, L' = PCy_3 (**1a**), PPh_3 (**2a**), PMe_2Ph (**3a**), PMe_3 (**4a**)) have been prepared by protonation of the corresponding neutral hydrides. Carbonyl free derivatives such as $[(\eta\text{-}C_5H_5)Ru(\widehat{P\ P'})(\eta^2\text{-}H_2)]BF_4$ ($\widehat{P\ P'}$ = 1,2-bis(dimethylphosphino)ethane (dmpe) (**5a**), (1,1-dimethyl-2,2-diphenylphosphino)ethane (dmdppe) (**6a**), (*R*)-(+)-1,2-bis(diphenylphosphino)propane ((*R*)-prophos) (**8a**), bis(PPh_3) (**9a**)) were similarly prepared. Pentamethylcyclopentadienyl analogues $[(\eta\text{-}C_5Me_5)Ru(\widehat{P\ P'})(\eta^2\text{-}H_2)]BF_4$ ($\widehat{P\ P'}$ = dmdppe (**7a**), $(PPh_3)_2$ (**10a**)) and $[(\eta\text{-}C_5Me_5)Ru(CO)(PCy_3)(\eta^2\text{-}H_2)]BF_4$ (**11a**) have also been prepared. Identification of these species as dihydrogen complexes is based upon observation of substantial H–D coupling (22–32 Hz) in the ^1H NMR spectra of the HD analogues, prepared by protonation of the corresponding deuterides. In every case studied in detail, the kinetic product of the protonation reaction is the dihydrogen complex, but an intramolecular isomerization occurs to give variable amounts of the transoid dihydride form at equilibrium. The composition of the equilibrium mixture and the rate at which the equilibrium is obtained depend upon the ligand environment. Facile rotation of the coordinated H_2 ligand in the ruthenium complexes is established by the study of chiral complexes. The coordinated H_2 in these complexes is substantially activated toward heterolytic cleavage. In the case of **5a**, the measured pK_a is 17.6 (CH_3CN), with the dihydrogen form deprotonated more rapidly than the dihydride.

Introduction

Although numerous reports of η^2-dihydrogen complexes have appeared in recent literature,[1] the chemistry of cationic half-sandwich complexes with pseudo-octahedral coordination has received relatively little attention. The exceptional stability of these η^2-dihydrogen complexes of ruthenium not only facilitates their study, but the rich and relatively well developed syntheses of (η^5-cyclopentadienyl)ruthenium halides[3] (and to a lesser extent the hydrides) allows for systematic variation in the ligand environment. Thus these complexes offer a unique opportunity to study the physical and chemical properties of coordinated dihydrogen as a function of the ligand environment about a metal center.

Scheme I



In this paper, we report on several complexes of the general form $[(\eta\text{-}C_5R_5)Ru(L)(L')(\eta^2\text{-}H_2)]BF_4$ (L, L' = CO and various phosphine ligands, vide infra), which are conveniently prepared by protonation of the corresponding neutral hydrides. These cationic complexes exist as rapidly equilibrating mixtures of the dihydrogen complex and the corresponding transoid dihydride form. The equilibrium composition and the rate at which equilibrium is obtained have been studied in detail in several cases and are found to be highly dependent on the ligand environment. The coordinated H_2 in these cationic complexes is highly activated toward heterolytic cleavage, with the dihydrogen form deprotonated in preference to the dihydride form. A preliminary account of portions of this work has been previously communicated.[4]

Results

Synthesis of Dihydrogen Complexes. Syntheses of the neutral ruthenium hydrides of the type CpRu(L)(L')H (L = CO; L' = PR_3; Cp = η^5-cyclopentadienyl) patterned after the report by Humphries and Knox for the PPh_3 complex[5] (**2**) allow for the convenient preparation of these hydrides from $Ru_3(CO)_{12}$, cy-

(1) For a comprehensive account of the development of this field, see: Kubas, G. J. *Acc. Chem. Res.* **1988**, *21*, 120–128. Since the review by Kubas several additional dihydrogen complexes have been reported.[2]

(2) (a) Arliguie, T.; Chaudret, B.; Morris, R. H.; Sella, A. *Inorg. Chem.* **1988**, *27*, 598–599. (b) Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 546–548. (c) Esteruelas, E. S.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1563–1564. (d) Hampton, C.; Cullen, W. R.; James, B. R.; Charland, J. *J. Am. Chem. Soc.* **1988**, *110*, 6918–6919. (e) Cotton, F. A.; Luck, R. L. *J. Chem. Soc., Chem. Commun.* **1988**, 1277–1278. (f) Bianchini, C.; Peruzzini, M.; Zanobini, F. *J. Organomet. Chem.* **1988**, *354*, C19–C22. (g) Bianchini, C.; Mealli, C.; Meli, A.; Peruzzini, M.; Zanobini, F. *J. Am. Chem. Soc.* **1988**, *110*, 8725–8726. (h) Jia, G.; Meek, D. W. *J. Am. Chem. Soc.* **1989**, *111*, 757–758. (i) Lundquist, E. G.; Huffman, J. C.; Folting, K.; Caulton, K. G. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1165–1167. (j) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sánchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431–7437. (k) Johnson, T. J.; Huffman, J. C.; Caulton, K. G.; Jackson, S. A.; Eisenstein, O. *Organometallics* **1989**, *8*, 2073–2074. (l) Albertin, G.; Antoniutti, S.; Bordignon, E. *J. Am. Chem. Soc.* **1989**, *111*, 2072–2077. (m) Nolan, S. P.; Marks, T. J. *J. Am. Chem. Soc.* **1989**, *111*, 8538–8540. (n) Cotton, F. A.; Luck, R. L. *Inorg. Chem.* **1989**, *28*, 2181–2186. (o) Mediati, M.; Tachibana, G. N.; Jensen, C. M. *Inorg. Chem.* **1990**, *29*, 3–5.

(3) (a) Bruce, M. I.; Hameister, C.; Swincer, A. G.; Wallis, R. C. *Inorg. Synth.* **1982**, *21*, 78–80. (b) Bruce, M. I.; Windsor, N. J. *Aust. J. Chem.* **1977**, *30*, 1601–1604.

(4) Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865–5867.

(5) Humphries, A. P.; Knox, S. A. R. *J. Chem. Soc., Dalton Trans.* **1975**, 1710–1714.

0002-7863/90/1512-5166$02.50/0

Table I. ^{1}H NMR Data (Hydride Region) for Compounds **1a–11a**[a]

compd	compd	δ(H-H)[b]	δ(H-D)[b]	J_{H-D}[c,e]	IS (ppb)[d]	$\delta(H)_2$[b]	$^2J_{P-H}$[c]
$CpRu(CO)(PCy_3)H_2^+$[f]	**1a**	−7.95	−7.97	28.5	19	−7.07	20.3
$CpRu(CO)(PPh_3)H_2^+$	**2a**	−7.10					
$CpRu(CO)(PMe_2Ph)H_2^+$	**3a**	−7.62					
$CpRu(CO)(PMe_3)H_2^+$[g]	**4a**	−7.91	−7.95	28.5	ca. 30		
$CpRu(dmpe)H_2^+$	**5a**	−10.06	−10.10	22.1[3.5]	32	−9.85	30.7
$CpRu(dmdppe)H_2^+$	**6a**	−9.60	−9.63	23.8[2.3]	33	−9.24	29.4
$Cp^*Ru(dmdppe)H_2^+$	**7a**	−9.83	−9.86	23.0	26	−9.26	30.1
$CpRu((R)\text{-prophos})H_2^+$[h]	**8a**	−8.78, −9.08[i]				−8.18, −8.54[i]	*i*
$CpRu(PPh_3)_2H_2^+$[j]	**9a**	−7.70	−7.71	26.5	ca. 10	−7.59	23.3
$Cp^*Ru(PPh_3)_2H_2^+$[k]	**10a**	−7.93	−7.95	24.0	24	−7.43	26.2
$Cp^*Ru(CO)(PCy_3)H_2^+$[l]	**11a**	−7.60	−7.61	29.2	12	−6.72	22.8

[a] All measurements were recorded at 298 K in a 250-MHz field (CD_2Cl_2 solution) except where noted. [b] Chemical shift in ppm. [c] Coupling constant in Hz. [d] Isotope shift ($\Delta\delta = \delta_{HH} - \delta_{HD}$). [e] [ ] = $^2J_{P-HD}$ coupling constant in Hz at 303 K. [f] 273 K. [g] 195 K. [h] 490 MHz. [i] See text. [j] 22 K, 500 MHz. [k] 253 K, 490 MHz. [l] 500 MHz.

clopentadiene, and the appropriate substituted phosphine. Thus the new complexes, $CpRu(CO)(L)H$ (L = PCy_3 (**1**), PMe_2Ph (**3**), PMe_3 (**4**)), as well as $CpRu(dmpe)H$ (**5**), can be readily prepared by phosphine substitution of $CpRu(CO)_2H$ (eq 1).

$$Ru_3(CO)_{12} + CpH \xrightarrow[\text{reflux}]{\text{heptane}} [CpRu(CO)_2H] \xrightarrow{PR_3} CpRu(CO)(PR_3)H + CO \quad (1)$$

PR_3 = PCy_3 1 PPh_3 2 PMe_2Ph 3 PMe_3 4

The carbonyl free chloride complexes were prepared by ligand substitution on $CpRu(PPh_3)_2Cl$.[6] Thermal ligand substitution affords the complexes $CpRu(\widehat{P\ P'})Cl$ (where $\widehat{P\ P'}$ = 1,2-bis(dimethylphosphino)ethane (dmpe), (1,1-dimethyl-2,2-diphenylphosphino)ethane (dmdppe), and (*R*)-(+)-1,2-bis(diphenylphosphino)propane ((*R*)-prophos)). These materials were isolated as yellow-orange to orange solids. The prophos complex has been previously reported.[7]

The hydrides and deuterides CpRu(dmpe)(H/D) (**5** and **5**-d_1), CpRu(dmdppe)(H/D) (**6** and **6**-d_1), CpRu((*R*)-prophos)H (**8**), and $CpRu(PPh_3)_2$(H/D) (**9** and **9**-d_1) can be easily prepared by heating the chloride complexes in methanol and sodium methoxide[8] to make the corresponding hydrides. Methanol-d_1 and sodium methoxide-d_3 can be employed to provide the analogous deuterides in good yields with ca. 90% deuterium incorporation at the metal hydride position.

Recent work by Suzuki[9] and Bercaw[10] has provided methodologies for the synthesis of Cp^*RuL_2Cl (Cp^* = η^5-pentamethylcyclopentadienyl; L = trimethylphosphine or L_2 = 1,2-bis(diphenylphosphino)ethane, dppe) from oligomeric $[Cp^*RuCl_2]_n$. We have prepared $Cp^*Ru(PPh_3)_2Cl$ by combination of $[Cp^*RuCl_2]_n$ with PPh_3 in absolute ethanol and refluxing *for at least 24 h* (Scheme I). A color change of the brown solution of $[Cp^*RuCl_2]_n$ to a reddish color is noted immediately after the addition of 2.5 equiv (based on Ru) of PPh_3. Prolonged stirring at ambient temperature and recrystallization from dichloromethane/hexanes yielded red needles. The ^{1}H NMR spectrum of this material exhibited broad resonances at 6.84 and 4.62 ppm presumably due to a paramagnetic Ru(III) complex.[11] If the rusty red reaction mixture obtained in the room temperature reaction was heated to reflux for 24 h, the precipitation of orange microcrystals of $Cp^*Ru(PPh_3)_2Cl$ was observed.

With use of the above methodology developed for the synthesis of phosphine-substituted Cp complexes, the Cp* analogues were similarly prepared. Ligand substitution of dmdppe for two triphenylphosphines in $Cp^*Ru(PPh_3)_2Cl$ proceeded smoothly in refluxing hexanes. Disappearance of the parent chloride was noted within 30 min when the reaction was followed by thin-layer chromatography. Isolation of the substituted chloride by cooling the reaction filtrate yielded clumps of red-orange needles of $Cp^*Ru(dmdppe)Cl$ (81% yield).

Conversion of the chlorides to the deuterides $Cp^*Ru(dmdppe)D$ (**7**-d_1) and $Cp^*Ru(PPh_3)_2D$ (**10**-d_1) was easily accomplished with use of the aforementioned sodium methoxide-d_3/methanol-d_4 methodology. Deuteride formation proceeds at room temperature in methanol-d_4, apparently due to the better electron donating properties of Cp* vs Cp, which further labilizes the chlorides toward heterolytic dissociation.

The synthesis of the carbonyl phosphine complex, $Cp^*Ru(CO)(PCy_3)D$ (**11**-d_1), was approached by phosphine substitution of the dicarbonyl bromide, $Cp^*Ru(CO)_2Br$. One of the carbonyl ligands could be substituted with PCy_3 by thermal displacement in refluxing toluene. After 24 h, the CO stretching region in the infrared spectrum showed a single band at 1925 cm^{-1} in toluene, consistent with formation of $Cp^*Ru(CO)(PCy_3)Br$. Heating $Cp^*Ru(CO)(PCy_3)Br$ in methanol-d_4 and sodium methoxide-d_3 provided **11**-d_1 in 60% yield.

Characterization of η^2-Dihydrogen Complexes by ^{1}H NMR. Protonation of the neutral hydrides (**1–11**) and certain of the corresponding deuterides with use of an excess (1.1–1.5 equiv) of 85% $HBF_4 \cdot Et_2O$ either at −78 °C in dichloromethane or by melting a frozen dichloromethane-d_2 solution of the hydride layered with acid in an NMR tube results in the observation of a broad resonance in the hydride region of the ^{1}H NMR spectrum. When a deficiency of acid was used, signals for neutral hydride as well as a cationic species were observed at low temperatures. Line widths of the Cp resonances ($v_{1/2} \cong 6$ Hz) at probe temperatures of ca. 195 K confirm that chemical exchange is slow compared to the NMR time scale, yet line widths as broad as 180 Hz were observed for the hydride signal of the protonated species, formulated as η^2-dihydrogen complexes, **1a–11a** (eq 2).

$$Cp^{(*)}Ru(L)(L')H \xrightarrow[CD_2Cl_2,\ 195\ K]{HBF_4 \cdot Et_2O} [Cp^{(*)}Ru(L)(L')(\eta^2\text{-}H_2)]BF_4 \quad (2)$$

1 - 11 1a - 11a

(L) = CO (L,L') = dmpe 5a

(L') = PCy_3 1a Cp^* = 11a dmdppe 6a Cp^* = 7a

PPh_3 2a (*R*)-prophos 8a

PMe_2Ph 3a $(PPh_3)_2$ 9a Cp^* = 10a

PMe_3 4a

^{1}H NMR spectra of partially deuterated η^2-dihydrogen complexes (H–D) exhibited a 1:1:1 triplet (J_{HD} = 22–32 Hz) (Table I) diagnostic of ^{1}H coupling to ^{2}H (I = 1), thereby establishing formulation of the H_2 ligand as an intact dihydrogen moiety. Line widths of the H–D resonances were typically a factor of 2 to 4 times narrower than the analogous H–H resonances at equivalent temperatures. Phosphorus–(η^2-HD) couplings ($^2J_{P-H}$) were observed for compounds **5a**-d_1 ($^2J_{P-H}$ = 3.5 Hz) and **6a**-d_1 ($^2J_{P-H}$ = 2.3 Hz). In most perprotio cases the η^2-dihydrogen resonance was too broad to resolve this coupling except at ambient tem-

(6) (a) Ashby, G. S.; Bruce, M. I.; Tomkins, I. B.; Wallis, R. C. *Aust. J. Chem.* **1979**, *32*, 1003–1016. (b) Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc. A* **1971**, 2376–2382.

(7) (a) Consiglio, G.; Morandini, F.; Bangerter, F. *Inorg. Chem.* **1982**, *21*, 455–457. (b) Morandini, F.; Consiglio, G.; Lucchini, V. *Organometallics* **1985**, *4*, 1202–1208.

(8) Davies, S. G.; Moon, S. D.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1983**, 1278–1279.

(9) (a) Suzuki, H.; Lee, D. H.; Oshima, N.; Moro-oka, Y. *Organometallics* **1987**, *6*, 1569–1575. (b) Oshima, N.; Suzuki, H.; Moro-oka, Y. *Chem. Lett.* **1984**, 1161–1164.

(10) Tilley, T. D.; Grubbs, R. H.; Bercaw, J. E. *Organometallics* **1984**, *3*, 274–278.

(11) Chaudret and Arliguie have reported observations of a similar compound: Arliguie, T.; Chaudret, B. *J. Chem. Soc., Chem. Commun.* **1986**, 985–986.

peratures and above for **5a** and **6a**.

When a mixture of H–H and H–D complexes was examined, a shift of the triplet H–D resonance to slightly higher field relative to the H–H resonance was noted. This isotope shift of the chemical shift for the H–D complexes is 30–33 ppb in the η^2-dihydrogen complexes of the bidentate phosphines (Table I). A slight temperature dependence of the chemical shifts was noted when complex **6a** was examined over a wide temperature range. The chemical shift of the η^2-dihydrogen resonance shifted downfield by 1.5 ppb per deg over a temperature range of 300–200 K.

Conformational Stability of η^2-Dihydrogen Complexes. The neutral hydride, CpRu(CO)(PMe_2Ph)H (**3**), has two diastereotopic methyl groups on the phosphine ligand. Thus two doublets, centered at 1.44 and 1.39 ppm ($^2J_{PH}$ = 9.7 Hz), were observed in the ^{1}H NMR spectrum (90 MHz, C_6D_6). Protonation at low temperature results in the formation of the dihydrogen complex, which exhibits two doublets in the methyl region of the ^{1}H NMR spectrum ($^2J_{PH}$ = 10.7 and 10.8 Hz, 250 MHz, 213 K). This signal persists without significant line broadening up to 283 K.

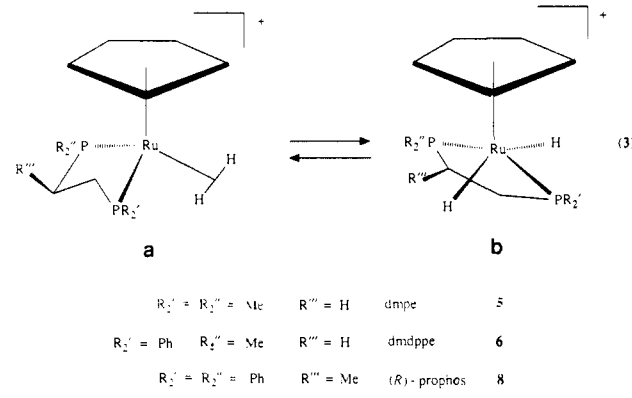
Another chiral complex, CpRu((*R*)-prophos)H (**8**),[7] possesses an asymmetric center on the chiral methine carbon of the ethenyl backbone and at the racemic metal center giving a pair of diastereomers whose configurations are designated as *R,R* and *S,R*.[12] At 490 MHz in $CDCl_3$, two upfield resonances are observed, one being assigned to each of the two diastereomeric hydrides. A triplet is observed at −13.65 ppm ($^2J_{P-H}$ = 32.8 Hz) and a doublet of doublets at −13.76 ppm ($^2J_{P-H}$ = 30.3 and 37.7 Hz). Only one unresolved Cp resonance at 4.57 ppm was observed for both diastereomers, however.[13] Protonation of a 40:60 mixture of these neutral hydride diastereomers (CD_2Cl_2) with subsequent warming results in the formation of dihydride **8b** and two spectroscopically distinguishable η^2-dihydrogen complexes (*R,R*)-**8a** and (*S,R*)-**8a**, each with dihydrogen resonances centered at −8.78 and −9.08 ppm ($\upsilon_{1/2}$ = 13 and 14 Hz, respectively) and Cp resonances (4.94 and 4.71 ppm) which integrated in a 30:70 ratio, respectively. Broadening due to epimerization appears to be insignificant for both η^2-dihydrogen and η^5-cyclopentadienyl resonances from 195 to 300 K.

Rotational Barrier of Hydrogen in η^2-Dihydrogen Complexes. Molecules possessing a center of asymmetry are chiral and therefore cannot have any symmetry elements that would equate the two η^2-dihydrogen atoms in a particular rotomer. Thus the two hydrogen atoms might be observed as chemically inequivalent if rotation could be frozen out or decoalescense might occur if intramolecular rotation of the η^2-dihydrogen ligand could be slowed to a rate comparable to the chemical shift difference (estimated at ca. 1 ppm at 298 K for **6a**) between the two ends of the H_2 ligand. However, with use of a 490-MHz magnet cooled to ca. 130 K (using a solvent mixture of $CHFCl_2/CD_2Cl_2$) only a single, broad resonance was observed for the η^2-HD resonance of **1a**-d_1, [Cp*Ru(CO)(PCy_3)(H–D)][BF_4] (**11a**-d_1), **6a**-d_1, and **7a**-d_1 whose line widths continued to increase upon decreasing the temperature from 190 to 130 K.

Reactivity of η^2-Dihydrogen Complexes. Decomposition of the dihydrogen complexes **2a–4a** proceeds cleanly near 0 °C to give dimeric complexes exhibiting two sets of upfield triplets in the region of −19 to −21 ppm and a resonance at 4.55 ppm assigned to free H_2. Further examination of these products by ^{1}H NMR and infrared spectroscopy allows the identification of these air-stable orange solids as bridging hydride dimers of the type {[CpRu(CO)(L)]$_2$(μ_2-H)}{BF_4} (L = PPh_3, PMe_2Ph, PMe_3). Four pairs of phosphorus coupled doublets observed for the decomposition products of **3a** in the ^{1}H NMR spectrum are consistent with the formation of *d,l*- and *meso*-diastereomers, each giving rise to two bridging hydride triplets in the ^{1}H NMR spectrum. These complexes are isoelectronic to the rhenium analogues recently reported by Gladysz and co-workers.[14]

Preliminary attempts to achieve hydrogenation reactions with the more thermally stable H_2 complex **5a** were not successful. Addition of 1 equiv of *tert*-butylethylene to the dmpe η^2-H_2 complex **5a** dissolved in CD_3CN showed no reaction after 18 h at 23 °C.

Observation of η^2-Dihydrogen ⇌ Dihydride Equilibria. When the chelating bidentate phosphine complexes of the type CpRu($R_2PCH_2CH_2PR_2'$)H (R = R′ = Me, **5**; R = Me, R′ = Ph, **6**) and CpRu((*R*)-prophos)H (**8**) were protonated at 195 K, the η^2-dihydrogen complexes (**5a**, **6a**, **8a**) were the sole products detectable by ^{1}H NMR. Upon warming to room temperature, a mixture of η^2-dihydrogen (**5a**, **6a**, **8a**) and dihydride (**5b**, **6b**, **8b**) complexes were observed (eq 3). The cationic metal dihydrides displayed characteristic sharp triplets 0.2 to 0.9 ppm downfield of the broad η^2-dihydrogen resonances in the ^{1}H NMR spectrum with phosphorus couplings ($^2J_{PH}$) ranging from 29.4 to 30.7 Hz at 298 K.



In order to measure the rate of this isomerization process, spin saturation transfer studies (SST) were performed on equilibrium mixtures of the η^2-dihydrogen and dihydride complexes, **5a** and **5b** or **6a** and **6b**. At ambient temperature in CD_2Cl_2 these mixtures exhibit product ratios of 86:14 and 66:34 of η^2-dihydrogen/dihydride, respectively, determined by integration of the Cp resonances. The ratio of the products was invariant with time and relatively insensitive to temperature changes (vide infra). The saturation transfer experiment was performed by irradiating the cyclopentadienyl resonance of the dihydride isomer and observing magnetization transfer into the η^2-dihydrogen cyclopentadienyl resonance. From the difference spectra, isomerization rate constants of 9.0 ± 1.4 × 10^{-2} s^{-1} (297 K, CD_3CN, 250 MHz) were obtained for **5b** → **5a** and 2.2 ± 0.3 × 10^{-2} s^{-1} (302 K, CD_2Cl_2, 490 MHz) for **6b** → **6a**. This corresponds to a free energy of activation for reductive coupling (dihydride → η^2-dihydrogen) of $\Delta G^{\ddagger}$ = 18.8 ± 0.2 and 19.9 ± 0.2 kcal mol^{-1} for **5b** → **5a** and **6b** → **6a**, respectively. In another saturation transfer experiment, the rate of oxidative scission (η^2-dihydrogen → dihydride) of **5a** → **5b** was measured by saturating the cyclopentadienyl peak of the η^2-dihydrogen complex and observing magnetization transfer into the dihydride cyclopentadienyl resonance. A rate of 1.6 ± 0.2 × 10^{-2} s^{-1} was obtained (302 K, CD_2Cl_2, 490 MHz) corresponding to a free energy barrier of 20.2 ± 0.2 kcal mol^{-1}.

Spin saturation transfer studies performed on a sample of **6a**/**6b** at various temperatures allowed the rate of the process **6b** → **6a** to be determined. An Eyring plot yielded the activation enthalpy and entropy, $\Delta H^{\ddagger}$ = 17.6 ± 0.9 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −7.8 ± 0.6 eu, respectively (Figure 1). The ratio of **6b**:**6a** was determined at several temperatures and used to determine the temperature dependence of the equilibrium. Rate of isomerization and van't Hoff data were gathered over a 45 deg temperature range and included data at lower temperatures from a CD_2Cl_2 sample and higher temperature data from a THF-d_8 sample. Equilibrium

(12) Assignment of configuration is based on the Baird/Sloan modification of the Cahn–Ingold–Prelog rules. The configuration of the metal center precedes that of the carbon center. Stanley, K.; Baird, M. C. *J. Am. Chem. Soc.* **1975**, *97*, 6598–6599.

(13) Two cyclopentadienyl resonances were previously reported for this compound in C_6D_6.[7b]

(14) Winter, C. H.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 219–225.

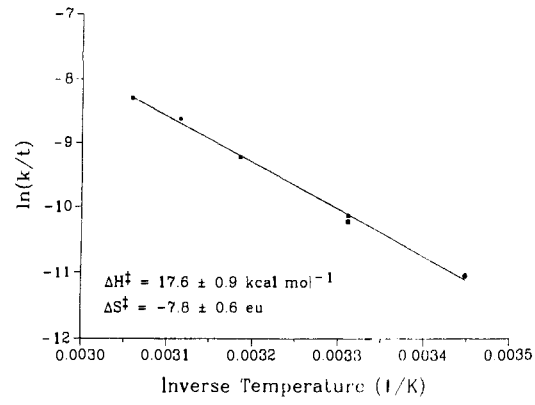


Figure 1. Eyring plot for the isomerization reaction **6a** → **6b**: (■) data from THF solution; (●) data from dichloromethane solution.

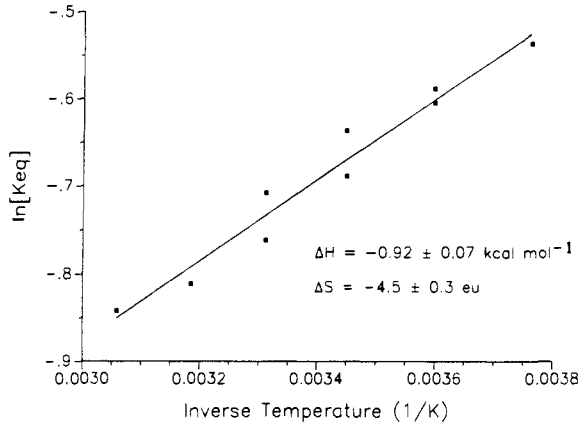


Figure 2. Plot of ln [K_{eq}] as a function of temperature for the equilibrium **6a** ⇌ **6b**.

constants were determined by using integration ratios collected after complete relaxation (delay of at least five T_1's after each 90° pulse) of either the cyclopentadienyl or H_2 resonances. A best fit line drawn to these data yielded $\Delta H = -0.92 \pm 0.07$ kcal mol^{-1} and $\Delta S = -4.5 \pm 0.3$ eu for the isomerization of **6a** → **6b** (Figure 2).

The SST data on the rate of approach to equilibrium were independently verified in the dmpe system (**5a**/**5b**). Isolation of the off-white precipitate obtained by adding diethyl ether to a concentrated dichloromethane solution of the **5a**/**5b** equilibrium mixture resulted in isolation of *only* the η^2-dihydrogen isomer (**5a**) as determined by dissolution of this solid in CD_2Cl_2 at −78 °C and observation of a single cyclopentadienyl and a broad η^2-dihydrogen resonance in the ^{1}H NMR. Qualitative kinetic measurements were obtained by rapidly warming this homogeneous sample from 195 to 253 K and holding this temperature constant. Another cyclopentadienyl resonance corresponding to the dihydride isomer **5b** appeared over time. These data yielded a half-life of isomerization of ca. 20 min.

The isomerization reactions (η^2-H_2 → dihydride) of the $(PPh_3)_2$ complexes **9a** and **10a** were studied by observation in real time. Protonation of the neutral hydrides (**9** and **10**) at 195 K leads to exclusive formation of the η^2-dihydrogen complexes (**9a** and **10a**). This assignment is based on the broad η^2-dihydrogen resonance upfield of a single, sharp singlet in the Cp or Cp* chemical shift region and the observed H–D coupling constants for the protonated deuteride. For **9a**-d_1, warming to 222 K produces a new 1:2:1 triplet at −7.59 ppm ($^2J_{PH}$ = 23.3 Hz) due to **9b**-d_1 whose intensity gains at the expense of the η^2-HD resonance due to **9a**-d_1. These observations are consistent with an isomerization of an η^2-dihydrogen complex to a metal dihydride cation.

Kinetic data acquired by following the rate of disappearance of the Cp resonance of the η^2-dihydrogen complex (**9a**) with time are consistent with a first-order process. When the natural logarithm of the intensity of the Cp resonance is plotted versus time, straight lines are obtained for data collected over 3 half-lives. The slope of the best-fit line, the first-order rate constant, is invariant with the starting concentration of the η^2-dihydrogen complex, a 12-fold increase of acid concentration, and a 5-fold excess of added triphenylphosphine. The rate constant calculated from the best-fit line at 222 K was $1.50 \pm 0.05 \times 10^{-4}$ s^{-1}, corresponding to a half-life of 77 min at this temperature. When this solution was examined by ^{1}H NMR at room temperature, only the ruthenium dihydride *trans*-**9b** was observed.[15] The rate of the isomerization **9a** → **9b** was studied over the temperature range 212–231 K. The enthalpy and entropy of activation $\Delta H^‡$ and $\Delta S^‡$ were calculated from the slope and intercept of the Eyring plot and were found to be 16.1 ± 1.8 kcal mol^{-1} and −2.8 ± 7.9 eu, respectively.

Isomerization of [Cp*Ru(PPh_3)$_2$(η^2-H_2)][BF_4] (**10a**) proceeds in a similar fashion. The η^2-dihydrogen complex **10a** is the sole product observed at 195 K upon protonation of the hydride, but isomerization to the transoid dihydride **10b** is not observed until 253 K and proceeds completely upon further warming to ambient temperatures. The rate of this rearrangement was investigated at 253 K. The disappearance of the η^2-dihydrogen complex was first order over 3 half-lives with no scrambling of the label in the H–D complexes. Best-fit lines drawn from the data yielded a rate constant of $2.39 \pm 0.06 \times 10^{-4}$ s^{-1}. The free energy of activation for isomerization of **10a** → **10b** was determined to be $\Delta G^‡_{253}$ = 18.9 ± 0.2 kcal mol^{-1}.

Intermolecular exchange of **9a**-d_1 with excess HBF_4·Et_2O appears to be slow at temperatures where the isomerization of **9a** → **9b** occurs. Protonation of a mixture of **9**-d_1 (90%) and **9** provides the corresponding products, **9a**-d_1 and **9a**. The relative ratio of these two products is difficult to determine precisely because the 1:1:1 H–D triplet of **9a**-d_1 is superimposed upon the broad η^2-dihydrogen resonance of **9a**. However, the relative amounts of **9a**-d_1 and **9a** remain unchanged at 222 K even in the presence of 12 equiv of HBF_4·Et_2O. As the isomerization of **9a**-d_1 → **9b**-d_1 proceeds, two triplets due to **9b**-d_1 and **9b** ($^2J_{PH}$ = 23 Hz for each) appear and are just resolved ($\Delta\delta$ = 11 ppb, 500 MHz). The ratio of these two triplets remains fairly constant over the 3 h course of isomerization while the overall intensity of the dihydride signals increases at the expense of **9a** resonances. The more downfield triplet is initially formed with greater intensity and remains more intense than the upfield triplet throughout the isomerization period. After 5 days at ambient temperature in the presence of a 0.3-equiv excess of HBF_4·Et_2O, the intensities of the **9b**-d_1 and **9b** triplets were approximately equal, the more upfield triplet gaining in intensity.

Heterolytic Activation of H_2. The deviation of J_{HD} of the dmpe complex **5a** (J_{HD} = 22.1 Hz) from that of free H–D (J_{HD} = 43 Hz)[16] suggested that the character of the H–D σ bond had changed significantly upon complexation. We therefore thought that the H–D (H–H) bond in the η^2-dihydrogen complex might be activated toward bond heterolysis representing the microscopic reverse for protonation of the neutral hydride. This pathway, however, may not necessarily apply to the transoid dihydride (vide infra).

As Norton and co-workers have previously demonstrated,[17] a convenient measure of the kinetic acidity of organometallic hydride compounds is to examine the self-exchange rate with its conjugate base. Thus SST experiments were performed on a mixture of **5a**/**5b** (0.047 mmol) and **5** (0.0094 mmol) dissolved in CD_3CN. SST experiments at 232 K were performed by irradiating one of the Cp rsonances and observing magnetization transfer in the subtraction spectrum. Saturation of the Cp resonance of the η^2-dihydrogen complex **5a** resulted in magnetization transfer to both the dihydride **5b** and neutral hydride **5**. Saturating the Cp

(15) (a) Conroy-Lewis, F. M.; Simpson, S. J. *J. Chem. Soc., Chem. Commun.* **1987**, 1675–1676. (b) Amaraskera, J.; Rauchfuss, T. B. *Inorg. Chem.* **1989**, *28*, 3875–3883.

(16) Nagaswara Rao, B. D.; Anders, L. R. *Phys. Rev.* **1965**, *140*, A112–A117.

(17) (a) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257–2263. (b) Jordan, R. F.; Norton, J. R. *J. Am. Chem. Soc.* **1982**, *104*, 1255–1263.

resonance of the neutral hydride **5** results in measurable magnetization transfer after subtraction to *only* the η^2-dihydrogen complex **5a**.

The thermodynamic acidity of the cationic complex was measured by adding 0.8 equiv of triethylamine to a CD_3CN solution of **5a**/**5b** at room temperature. The ^1H NMR showed dramatic line broadening of both Cp and η^2-dihydrogen resonances of **5a** and an upfield shift of these signals. Both η^5-cyclopentadienyl and dihydride resonances for the dihydride **5b** remained sharp, however. The pK_a can be calculated from the equilibrium

$$L_nM(\eta^2\text{-}H_2)^+ + B \rightleftharpoons L_nMH + BH^+$$

then

$$K_{eq} = [L_nMH][BH^+]/[L_nM(\eta^2\text{-}H_2)^+][B]$$

in dilute solution. It follows that

$$pK_{eq} = pK_a - pK_{BH^+}$$

or

$$pK_a = pK_{eq} + pK_{BH^+}$$

where pK_{BH^+} for $HNEt_3$ in CH_3CN is known.[18] Because $[L_nMH] = [BH^+]$, pK_{eq} can be calculated if $[L_nMH]$, [B], and $[L_nM(\eta^2\text{-}H_2)^+]$ are known. The *relative* concentration, $[L_nMH]/[L_nM(\eta^2\text{-}H_2)^+]$, can be found by ^1H NMR integration, and $1/[B]$ can be calculated from the starting quantity of B and $[L_nMH]/[L_nM(\eta^2\text{-}H_2)^+]$ at equilibrium. In this manner the pK_a for **5a** was found to be 17.6.

Addition of D_2O to a sample of **5a** dissolved in acetone-d_6 at 263 K resulted in the loss of signal intensity for the η^2-dihydrogen resonance. The broad resonance of the η^2-dihydrogen ligand was replaced with a 1:1:1 triplet (J = 21.6 Hz) of diminished intensity. A concomitant increase in the intensity of the H_2O resonance is also observed. Upon warming to 297 K, further incorporation of deuterium had occurred. Only a weak 1:1:1 triplet was observed and an isotope shift (1.4 Hz) of the Cp resonance of complex **5a**-d_2 was noted. Extensive deuterium incorporation into complex **5b** was also noted. No loss of intensity attributable to deuterium incorporation into the cyclopentadienyl resonances was observed.

Discussion

H–D Coupling in η^2-Dihydrogen Complexes. Observable H–D couplings in these complexes provide the best evidence for the retention of the H–D bond. It is likely that the Fermi contact term dominates the scalar coupling interaction, as is the case with free H_2. As the σ bonding character between the H–H (H–D) nuclei changes, the magnitude of the coupling constant should vary in a corresponding fashion. Thus if the bond distance of the η^2-dihydrogen ligand is affected by changing the ligand environment around the metal, a concomitant change in the H–D coupling constant should be observed if the σ framework of the H–H (H–D) ligand is altered. There is very little data in the literature that can shed light on this question. Although Morris and co-workers[19] have not observed a consistent trend correlating J_{HD} and complex basicity within the iron triad, their results within a single element (Fe or Ru) demonstrated that the substitution of diphos with the more basic depe ligand (depe = 1,2-bis(diethylphosphino)ethane) consistently decreased J_{HD} from 30 to 28 Hz for iron and 32.9 to 32.0 Hz for ruthenium complexes. Hence a systematic decrease in the H–D coupling constant (J_{HD}) is expected as the basicity is increased at the ruthenium center.

This expectation is confirmed to some extent by the data in Table I. The least basic metal centers are found in the carbonyl-containing complexes such as **1a** and **4a**, which have the largest values of J_{H-D}. For chelating bidentate phosphine complexes, our data for **5a** (dmpe, J_{H-D} = 22.1 Hz) and **6a** (dmdppe, J_{H-D} = 23.8 Hz) can be compared with the previously reported value of J_{H-D} of 24.9 Hz for $(\eta\text{-}C_5H_5)Ru(diphos)(\eta^2\text{-}H_2)^+$ (ref 15a). The expected decrease in J_{H-D} with increasing basicity of the metal center is observed. An appropriate decrease in J_{H-D} is observed when the cyclopentadienyl ligand is replaced with pentamethylcyclopentadienyl (**10a** versus **9a**). However, a similar comparison of **1a** and **11a** shows that in the carbonyl-containing complexes, this substitution has the effect of *increasing* J_{H-D}. It is possible that factors other than simple ligand basicity are involved in determining J_{H-D} values.

Equilibria between Dihydrogen and Dihydride Tautomers. If J_{HD} is a good indicator of the basicity of the metal center then it might also be expected to reflect the position of equilibrium between η^2-dihydrogen and dihydride tautomers for the bis(phosphine) chelate complexes. Defining an equilibrium constant for this equilibrium as in eq 3, i.e. $K_{eq} = [RuH_2]/[Ru(\eta^2\text{-}H_2)]$, we find that K_{eq} = 0.17 for the dmpe complex **5a**/**5b** and that K_{eq} = 0.67 for the presumably less basic dmdppe complex **6a**/**6b**. An extension of this comparison can be made by noting that K_{eq} = 2 has been previously reported for the diphos complex.[15a]

In these ruthenium compounds, however, an opposite trend is observed. As basicity at the metal center is increased by virtue of the more basic phosphine ligands ($CpRu(dppe)H_2$[15a] < **6** < **5**), J_{HD} decreases as expected, but an *increasing* amount of η^2-dihydrogen complex is also observed. These arguments consider only electronic interactions and neglect the steric demands of a cisoid chelate in the case of the η^2-dihydrogen complexes versus a transoid chelate of the dihydrides. The interactions of phosphine substituents with the Cp (Cp*) ring may be significant in determining the position of the equilibrium. The smaller methyl groups in compound **5a** will have little interaction with Cp hydrogens when positioned in a cisoid chelate whereas interactions between bulkier phenyl substituents and the Cp ring in **6a** favor the transoid arrangement of the dihydride complex **6b**. The free energy differences between η^2-dihydrogen complexes and their dihydride isomers and the relative position of this equilibrium within the series of bidentate phosphine complexes are consistent with the predominance of steric rather than electronic factors.

Viewed in this context, Simpson's data[15a] show that the number of methylene groups in the chelate bridge can drastically alter the thermodynamics of the η^2-dihydrogen $\rightleftharpoons$ dihydride equilibrium. Thus the dppp ligand can easily span transoid positions of a four-legged piano stool dihydride arrangement and avoid phosphine-ring interactions, but the smaller dppm ligand would be destabilized more by angle strain within a metallacyclobutane in a transoid conformation relative to phosphine–ring interactions in the cisoid conformation. If the basicity of the metal center is changed while minimizing steric differences between isomeric forms, an expected inverse relationship between J_{HD} and K_{eq} is observed, as is the case when going from monophosphine complex **4** to bis(phosphine) **9**.

Barrier to H_2 Rotation. Hydrogen rotation in complexes of the type $W(CO)_3(PR_3)_2(\eta^2\text{-}H_2)$ has been studied by Eckert using inelastic neutron scattering, with the conclusion that thermally activated rotation is facile, and a quantum mechanical process (rotational tunneling) is also significant.[20] In the many dihydrogen complexes now known, there has been no report of barriers to H_2 rotation that were of sufficient magnitude to allow thermal rotation to be observed on the time scale of the solution NMR experiment. In principle, the ruthenium compounds under study here should provide an opportunity to observe this phenomenon. The values of J_{H-D} are quite low, which may indicate that there is substantial back-donation into the σ^* orbital of the H_2 ligand. In addition, chiral complexes are readily prepared in this system.

Since we anticipated a requirement for quite low temperatures, we chose to study the HD derivatives rather than the H_2 complexes, since very efficient dipole–dipole relaxation in the latter is expected to lead to broad resonances at low temperatures, which would obscure any changes in the NMR spectrum due to hindered rotation.[21] The principle of the experiment is exemplified by the

(18) Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45.
(19) Bautistia, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* **1988**, *110*, 7031–7036.
(20) Eckert, J.; Kubas, G. J.; Dianoux, A. J. *J. Chem. Phys.* **1988**, *88*, 466–469.

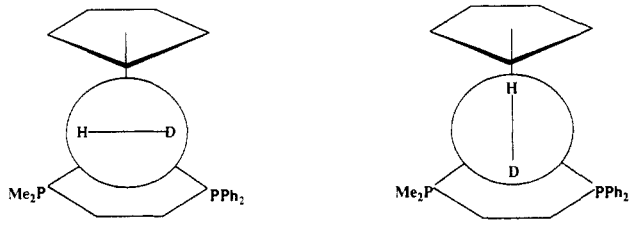


Figure 3. Projections along the Ru–dihydrogen axis of two rotamers of complex **6a**-d_1.

sketch of complex **6a**-d_1 shown in Figure 3 in which the view is along the metal ligand axis that is perpendicular to the H–D axis. The proton NMR spectrum of **6a**-d_1 at 190 K exhibits a slightly broadened 1:1:1 triplet (J_{H-D} = 24 Hz), which continues to broaden on further cooling to 130 K. All of the observed line broadening was accounted for by relaxation effects. No evidence for hindered rotation was obtained. Similar results were obtained in studies of **1a**-d_1, **7a**-d_1, and **11a**-d_1. We conclude that the barriers to rotation of bound H_2 in these ruthenium complexes are less than 6 kcal mol^{-1}.

Stability of Metal Centers toward Epimerization. Diastereotopic methyl groups on the dimethylphenylphosphine ligand of **3a** provide a molecular "tag" sensitive to the configuration of the metal center. If the metal center of the cationic η^2-dihydrogen complex were to epimerize at a rate greater than the chemical shift difference between the two methyl resonances, then only a single doublet whose net chemical shift would represent the average of the two anisochronus methyl environments should be observed. In the ^{1}H NMR of **3a**, two distinct doublets are observed in the methyl region in the ^{1}H NMR, until decomposition occurs from −10 to 0 °C (CD_2Cl_2). This observation implies that the η^2-dihydrogen complex does not epimerize rapidly on the NMR time scale.

Lack of epimerization is perhaps better illustrated when the diastereomeric mixture (*R,R*)/(*S,R*)-**8a** is examined. A mixture of these diastereomeric dihydrogen complexes clearly shows *two* distinct broad resonances. These broad resonances are well separated (0.3 ppm) at 300 K and show no evidence of coalescence (490 MHz). Thus epimerization of the metal center in **8a** is slow compared to the NMR time scale.

Structure of the Dihydride Cations. There are two possible structures for the dihydride cations formed by isomerization of the dihydrogen complexes. The first possibility is to consider these complexes as transoid metal dihydrides having four-legged piano stool structures with a symmetry plane containing both hydrides, the metal center, and the centroid of the Cp ring or both symmetrical phosphines. An alternative structure is a cisoid dihydride structure. The cisoid structure should give rise to two distinct hydride resonances in most of the complexes studied here. The observation of a single triplet resonance in the ^{1}H NMR spectrum of these cations is not conclusive evidence for the trans structure, since the observed triplet resonance could be due to a rapid fluxional process occurring in a cis dihydride, which would render the hydrides equivalent. Under this assumption, the observed coupling to ^{31}P would be the average of J_{cis} and J_{trans}.

No firm conclusion as to the structure of these complexes is possible based on the magnitude of the observed P–H coupling. Faller and Anderson have shown that in complexes of the type *cis*-(η-C_5H_5)Mo(CO)$_2$(PR_3)H, J_{H-P} values of 66–73 Hz are observed. In the trans form of these complexes, J_{H-P} is 24–29 Hz.[22] The magnitude of $^2J_{P-H}$ observed in **1b** and **5b–11b** is 20–31 Hz. While these data seem to favor the cisoid dihydride structure, this assumes that a direct comparison between neutral molybdenum and cationic ruthenium complexes is valid.

With use of the chiral phosphine ligand, (*R*)-prophos, a new center of asymmetry is introduced breaking the local symmetry once present at the metal center. This results in two chemically inequivalent hydride environments in any static structure. The ^{1}H NMR of the (*R*)-prophos dihydride **8b** in the hydride region consists of two distinct signals, each a well-resolved doublet of doublet of doublets, consistent with an ABXY spin system (X, Y = ^{31}P). This observation clearly rules out the possibility of the rapidly fluxional cisoid structure. The structure of the cation **8b** is most likely a transoid dihydride. By comparison of the magnitude of J_{H-P} values, it is likely that all the cationic dihydrides observed in this work have similar structures and that the molecules are not dynamic on the NMR time scale at ambient temperatures.

Observation of the number of methyl resonances in the ^{1}H NMR of **5b** and **6b** further supports this structural assignment. Considering the fixed arrangement of a static cisoid dihydride as a possible structure, the methyl groups are chemically and magnetically inequivalent, analogous to the η^2-dihydrogen complex. The observed single resonance for the methyl groups in the dihydrides **5b** and **6b** implies that either the two methyl groups are equivalent by some symmetry operation of the molecule or an average resonance is observed by virtue of a fluxional process. Because the observations of **8b** indicate that this molecule is not rapidly fluxional on the NMR time scale, a transoid structure that results in the equivalency of the methyl groups is confirmed for these dihydride complexes.

Mechanism of the Isomerization of an η^2-Dihydrogen Complex to a Metal Dihydride. Saturation transfer experiments establish that the η^2-dihydrogen and dihydride isomers **5a**/**5b** interconvert rapidly on the laboratory time scale.[4] This is consistent with the observation that the relative concentrations of materials are invariant over prolonged periods within ^{1}H NMR detection limits. The free energy of activation calculated for the isomerization of **5a** → **5b** at 298 K is $\Delta G^{\ddagger}$ = 20.2 ± 0.2 kcal mol^{-1}. This relatively large barrier to isomerization re-emphasizes the point made by Kubas[1,23] that these molecules represent highly stabilized intermediates along the pathway of oxidative addition of dihydrogen. The lack of a pronounced isotope effect on the rate of the isomerization suggests the lack of extensive H–H (H–D) bond cleavage in the transition state. However, for bent transition states expected along the pathway of oxidative addition of dihydrogen, kinetic isotope effects have been shown[24] to be small ($k_{HH}/k_{DD} < 1.5$).

In none of the ligand systems that we have studied was it possible to directly observe a *cis*-dihydride complex. Rapid equilibrium between an η^2-dihydrogen complex and small amounts of a *cis*-dihydride species cannot be excluded on the basis of our data, however.

More extensive kinetic studies carried out on [CpRu(dmdppe)(η^2-H_2)][BF_4] and the corresponding dihydride (**6a**/**6b**) are consistent with the kinetic measurements on **5a**/**5b**. Summing the activation parameters measured from saturation transfer kinetics for the process **6b** → **6a** with the van't Hoff reaction parameters for **6b** ⇌ **6a** (the inverse of **6a** ⇌ **6b**) yields the activation parameters for **6a** → **6b**. This gives an enthalpy of activation of $\Delta H^{\ddagger}$ = 18.5 ± 0.9 kcal mol^{-1} and $\Delta S^{\ddagger}$ = −3.3 ± 0.7 eu with $\Delta G^{\ddagger}_{302}$ = 19.5 ± 0.9 kcal mol^{-1} for the isomerization of **6a** → **6b**. The data used in calculation of the activation parameters were obtained in two different solvents, THF-d_8 and CD_2Cl_2, and were collected over a 37 deg temperature range. The agreement of data in solvents of different polarity and lack of H–D label scrambling is consistent with an intramolecular rearrangement.

Reaction parameters from the van't Hoff plot afford thermochemical data for this η^2-dihydrogen ⇌ dihydride isomerization in [CpRu(dmdppe)H_2][BF_4]. A small but negative entropy for this isomerization process is consistent with the loss of rotational freedom of a rotor-like η^2-dihydrogen complex upon rearrangement to a static metal dihydride, assuming little entropy change is realized in going from a cisoid to a transoid bidentate phosphine. The small enthalpy change suggests little difference in the overall

(21) Crabtree, R. H.; Hamilton, D. G. *J. Am. Chem. Soc.* **1988**, *110*, 4126–4133.
(22) Faller, J. W.; Anderson, A. S. *J. Am. Chem. Soc.* **1970**, *92*, 5852–5860.
(23) Kubas, G. J. *Comments Inorg. Chem.* **1988**, *7*, 17–40.
(24) Zhou, P.; Vitale, A. A.; Filippo, J. S., Jr.; Saunders, W. H. *J. Am. Chem. Soc.* **1985**, *107*, 8049–8054.

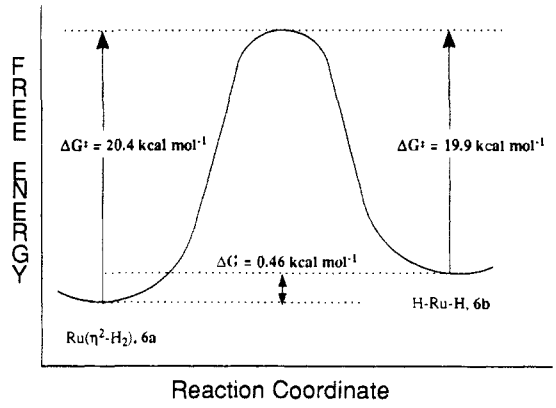


Figure 4. Reaction coordinate diagram for the isomerization **6a** ⇌ **6b**.

bond energies of both molecules. This suggests that the sum of the remaining H–H bond energy and Ru(η^2-H_2) bond energy is approximately equal to the Ru–dihydride bond energies. These kinetic and thermodynamic observations are summarized in the reaction coordinate diagram of Figure 4.

Observations on the irreversible isomerization of [CpRu(PPh_3)$_2$(η-H_2)][BF_4] (**9a**) to [CpRu(PPh_3)$_2$(H)$_2$][BF_4] (**9b**) add further support for an intramolecular rearrangement process. The isomerization is first order in the disappearance of η^2-dihydrogen complex. No scrambling of deuterium label in the H–D complexes was observed on the time scale of isomerization. The observed rate is independent of excess acid and excess phosphine concentration. All of these observations strongly support an intramolecular isomerization mechanism in which hydrogen (or proton) migration occurs to give the observed product. An intermolecular proton-transfer mechanism where neutral hydride is protonated backside to the hydride to form a trans-dihydride cation must then be ruled out as a plausible mechanism for dihydride formation. Phosphine dissociation to open a coordination site for hydrogen migration as the rate-determining step can also be discounted since the rate of disappearance of η^2-dihydrogen complex is invariant upon addition of a 5-fold excess of triphenylphosphine. Eyring studies over a 19 deg range yield an activation enthalpy $\Delta H^{\ddagger}$ = 16.1 ± 1.8 kcal mol^{-1} and activation entropy $\Delta S^{\ddagger}$ = −2.8 ± 7.9 eu for the isomerization of the η^2-dihydrogen complex **9a** to the dihydride form **9b**. The free energy of isomerization of the monodentate bis(phosphine) complex is very similar to that of the bidentate bis(phosphine) complexes, strongly suggestive of a similar mechanism of isomerization. Small entropies of activation for η^2-dihydrogen → dihydride are also consistent with an intramolecular mechanism for isomerization.

Deuterium incorporation as evidenced by elimination of the η^2-dihydrogen resonance of **5a** in the presence of D_2O, and appearance of an new single Cp resonance due to **5a**-d_2 is consistent with the acidity of **5a** (vide infra). Lack of deuterium incorporation into the Cp ring as evidenced by retention of η^5-cyclopentadienyl line intensity suggests that isomerization via a ring-protonated intermediate (D^+ in an exo position) is not an important pathway, but this does not rule out formation of an endo-deuterated species as an intermediate for hydrogen migration since no net deuterium incorporation into the ring would result upon isomerization.

For systems in which hydrogen migration is observed from the metal center to the cyclopentadienyl ring, much higher temperatures are required. For example, such a process has been recently considered by Parkin and Bercaw[25] to account for the scrambling of H and D labels in $Cp_2WH_2D^+$. Green and co-workers[26] have invoked a metal hydride intermediate to facilitate the isomerization of [Mo(η^6-C_7H_8)$_2$][BF_4] to [Mo(η^7-C_7H_7)(η^5-C_7H_9)][BF_4]. The proposed rate-determining step of carbon–hydrogen bond cleavage

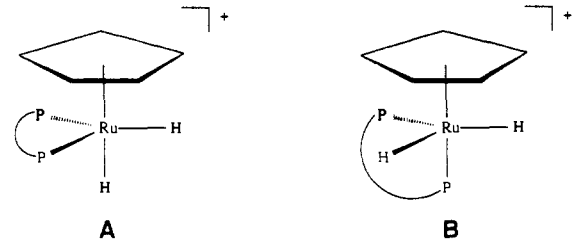


Figure 5. Two suggested structures for the transition state in the isomerization reaction of the dihydrogen complex to the trans dihydride form.

to form an unobserved ruthenium hydride represents the microscopic reverse postulated for hydride transfer in our system. For rate constants comparable to those observed for the isomerization **9a** → **9b** at 222 K (ca. 10^{-5} s^{-1}), a much higher temperature of 332.6 K (k_{obs} = 1.4 × 10^{-5} s^{-1}) is required. Similarly, Whitesides and Shelly have shown[27] that migration of a hydrogen atom to the metal in {η^4-C_5H_5(*exo*-D)}Fe(CO)$_3$ is achieved by prolonged heating to reflux in methylcyclohexane. Presumably C–H bond cleavage occurs slowly to form $CpFe(CO)_2H$ which further decomposes to [$CpFe(CO)_2$]$_2$. In other work Whitesides and Neilan[28] have reported that isomerization of Fe(CO)$_3$(η^4-C_6H_7Ph) occurs through an iron hydride intermediate but proceeds at 145 °C with a half-life of 4 h. Thus it seems extremely unlikely that the cyclopentadienyl ring is involved in the relatively facile isomerizations observed in the H_2 complexes considered here.

In summary, a mechanism for this η^2-dihydrogen ⇌ dihydride isomerization must be consistent with the following observations: (1) an intramolecular rearrangement independent of external acid or phosphine concentration, (2) a barrier to rearrangement that differs only slightly between chelating and nonchelating phosphines, (3) a slightly higher barrier for Cp* vs Cp complexes. We propose that the mechanism of isomerization consists of a simple first-order process in which the ground-state η^2-dihydrogen complex traverses a relatively high energy transition state along the pathway to dihydride product. In the case of the chelating phosphines, energy differences between η^2-dihydrogen complex and dihydride are small and are reflected as an observable equilibrium distribution of products. For the (PR_3) complexes, the dihydride form is more stable thermodynamically than the H_2 complex. The apparent "irreversible" isomerizations of **9a** and **10a** imply that the dihydride must be at least ca. 3 kcal mol^{-1} more stable than the H_2 complex at ambient temperatures since no remaining H_2 complex can be detected by ^{1}H NMR. Our data do not rule out the possibility of formation of an unstable intermediate (possibly a cis dihydride).

Two plausible models for the transition state are shown in Figure 5. These proposed structures are cationic analogues to transition states invoked in the rearrangement of fluxional four-legged piano stool complexes $CpMo(CO)_2(PPh_3)H$, in which a barrier for cis ⇌ trans isomerization was measured as 13.1 kcal mol^{-1} (25 °C in $CDCl_3$).[22]

Of these two potential models structure B is favored in light of the facile rearrangement of chelating phosphine complexes. Structure A would require the hydride to "poke through" the metallacyclophosphane ring in order for the dihydrides to adopt a transoid geometry. Structure B would allow the phosphine

(25) Parkin, G.; Bercaw, J. E. *J. Chem. Soc., Chem. Commun.* **19898** 225–257.
(26) Green, M. L. H.; Newman, P. A.; Bandy, J. A. *J. Chem. Soc., Dalton Trans.* **1989**, 331–343.
(27) Whitesides, T. H.; Shelly, J. *J. Organomet. Chem.* **1975**, *92*, 215–226.
(28) Whitesides, T. H.; Neilan, J. P. *J. Am. Chem. Soc.* **1973**, *95*, 5811–5813.
(29) Erikson, T. K. G.; Mayer, J. M. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1527.
(30) King, R. B.; Cloyd, J. C., Jr. *J. Am. Chem. Soc.* **1975**, *97*, 53–60.
(31) Nelson, G. O. *Organometallics* **1983**, *2*, 1474–1475.
(32) Conroy-Lewis, F. M.; Simpson, S. J. *J. Organomet. Chem.* **1987**, *322*, 221–228.
(33) Bercaw, J. E.; Bergman, R. G.; Seidler, P. F.; Stryker, J. M.; Threlkel, R. S. *Org. Synth.* **1987**, *65*, 42–45.
(34) Faller, J. W. In *Determination of Organic Structures by Physical Methods*; Nachod, F. C., Zuckerman, J. J., Eds.; Academic Press: New York, 1973; Vol. 5, Chapter 2.

chelate to "slide between" the two hydrides thus completing the isomerization. The smaller angle that the chelating phosphine needs to span in B would also stabilize this transition state relative to A. As expected for the bulkier Cp* ligand, steric interactions between large phosphines and the ring methyl groups would be enhanced upon adopting this approximate trigonal-bipyramidal geometry. This could account for the observed increased free energy of activation for the isomerization of **10a** → **10b** compared to **9a** → **9b**.

Heterolytic Activation of H_2. Observations gathered from SST experiments show that the H_2 complex **5a** undergoes proton exchange with its conjugate base (**5**) much faster than does the dihydride isomer **5b**. Similarly, when an equilibrium mixture of **5a**/**5b** was reacted with Et_3N, line broadening of only the signals due to **5a** was noted. These observations establish that the kinetic acidity of **5a** is greater than that of **5b**. Similar observations have been recently reported for rhenium H_2 complexes.[35]

A quantitative assessment of the acidity of the coordinated hydrogen in **5a** was carried out in acetonitrile, affording a pK_a value of 17.6. This indicates that coordination of H_2 to the Lewis acidic ruthenium cation has substantially activated the H_2 toward heterolysis, since hydrogen itself is a very weak acid.[36] This heterolysis does not involve the dihydride form. Similar heterolytic activation of hydrogen may be involved in certain hydrogenation and hydrogenolysis reactions.[37] Deprotonation of coordinated H_2 by relatively weak bases has been recently invoked by Morris and co-workers in the reaction of iron group dichloride complexes with hydrogen.[38] A recent report of hydrogenation of hindered alkenes *may* involve H_2 complexes of molybdenum.[39]

Conclusions

Coordination of H_2 to cationic ruthenium centers leads to a substantial activation of H_2 toward heterolysis. The observation of greater kinetic acidity of the H_2 complexes with respect to the dihydride isomers is consistent with the observation that the H_2 complexes are the *kinetic* products of protonation of the neutral hydride precursors. The initially formed H_2 complexes then undergo isomerization by an *intramolecular* rearrangement to afford equilibrium mixtures of the dihydride and dihydrogen complexes. The dihydride complexes adopt a pseudo-square-pyramidal geometry with the hydride ligands in transoid positions. The position of the equilibrium is a function of the ligand set. For monodentate ligands, the equilibrium is determined by the basicity of the ligand set, with the more basic ligands favoring formation of the dihydride. The basicity of the ligand set shows the expected inverse correlation with the observed values of J_{H-D}. For complexes containing bidentate chelating phosphine ligands, the position of the equilibrium is apparently determined by both steric and electronic factors. Observations on chiral complexes have established that the metal centers are configurationally stable on the NMR time scale. Rotation of coordinated H_2 is facile, and the rate of this process could not be measured by solution NMR.

Our observations are not in agreement with those of Simpson and Conroy-Lewis (SC) on related complexes.[15a] In the protonation of the hydrides $CpRu(Ph_2(CH_2)_nPPh_2)H$ (n = 1–3) *at room temperature*, SC reported that the ratio of dihydrogen to dihydride complex depends on the value of n, with larger values of n favoring the dihydride form. SC did *not* observe saturation transfer between corresponding η^2-dihydrogen and dihydride forms (n = 2). On the basis of these observations, SC proposed that the pathway of protonation was *kinetically* controlled and that the two products arose by two different protonation pathways. In the light of our results, it seems likely that the product mixtures observed by SC are actually thermodynamically determined and that the kinetic product of protonation is always the dihydrogen complex.

Experimental Section

General Considerations. All solvents were purified by distillation from sodium/benzophenone (toluene), potassium/benzophenone (heptane, THF), Na/K alloy/benzophenone (diethyl ether, pentane), or sodium/lead alloy (dichloromethane) under oxygen- and water-free N_2 (deoxygenated over BASF R3-11 CuO catalyst and dried by passing through a column of P_2O_5). Toluene, heptane, and pentane required the addition of tetraglyme (Aldrich). Deuterated solvents used in NMR experiments were dried and degassed by vacuum transfer of solvent onto activated molecular sieves or Na/K alloy/benzophenone. All reactions were performed under an atmosphere of nitrogen or argon utilizing standard Schlenk techniques. Air-sensitive materials were stored and manipulated in a Vacuum Atmospheres drybox equipped with a HE-493 dry train.

Infrared spectra were recorded on either a Perkin-Elmer 337 grating spectrophotometer or a Nicolet FT DX-5 spectrophotometer with 0.1 mm path length NaCl cells or KBr pellets. Routine ^1H NMR spectra were recorded on a Bruker WM-250 or a JEOL FT-90Q spectrometer with benzene-d_6, chloroform-d_1, or dichloromethane-d_2 (predried over molecular sieves). ^1H NMR spectra were referenced to the residual proton resonance of the deuterated solvent. ^{31}P NMR spectra were obtained on a Bruker WM-500 instrument, employing a spectrometer frequency of 202.45 MHz. ^{31}P chemical shifts were externally referenced to 85% H_3PO_4.

$CpRu(PPh_3)_2Cl$[3] and $CpRu(PPh_3)_2H$[8] were prepared by the reported procedures. $CpRu(CO)(PPh_3)H$ was synthesized according to Humphries and Knox,[5] while the chlorides $CpRu(CO)(PCy_3)Cl$, $CpRu(CO)(PMe_3)Cl$, and CpRu(dmpe)Cl were prepared with minor modifications of this procedure. $[Cp^*Ru(Cl)_2]_n$ was prepared by the method of Suzuki.[9] CpRu((*R*)-prophos)Cl and CpRu((*R*)-prophos)H were prepared according to the methods of Consiglio and co-workers.[7] (*R*)-prophos was purchased from Strem Chemicals, Inc., and dmdppe was prepared according to the procedure given by King and Cloyd.[30] $Cp^*Ru(CO)_2Br$ was prepared by bromination of the dimer as reported for the corresponding iodide.[31] $Cp^*Ru(PPh_3)_2H$ was prepared by the method of Conroy-Lewis and Simpson.[32] Pentamethylcyclopentadiene was prepared by the method of Bercaw and co-workers.[33]

Synthesis of Neutral Hydrides. $CpRu(CO)(PCy_3)H$ (1). Freshly cracked cyclopentadiene (3 mL), 250 mg of $Ru_3(CO)_{12}$, and 150 mL of freshly distilled heptane were combined in a 250-mL Schlenk flask. After 2 h of reflux under N_2, the initially deep red solution had lightened to the lemon yellow color of $CpRu(CO)_2H$. Against a stream of N_2, 420 mg (1.5 mmol) of PCy_3 was added. The solution was heated to reflux for 30 min. After the mixture was cooled, the solvent was removed by rotary evaporation to afford a yellow liquid. Addition of pentane to this yellow liquid afforded tan crystals in 70% yield. This material could be further purified by chromatography on neutral alumina(I) with benzene as the eluent or recrystallized from benzene/pentane. Yield: 350 mg (0.74 mmol, 60%). ^1H NMR (C_6D_6) δ 4.94 (s, 5 H, C_5H_5), 2.1–0.8 (br, 33 H, C_6H_{11}), −12.00 (d, 1 H, J_{PH} = 30.4 Hz, Ru–H). IR: ν_{CO} = 1920 cm^{-1} (heptane). This material was converted to the corresponding chloride $CpRu(CO)(PCy_3)Cl$ by the method of Humphries and Knox.[5]

$CpRu(CO)(PCy_3)D$ (1-d_1). A 15-mL Schlenk flask was charged with 54 mg (0.10 mmol) of $CpRu(CO)(PCy_3)Cl$, 19 mg (0.3 mmol) of $NaOCD_3$, and 0.8 mL of CD_3OD. This orange suspension was heated to reflux for 4 h, affording a yellow solution. The solution was cooled, and the solvent was removed in vacuo. The residue was extracted with 2 × 5 mL of toluene. Evaporation of the toluene afforded the product as colorless crystals in 50% yield. ^1H NMR showed <15% protium in the hydride position.

$CpRu(CO)(PMe_2Ph)H$ (3). PMe_2Ph (0.2 mL, ca. 1.4 mmol) was added to a solution of 1.28 mmol of $CpRu(CO)_2H$ prepared as above. After 10 min of reflux, the solvent was removed by rotary evaporation to give a red oil. Chromatography on neutral alumina(III) was carried out under N_2 (elution with 50/50 dichloromethane/hexanes). The solvents were removed, and sublimation of the residues at 40 °C (5 × 10^{-3} mm) gave a yellow oil that crystallized on a cold probe. Finally 90 mg of yellow solid was recovered for a 22% yield. ^1H NMR (C_6D_6) δ 7.5–7.1 (br, 5 H, C_6H_5), 4.73 (s, 5 H, C_5H_5), 1.43 (d, 3 H, J_{PH} = 9.7 Hz, CH_3), 1.39 (d, 3 H, J_{PH} = 9.7 Hz, CH_3'), −11.70 (d, 1 H, J_{PH} = 35.3 Hz, Ru–H). IR: ν_{CO} = 1925 cm^{-1} (heptane).

$CpRu(CO)(PMe_3)H$ (4). To a solution of 1.2 mmol of $CpRu(CO)_2H$ prepared as above was added 0.30 mL of PMe_3. This solution was refluxed for 10 min. The solvent was removed by rotary evaporation. The remaining volatiles were removed in vacuo. The pale yellow product was sublimed onto a water-cooled probe at 50 °C (5 × 10^{-3} mm). Yield: 210 mg, 65%. ^1H NMR (C_6D_6) δ 4.78 (br s, 5 H, C_5H_5), 1.06 (d, 9 H,

(35) Heinekey, D. M.; Chinn, M. S.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824–1826.
(36) pK_a = 35 for free H_2 in tetrahydrofuran has been reported: Buncel, E.; Menon, B. *J. Am. Chem. Soc.* **1977**, *99*, 4457–4461.
(37) Cf.: Brothers, P. J. *Prog. Inorg. Chem.* **1981**, *28*, 1–61.
(38) Cappellani, E. P.; Maltby, P. A.; Morris, R. H.; Schweitzer, A. T.; Steele, M. R. *Inorg. Chem.* **1989**, *28*, 4437–4438.
(39) Bullock, R. M.; Rapolli, B. J. *J. Chem. Soc., Chem. Commun.* **1989**, 1447–1448.

J_{PH} = 9.7 Hz, CH_3), -12.05 (d, 1 H, J_{PH} = 36.1 Hz, Ru-H). IR: ν_{CO} = 1910 cm^{-1} (heptane). Anal. Calcd for $C_9H_{15}OPRu$: C, 39.84; H, 5.58. Found: C, 40.19; H, 5.56.

CpRu(dmpe)H (5). Under N_2, 0.2 mL of dmpe was added to a solution of 1.2 mmol of $CpRu(CO)_2H$ prepared as above. The solution was heated to reflux for 20 min. The yellow solution was cooled under N_2, and the solvent was removed by rotary evaporation. The residue was pumped dry in vacuo. Sublimation at 45 °C (5×10^{-3} mm) onto a water-cooled probe afforded a pale yellow solid. Yield: 236 mg, 64%. ^1H NMR (C_6D_6) δ 4.82 (br s, 5 H, C_5H_5), 1.38 (virtual t, 6 H, CH_3), 1.22 (virtual t, 6 H, CH_3'), -14.05 (t, 1 H, J_{PH} = 36.8 Hz, Ru-H).

CpRu(dmdppe)Cl. A solution of $CpRu(PPh_3)_2Cl$ (500 mg, 0.69 mmol), 0.35 mL of $Ph_2PCH_2CH_2PMe_2$ (d_{20} = 1.08 g mL^{-1}, 1.4 mmol), and 25 mL of freshly distilled toluene were combined under N_2 in a 50 mL Schlenk flask. After the mixture was heated for 10 h in a 100 °C oil bath, a noticeable amount of pale yellow precipitate separated from the orange supernatant. This was removed by cannula filtration, and the solvent was removed by rotary evaporation to yield an orange crystalline material in an oil. The desired product was recrystallized from CH_2Cl_2/heptane by partial evaporation of CH_2Cl_2 until an orange precipitate had formed. This material was isolated by filtration and washed with 3 × 10 mL of pentane. Yield: 240 mg (72%). ^1H NMR (CD_2Cl_2) δ 7.8-7.0 (m, 10 H, C_6H_5), 4.52 (s, 5 H, C_5H_5), 1.85-2.55 (m, 4 H, methylene) 1.77 (d, 3 H, J_{PH} = 8.9 Hz, CH_3), 1.68 (d, 3 H, J_{PH} = 9.8 Hz, CH_3'). Anal. Calcd for $C_{21}H_{25}ClP_2Ru$: C, 52.99; H, 5.31. Found: C, 52.95; H, 5.30.

Cp*Ru(PPh$_3$)$_2$Cl. A 100-mL schlenk flask was charged with ca. 50 mL of absolute ethanol and 2.3 g (0.9 mmol) of PPh_3. $[Cp^*RuCl_2]_n$ (500 mg) was added to this mixture. A dark red solid replaced the brown color of starting material within minutes. This mixture was heated to reflux. After 24 h, orange microcrystals had separated leaving a transparent, light-orange supernatant. The mixture was cooled to -20 °C, and the orange microcrystalline product was isolated by filtration and washed with 3 × 5 mL of cold pentane. Yield: 1.17 g (90%). ^1H NMR (see text).

Cp*Ru(dmdppe)Cl. A 35-mL Schlenk flask was charged with 250 mg (0.31 mmol) of $Cp^*Ru(PPh_3)_2Cl$ and 20 mL of benzene. $Ph_2PCH_2CH_2PMe_2$ (85 μL, 0.33 mmol) was added to this mixture and heated to reflux for 2 h. The reaction mixture was cooled and the solvent removed to afford an orange solid that was chromatographed on a 10-cm plug of silica with CH_2Cl_2 as the eluent. Evaporation of solvent followed by recrystallization from hot hexane affords the product as orange crystals. Yield: 58 mg (34%). ^1H NMR ($CDCl_3$) δ 7.8-7.0 (br, 10 H, Ph), 1.57 (d, 3 H, J_{PH} = 8.8 Hz, CH_3), 1.53 (br s, ca. 18 H, Cp* and CH_3'), 2.55 (m), 2.10 (m), 1.85 (m) (methylene resonances). Anal. Calcd for $C_{26}H_{35}ClP_2Ru$: C, 57.18; H, 6.47. Found: C, 56.99; H, 6.49.

Synthesis of Bis(phosphine) Hydrides and Deuterides from Their Chlorides. The methodology followed for this transformation was adapted from Davies, Simpson, and Moon.[8] Representative examples are outlined below.

CpRu(dmdppe)H (6). A 35-mL Schlenk flask was charged with 5 mL of dry MeOH, 90 mg (1.3 mmol) of NaOEt, and 99 mg (0.21 mmol) of CpRu(dmdppe)Cl. The reaction proceeded and was worked up as above. Recrystallization from Et_2O/pentane affords the product as white crystals. Yield: 30 mg (33%). ^1H NMR (C_6D_6), δ 8.0-7.0 (br, 10 H, C_6H_5), 4.78 (s, 5 H, C_5H_5), 1.31 (d, 3 H, J_{PH} = 8.9 Hz, CH_3), 1.28 (d, 3 H, J_{PH} = 8.3 Hz, CH_3'), -14.44 (d, J_{PH} = 35.6 Hz, Ru-H). Anal. Calcd for $C_{21}H_{26}P_2Ru$: C, 57.13; H, 5.95. Found: C, 57.16; H, 6.01.

CpRu(dmdppe)D (6-d_1). A 10-mL pear-shaped Schlenk flask (rinsed with D_2O and oven dried) was charged with 36 mg (0.6 mmol) of $NaOCD_3$, 49 mg (0.11 mmol) of CpRu(dmdppe)Cl, and 1.0 mL of CD_3OD (99.9% d_4). The solids dissolved upon heating to reflux. After 15 min of reflux, the solution changed from an orange to a yellow color. The solution was refluxed for another 6 h and then cooled. The solvent was removed in vacuo. The remaining yellow solid was extracted with 8 mL of toluene. The yellow supernatant was filtered, and the solvent was removed in vacuo. Recrystallization from ether/pentane and cooling to -20 °C yielded 15 mg (31%) of white crystals.

Cp*Ru(dmdppe)H (7). A 25-mL pear-shaped Schlenk flask was charged with 101 mg (0.18 mmol) of Cp*Ru(dmdppe)Cl, 100 mg of $NaOCH_3$, and 10 mL of dry MeOH. This orange solution was refluxed for 3 h, during which time the color changed to yellow. The solvent was removed and the residue dried overnight in vacuo. The yellow residue was extracted with a 10-mL portion of heptane and with 2 × 5 mL of ether. After filtration, the volume of the yellow solution was reduced to ca. 10 mL in vacuo. Small yellow crystals formed upon cooling to -20 °C. The supernatant was removed and the yellow crystals dried in vacuo. Yield: 60 mg (60%). ^1H NMR (C_6D_6) δ 7.8-6.9 (br, 10 H, C_6H_5), 1.88 (t, 15 H, $^4J_{PH}$ = 1.4 Hz, Cp*), 1.28 (d, 3 H, J_{PH} = 8.7 Hz, CH_3), 1.21 (d, 3 H, J_{PH} = 7.8 Hz CH_3'), -13.98 (d, J_{PH} = 35.4 Hz, Ru-H). Anal. Calcd for $C_{26}H_{36}P_2Ru$: C, 61.03; H, 7.11. Found: C, 60.70; H, 7.09.

Cp*Ru(dmdppe)D (7-d_1). A 35-mL pear-shaped Schlenk flask was charged with 50 mg (0.091 mmol) of Cp*Ru(dmdppe)Cl, 14 mg (0.24 mmol) of $NaOCD_3$, and 0.9 mL of CD_3OD. After 1 h of heating to reflux, the reaction was cooled to room temperature and the solvent removed in vacuo to afford a pale yellow solid. The solid was extracted with 2 × 10 mL of heptane. Evaporation of solvent followed by drying left 35 mg (74%) of bright yellow crystals.

CpRu(PPh$_3$)$_2$D (9-d_1). A 10-mL pear-shaped Schlenk flask was charged with 25 mg (0.40 mmol) of $NaOCD_3$, 1.0 mL of CD_3OD, and 100 mg (0.14 mmol) of $CpRu(PPh_3)_2Cl$. After being heated to reflux for 8 h, the mixture was cooled, the solvent removed, and the resulting yellow solid dried in vacuo overnight. The residue was extracted with 2 × 5 mL of toluene to give a clear, yellow solution. The solvent was removed in vacuo. Recrystallization from Et_2O/heptane affords the product as a pale yellow crystalline solid. Yield: 66 mg (68%). ^1H NMR in benzene-d_6 showed no detectable hydride resonance.

Cp*Ru(PPh$_3$)$_2$D (10-d_1). A 35-mL pear-shaped Schlenk flask (rinsed with D_2O and oven dried) was charged with 1 mL of CD_3OD, 57 mg (1 mmol) of $NaOCD_3$, and 100 mg (0.12 mmol) of $Cp^*Ru(PPh_3)_2Cl$. After heating to reflux for 24 h, the mixture was cooled and the solvent removed in vacuo. The yellow solid residue was extracted with 10 mL and 2 × 5 mL portions of toluene. The solvent was removed in vacuo to afford a yellow crystalline residue. The ^1H NMR spectrum was identical with that reported[32] for **10**, with the exception of the metal hydride resonance, which was diminished to about 2% of the expected intensity.

Cp*Ru(CO)(PCy$_3$)H (11). A 35-mL pear-shaped Schlenk flask was charged with 96 mg (0.26 mmol) of $Cp^*Ru(CO)_2Br$, 101 mg (0.36 mmol) of PCy_3, and 15 mL of freshly distilled toluene. The mixture was heated to reflux for 24 h. During this period, the solution developed an orange color. After 24 h the solution exhibited a single band in the infrared spectrum (ν_{CO} = 1925 cm^{-1}). Removal of solvent by rotary evaporation followed by recrystallization from dichloromethane/hexane affords the product as orange microcrystals. Yield: 100 mg (62%). Anal. Calcd for $C_{29}H_{48}BrOPRu$: C, 55.75; H, 7.76. Found: C, 56.06; H, 7.71.

Syntheses of η^2-Dihydrogen Complexes. A 50-mL pear-shaped Schlenk flask was charged with 100 mg (ca. 0.2 mmol) of neutral hydride. This yellow solid was dissolved in ca. 30 mL of freshly distilled diethyl ether (Et_2O). The resulting pale yellow solution was cooled to -30 °C and ca. 5 μL of 85% $HBF_4 \cdot Et_2O$ (Aldrich) was added. A flocculent, white precipitate was noted in these solutions soon after the addition of acid. The mixture was warmed to 0 °C in order to digest the precipitate for filtration. The supernatant was removed by cannula filtration, leaving an off-white to yellow colored solid. This solid was dried in vacuo. Further purification by recrystallization from acetone/Et_2O could be achieved if desired. **1a/1b**: Yield 45%. Anal. Calcd for $C_{24}H_{40}BF_4OPRu$: C, 51.15; H, 7.17. Found: C, 48.61; H, 7.14. IR (KBr disk): 2020 (m), 1965 (s), 1940 (s), 1910 cm^{-1} (m sh). ^1H NMR (CD_2Cl_2, 250 MHz): **1a** δ 5.62 (s, 5 H, C_5H_5), 2.48-1.31 (br m, ca. 33 H, C_6H_{11}); **1b** δ 5.74 (s, 5 H, C_5H_5), 2.48-1.31 (br m, ca. 33 H, C_6H_{11}). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): **1a** δ 68.5 (s); **1b** δ 76.7 (s). With selective decoupling of the ligand protons only, the resonance at 76.7 ppm is a triplet with $^2J_{P-H}$ = 20 Hz. **5a/5b**: Yield 60%. Anal. Calcd for $C_{11}H_{23}BF_4P_2Ru$: C, 32.61; H, 5.73. Found: C, 28.86; H, 5.42. ^1H NMR (CD_2Cl_2, 250 MHz): **5a** δ 5.15 (s, 5 H, C_5H_5), 1.74 (d, 6 H, J_{P-H} = 11 Hz, CH_3), 1.73 (d, 6 H, J_{P-H} = 11 Hz, CH_3'); **5b** δ 5.31 (s, 5 H, C_5H_5), 1.86 (d, 12 H, J = 13 Hz, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): **5a** δ 55.8 (s); **5b** δ 71.5 (s). **6a/6b**: Yield 23%. Anal. Calcd for $C_{21}H_{27}BF_4P_2Ru$: C, 47.65; H, 5.15. Found: C, 45.15; H, 4.96. ^1H NMR (CD_2Cl_2, 500 MHz): **6a** δ 7.74-7.43 (m, 10 H, C_6H_5), 5.02 (s, 5 H, C_5H_5), 1.95 (d, J_{PH} = 10.3 Hz, 3 H, CH_3), 1.82 (d, J_{PH} = 11.2 Hz, 3 H, CH_3'); **6b** δ 7.74-7.43 (m, 10 H, C_6H_5), 5.44 (s, 5 H, C_5H_5), 1.77 (d, J_{PH} = 10.5 Hz, 6 H, CH_3), 2.67, 2.45, 2.24, 2.09, 1.87 (m, 4 H, CH_2). **8a/8b**: Yield 80%. Anal. Calcd for $C_{32}H_{33}BF_4P_2Ru$: C, 57.58; H, 4.99. Found: C, 55.13; H, 5.03. ^1H NMR (CD_2Cl_2, 490 MHz): **8a-*RR*** δ C_6H_5 7.65-7.37 (m, 20 H, C_6H_5), 4.94 (s, 5 H, C_5H_5), 1.18 (dd, ^3J_PH = 6.1 Hz, 3 H, CH_3); **8a-*SR*** δ 7.65-7.37 (m, 20 H, C_6H_5) 4.71 (s, 5 H, C_5H_5), 0.85 (d of d, $^3J_{PH}$ = 7.0 Hz, J_{HH} = 14.2 Hz, 3 H, CH_3); **8b** δ 7.65-7.37 (m, 20 H, C_6H_5), 5.40 (s, 5 H, C_5H_5), CH_3 0.94 (dd, $^3J_{PH}$ = 6.7 Hz, J_{HH} = 14.6 Hz, 3 H), 3.36, 3.0-2.7, 2.4-2.0 (br m, 3 H, CH_2 and CH). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 202 MHz): **8a-*RR*** δ 81.8 (d) and 65.2 (d) (J_{PP} = 33.5 Hz); **8a-*RS*** δ 87.1 (d) and 70.6 (d) (J_{PP} = 30.2 Hz); **8b** δ 78.9 (d) and 61.6 (d) (J_{PP} = 29.0 Hz).

In Situ Preparation of η^2-Dihydrogen Complexes. Samples of **2a, 3a, 4a, 7a, 9a, 10a,** and **11a** were prepared by charging a 5-mm NMR tube (New Era NE-M5 or Wilmad 507) sealed onto a glass 4-mm Kontes valve with a Teflon stopcock with 10-15 mg of the appropriate hydride. This apparatus was attached to a vacuum line by means of a $^3/_8$ in. Cajon Ultra-Torr seal. The apparatus was evacuated, and the sample was

cooled in liquid N_2 or dry ice/2-propanol. Anhydrous CD_2Cl_2 (dried over 4Å molecular sieves), which had been degassed by at least 3 freeze/pump/thaw cycles, was vacuum transferred onto the solid sample. The sample was warmed to −78 °C in dry ice/2-propanol, and ambient pressure was reestablished by opening the valve to an argon bubbler. $HBF_4 \cdot Et_2O$ (1.2–1.5 equiv of 85%; Aldrich) was added under argon purge with a 10-μL syringe to the wall of the NMR tube. The sample solution and acid were frozen upon cooling with liquid N_2, and the argon atmosphere was removed under vacuum. The apparatus was shut off from dynamic vacuum, and the $HBF_4 \cdot Et_2O$ was transferred to a level just above the frozen sample solution by gentle heating, being careful not to melt the frozen solution below during this transfer process. The NMR tube was then flame sealed under vacuum, plunged into a dry ice/2-propanol bath to melt the frozen sample, and gently agitated to mix the reagents. In cases where an excess of acid was employed, ^1H NMR showed complete consumption of neutral hydride at 195 K. ^1H NMR (CD_2Cl_2, 250 MHz, 298 K) (resonances due to coordinated hydrogen and ruthenium hydrides are listed in Table I): **2a** 7.56–7.31 (br m, 15 H, C_6H_5), 5.44 (s, 5 H, C_5H_5); **3a** δ C_6H_5 7.67–7.46 (br m, 10 H, C_6H_5), 5.44 (s, 5 H, C_5H_5), 2.12 (d, J_{PH} = 10.8 Hz, 3 H, CH_3), 2.09 (d, J_{PH} = 10.7 Hz, 3 H, CH_3'); **4a** (293 K) δ 5.49 (s, 5 H, C_5H_5), 1.78 (d, J_{PH} = 10.9 Hz, 6 H, CH_3); **7a** ($CD_2Cl_2/CHFCl_2$ [1:5], 490 MHz, 195 K) δ 1.71 (s, 15 H, C_5Me_5), 1.76 (d, J_{PH} = 8.7 Hz, 6 H, CH_3), 2.64, 2.26 (br m, 4 H, CH_2); **7b** ($CD_2Cl_2/CHFCl_2$ [1:5], 490 MHz, 298 K) δ 1.92 (s, 15 H, C_5Me_5), CH_3 1.76 (d, J_{PH} = 10.5 Hz, 6 H), 2.41 (q, J_{PH} = 7.5 Hz, 2 H, CH_2), 2.38 (q, J_{PH} = 7.4 Hz, 2 H, CH_2'). The phenyl resonances for **7a**/**7b** are not reported due to overlap with the freon solvent. **9a** (CD_2Cl_2, 500 MHz, 222 K) δ 7.40–6.95 (br m, 30 **H**, C_6H_5), 4.83 (s, 5 H, C_5H_5); **9b** (CD_2Cl_2, 500 MHz, 298 K) δ 7.49–7.29 (br m, 30 H, C_6H_5), 4.91 (s, 5 H, C_5H_5); **10a** (CD_2Cl_2, 250 MHz, 266 K) δ 7.5–7.1 (br m, 30 H, C_6H_5), 1.30 (s, 15 H, C_5Me_5); **10b** (CD_2Cl_2, 250 MHz, 266 K) δ 7.5–7.1 (br m, 30 H, C_6H_5), 1.34 (s, 15 H, C_5Me_5); **11a** ($CD_2Cl_2/CHFCl_2$ [1:5], 250 MHz, 298 K) δ 2.10 (s, 15 H, C_5Me_5), 2.0–1.3 (br m, 33 H, C_6H_{11}); **11b** ($CD_2Cl_2/CHFCl_2$ [1:5], 250 MHz, 298 K) δ 2.19 (s, 15 H, C_5Me_5), 2.0–1.3 (br m, 33 H, C_6H_{11}).

Kinetics of the Isomerization of 9a → 9b. Samples were prepared by charging a 5-mm NMR tube sealed onto a Kontes Teflon tap with the neutral hydride **9** and a slight excess of 85% $HBF_4 \cdot Et_2O$. ^1H NMR showed complete consumption of neutral hydride at 195 K. Similar experiments were carried out with the corresponding deuteride **9**-d_1 to study the rate of isomerization of **9a**-d_1 → **9b**-d_1.

The ^1H probe in a Bruker WM-500 or Yale 490 NMR spectrometer was cooled to 195 K and its temperature monitored with the Bruker BVT-1000 temperature controller unit. The sample was removed from the dry ice/2-propanol bath, inserted into the spinner, and lowered into the probe. The shims were adjusted and the probe warmed to the desired temperature of the kinetics experiment. Data collection was carried out with a microprogram that utilized variable delay (VD) and variable counter (VC) lists so that the initial rates of isomerization as well as long reaction times could be well characterized by a sufficient amount of data.

Peak intensities were analyzed from stacked plots of the cyclopentadienyl resonances of the ^1H NMR spectra. It was assumed that peak intensities were proportional to concentration since the line widths of resonances due to starting material and products were similar throughout the observed course of isomerization. A best-fit line generated from a least-squares fit of ln [peak intensity] versus time provided the first-order rate constant k_{obs}.

The major sources of error considered from these kinetic experiments included the accuracy and reproducibility of the BVT-1000 temperature controller, which was calibrated against a methanol sample for the probe in use. Corrected temperature values were interpolated from a quadratic function that corrolated the dial temperature of the BVT-1000 controller with the temperature calculated from the chemical shift difference of the hydroxyl and methyl resonances in CH_3OH. Reproducibility of dial temperatures was ±0.2 deg. Errors in time measurements under computer control were assumed to be negligible relative to temperature uncertainties. Uncertainties in peak intensities were estimated as ±10%. However, uncertainties derived from statistical analysis of least-squares residuals were consistently smaller than propagated uncertainties with use of the above estimates. The reported uncertainty in the isomerization rate therefore represents one standard deviation (±σ) derived from the slope of the best-fit line.

Spin Saturation Transfer Experiments. Samples of mixtures of **5a**/**5b** or **6a**/**6b** were either prepared as detailed above or isolated as mixtures of the η^2-dihydrogen and dihydride cations. Samples were prepared with carefully degassed solvents in flame-sealed 5-mm NMR tubes. T_1's for the Cp resonances of each sample were determined by the 180–τ–90 pulse sequence. Decoupler power was adjusted so that complete saturation of the irradiated peak was observed after irradiating for at least five T_1's. The extent of saturation transfer was ascertained by examining difference spectra resulting from subtraction of data collected with and without saturation at the resonance of interest. Rates of exchange were calculated as previously outlined for a two-site-exchange process.[34] By using the Eyring equation, $\ln (k_{obs}) = \kappa k T h^{-1} \exp(-\Delta G^{\ddagger}/RT)$, and assuming a transmission coefficient $\kappa = 1$, the free energies of activation could be calculated. Uncertainty in the rate constant was calculated from the residuals of the best-fit line drawn to the data. The uncertainties in rates and temperatures could be propagated to find the uncertainty in $\Delta G^{\ddagger}$. A 20% uncertainty in the rate propagated with a 1% uncertainty in temperature resulted in ca. 2% uncertainty in $\Delta G^{\ddagger}$.

Eyring Plots of Spin Saturation Transfer Kinetics. Spin saturation transfer experiments were used to probe the rate of isomerization over a 40 deg range spanned by samples of **6a**/**6b** in two different solvents (THF-d_8 and CD_2Cl_2). Temperature control was monitored as described above. A period of at least 5 half-lives was allowed for the sample to reestablish equilibrium when the temperature was changed. Eyring plots of $\ln (k_{obs}/T)$ vs $1/T$ were constructed. A best-fit line drawn from a least-squares analysis of the data provided the enthalpy and entropy of activation from the slope and intercept, respectively, of the best-fit line. Uncertainties in the activation enthalpy and entropy were calculated from the uncertainties in the slope and intercept of the best-fit line.

van't Hoff Plots. Product ratios of **6b**/**6a** corresponding to the process **6a** ⇌ **6b** were determined from 278–302 K in CD_2Cl_2 and from 303–323 K in THF-d_8 by integration of the Cp resonances after applying a 90° observation pulse and waiting at least five T_1's to allow for complete signal relaxation. Temperature control was monitored as previously described. A period of 5 half-lives to allow for chemical equilibration at the new temperature was used. Plotting $\ln K_{eq}$ vs $1/T$ provided the enthalpy and entropy of reaction from the slope and intercept, respectively, of the best-fit line determined from least-squares analysis. Uncertainties in ΔH and ΔS were determined by propagating the uncertainties in the slope and intercept of the best-fit line.

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