

# Effect of the Ligand and Metal on the $pK_a$ Values of the Dihydrogen Ligand in the Series of Complexes $[M(H_2)H(L)_2]^+$ , $M = Fe, Ru, Os$ , Containing Isosteric Ditertiaryphosphine Ligands, L

E. Paul Cappellani, Samantha D. Drouin, Guochen Jia, Patricia A. Maltby, Robert H. Morris,\* and Caroline T. Schweitzer

Contribution from the Department of Chemistry and the Scarborough Campus, University of Toronto, Toronto, Ontario M5S 1A1, Canada

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**Abstract:** The new dihydrogen complexes *trans*- $[MH(H_2)L_2]BF_4$ ,  $L = P(C_6H_4-4-R)_2CH_2CH_2P(C_6H_4-4-R)_2$ ,  $R = CF_3$ ,  $M = Fe, Ru$ , and  $Os$ ,  $R = CH_3$ ,  $M = Fe$ ,  $R = OMe$ ,  $M = Ru$ , are prepared by reaction of the dihydride complexes  $MH_2L_2$  with  $HBF_4$ . The H-H bond length of the spinning  $H_2$  ligand does not change significantly as a function of R (from  $CF_3$  to  $CH_3$  when  $M = Fe$  and from  $CF_3$  to  $OCH_3$  for  $M = Ru$ ) according to  $^1H$  NMR  $T_1$  and  $^1J(HD)$  measurements while there is a lengthening for the Os complexes. The rate constants for H atom exchange (reflecting the ease of homolytic splitting of  $H_2$ ) increase with the increasing donor ability of R for a given metal as do the  $pK_a$  values (reflecting a decrease in ease of heterolytic splitting). The electrochemical properties of some complexes  $MH(Cl)L_2$  and  $MH_2L_2$  are reported. As expected  $H_2$  acidity decreases as the parent hydride becomes easier to oxidize with this change in R (same M). The trend in dihydrogen  $pK_a$  values as a function of the metal,  $Fe < Os < Ru$ , is distinctively different to the trend in  $pK_a$  values of the dihydride complexes  $M(H_2)(CO)_4$ ,  $Fe < Ru < Os$ , and  $[M(C_5H_5)(H)_2(PPh_3)_2]^+$ ,  $Ru < Os$ . The high H-H bond energy of the  $Ru^{2+}$  complexes *trans*- $[RuH(H_2)L_2]BF_4$  is probably the reason why they are less acidic than corresponding  $Os^{2+}$  complexes. A consideration of the  $pK_a$  values correctly indicated that a  $RuH_2L_2/[RuH(H_2)L_2]^+$  mixture would be more effective at H/D exchange between  $D_2$  and  $HO^dBu$  than the dihydrogen complex alone.

## Introduction

The reactions of transition metal dihydrogen complexes<sup>1</sup> is a growing field.<sup>2</sup> We are interested in gaining a semiquantitative understanding of reactions which involve the homolytic and heterolytic splitting of the dihydrogen ligand in order to rationally design new soluble metal catalysts and to discover new reactions, such as the protonation of coordinated dinitrogen by dihydrogen.<sup>3</sup> This work describes the preparation and reactions of the dihydrogen complexes *trans*- $[MH(H_2)L_2]^+$ , where M is Fe, Ru, and Os and where L is a bidentate ligand:

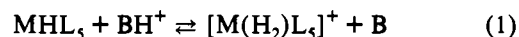
$$L = (4-RC_6H_4)_2PCH_2CH_2P(C_6H_4-4-R)_2$$

R	ligand abbreviation
$CF_3$	dtfpe
H	dppe
$CH_3$	dtpe
$CH_3O$	dape

The ligands are listed according to increasing electron-donating ability on the basis of studies of complexes of Mo,<sup>4</sup> W,<sup>4</sup> and Re.<sup>5</sup> The electronics at the metal can be altered greatly while maintaining constant steric interactions in the complex by use of this series of ligands. The properties of the dihydrogen ligands in the complexes *trans*- $[MH(H_2)L_2]^+$  have already been examined in detail for the ligands dppe and depe ( $PEt_2CH_2CH_2PEt_2$ ),<sup>6,7</sup> but there was the problem of separating the electronic and steric effects of the two ligands; in addition, the  $pK_a$  of these complexes had not been examined. The present work examines how the properties of the dihydrogen ligand change with a change in R. The reactions of the  $H_2$  ligand examined here as a function of

R include the kinetics of H atom exchange between dihydrogen and hydride sites and the kinetics and thermodynamics of the acidity of the dihydrogen ligand. The former is thought to involve the homolytic splitting of the  $H_2$  ligand,<sup>6,7</sup> while the latter involves the heterolytic splitting. Part of this work has been communicated.<sup>8</sup>

Previous studies of the complexes  $[Ru(C_5R'_5)(H_2)L]^+$ ,  $R' = H, Me$  have revealed how sensitive dihydrogen acidity is to the nature of L.<sup>9-11</sup> Approximate  $pK_a$  values for these and other dihydrogen complexes have been obtained by measuring the equilibrium constant by NMR for the reaction between a suitable acid of known  $pK_a$ ,  $BH^+$ , and the conjugate base hydride  $MHL_5$  of the dihydrogen complex  $[M(H_2)L_5]^+$  (eq 1).



A wide range of  $pK_a$  values (<0 to >16) of dihydrogen complexes has been reported,<sup>10-15</sup> and this work has been recently reviewed.<sup>2,16</sup>

Tilset and Parker have shown how electrochemical data can be combined with  $pK_a$  data in a thermochemical cycle to give

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metal-hydride bond dissociation enthalpies ( $\Delta H_{\text{BDE}}\{\text{MH}\}$ ) of transition-metal-hydride complexes in  $\text{CH}_3\text{CN}$ .<sup>17,18</sup> For example the complex  $\text{Mn}(\text{CO})_5\text{H}$  is reported to have a  $\Delta H_{\text{BDE}}\{\text{MnH}\}$  of 68 kcal mol<sup>-1</sup>, while complexes  $\text{M}(\text{C}_5\text{H}_5)(\text{CO})_2\text{H}$ ,  $\text{M} = \text{Fe}, \text{Ru}$ , have  $\Delta H_{\text{BDE}}$  of 58 and 65 kcal mol<sup>-1</sup>, respectively; the first value agrees fairly well with calorimetric determinations. A useful equation for understanding the acidity of dihydrogen complexes in THF or  $\text{CH}_2\text{Cl}_2$  has been derived from an identical thermochemical cycle (eq 2).<sup>11</sup>

$$1.37\text{p}K_a\{\text{M}(\text{H}_2)\} = \Delta H_{\text{BDE}}\{\text{M}(\text{H}_2)\} - 23.1E_{1/2}(\text{MH}/\text{MH}^-) - C \quad (2)$$

It relates the  $\text{p}K_a$  (pseudoaqueous scale<sup>19</sup>) of a dihydrogen complex  $\text{M}(\text{H}_2)\text{L}'_5$  (all  $\text{L}'$  not necessarily the same) to the electrochemical potential  $E_{1/2}(\text{MH}/\text{MH}^-)$  for the oxidation of the hydride  $[\text{MHL}'_5]^-$  in THF or  $\text{CH}_2\text{Cl}_2$  (versus  $\text{Fe}(\text{C}_5\text{H}_5)_2^+/\text{Fe}(\text{C}_5\text{H}_5)_2$  reference potential). The bond dissociation energy,  $\Delta H_{\text{BDE}}\{\text{M}(\text{H}_2)\}$  is the energy required to take an H atom from the  $\text{M}(\text{H}_2)$  unit in solution (eq 3).

$$\Delta H_{\text{BDE}}\{\text{M}(\text{H}_2)\text{L}'_5\} = \Delta H_{\text{f}}\{\text{H}^*\} + \Delta H_{\text{f}}\{\text{MHL}'_5\} - \Delta H_{\text{f}}\{\text{M}(\text{H}_2)\text{L}'_5\} \quad (3)$$

Such a  $\Delta H_{\text{BDE}}$  energy has been measured in the gas phase to be 83.5 kcal mol<sup>-1</sup> for the postulated species  $[\text{Mn}(\text{H}_2)(\text{CO})_5]^+$ ; this value should also apply approximately for the complex in nonpolar solvents.<sup>20</sup> The reason why this value is much higher than the  $\Delta H_{\text{BDE}}\{\text{MnH}\}$  for  $\text{MnH}(\text{CO})_5$  mentioned above is probably because a strong H-H bond as well as the Mn-H interactions have to be broken in  $[\text{Mn}(\text{H}_2)(\text{CO})_5]^+$ ; presumably the coordinated H-H bond is weakened somewhat from the  $\Delta H_{\text{BDE}}\{\text{H}_2(\text{g})\}$  value of 104 kcal mol<sup>-1</sup>. Therefore it may be possible to obtain important information on the strength of H-H bonding in dihydrogen complexes by determining the magnitude of such  $\Delta H_{\text{BDE}}\{\text{M}(\text{H}_2)\}$  values.

Initially  $C$  in eq (2) was evaluated as 59 kcal mol<sup>-1</sup> on the assumption that the  $\Delta H_{\text{BDE}}(\text{Ru}-\text{H})$  values of the complexes  $[\text{Ru}(\text{C}_5\text{R}_5)(\text{H})_2\text{L}]^+$  in THF or  $\text{CH}_2\text{Cl}_2$  were approximately 65 kcal mol<sup>-1</sup>.<sup>11,15</sup> This gave  $\Delta H_{\text{BDE}}\{\text{M}(\text{H}_2)\}$  values of about 65 kcal mol<sup>-1</sup> for the dihydrogen complexes  $[\text{Ru}(\text{C}_5\text{R}_5)(\text{H}_2)\text{L}]^+$  in solution which are close in energy to the dihydride tautomers just mentioned.<sup>11</sup> However recent work indicates that these  $\Delta H_{\text{BDE}}$  values should be about 72 kcal mol<sup>-1</sup>,<sup>21-24</sup> and so a better value of  $C$  in eq 2 is 66 kcal mol<sup>-1</sup>. Equation 2 with  $C = 66$  should now provide  $\Delta H_{\text{BDE}}$  values which can be compared to other  $\Delta H_{\text{BDE}}$  values determined by Tilset, Parker, and co-workers. As absolute values, the energies are only as good as the assumptions which were described by these workers.<sup>17</sup> How the energy  $\Delta H_{\text{BDE}}$  in eq 3 varies with the metal and ligands and how it compares to metal hydride BDE values is a subject of this study.

Dihydrogen complexes of the correct acidity and lability with respect to  $\text{H}_2$  loss/coordination are known to catalyze H/D exchange between  $\text{D}_2$  and alcohols.<sup>25</sup> Albeniz et al. found that *trans*- $[\text{Ru}(\text{H}_2)(\text{H})(\text{dppe})_2]\text{BF}_4$  was not as effective a catalyst as  $[\text{Ir}(\text{bq})(\text{PPh}_3)_2\text{H}(\text{H}_2\text{O})]\text{SbF}_6$ ; the latter complex is known to react with  $\text{H}_2$  to give  $[\text{Ir}(\text{bq})(\text{PPh}_3)_2\text{H}(\text{H}_2)]\text{SbF}_6$ . Our acidity studies

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suggested that a mixture of *trans*- $[\text{Ru}(\text{H}_2)(\text{H})(\text{dppe})_2]\text{BF}_4$  and  $\text{RuH}_2(\text{dppe})_2$  might be a more efficient catalyst system than just *trans*- $[\text{Ru}(\text{H}_2)(\text{H})(\text{dppe})_2]\text{BF}_4$  on its own, and so this is also studied here.

## Experimental Section

All operations were conducted under a purified nitrogen or argon atmosphere using vacuum line or glovebox techniques. Solvents were dried and degassed before use. Tetrahydrofuran (THF), diethyl ether ( $\text{Et}_2\text{O}$ ), and hexane were dried over and distilled from sodium benzophenone ketyl. Methanol (MeOH) and ethanol (EtOH) were distilled from magnesium methoxide and magnesium ethoxide, respectively. Acetone was dried over potassium carbonate. Dichloromethane was distilled from calcium hydride. Deuterated solvents were dried over Linde type 4 Å molecular sieves and degassed prior to use. The phosphorus ligands dppe and depe and the precursor compound  $\text{PCl}_2\text{CH}_2\text{CH}_2\text{PCl}_2$  were purchased from Digital Specialty Ltd. All other reagents were purchased from Aldrich Chemical Company Inc. Osmium tetroxide was received as a loan from Johnson-Matthey Co. The method of Chatt and Hayter<sup>26</sup> was used to prepare  $[\text{Os}_2\text{Cl}_3(\text{PEtPh}_2)_6]\text{Cl}\cdot 2\text{H}_2\text{O}$ . Complexes  $\text{MH}_2\text{L}_2$  and *trans*- $[\text{MH}(\text{H}_2)\text{L}_2]\text{BF}_4$  were prepared by the method of Bautista et al.<sup>6</sup> ( $\text{M} = \text{Fe}, \text{Ru}$ ,  $\text{L} = \text{dppe}, \text{depe}$ ) or Earl et al.<sup>7</sup> ( $\text{M} = \text{Os}$ ,  $\text{L} = \text{dppe}, \text{depe}$ ). Ditertiaryphosphines  $\text{P}(\text{C}_6\text{H}_4\text{-}4\text{-R})_2\text{CH}_2\text{CH}_2\text{P}(\text{C}_6\text{H}_4\text{-}4\text{-R})_2$ ,  $\text{R} = \text{Me}$  (dtpe) and  $\text{R} = \text{MeO}$  (dape), were prepared by the method of Chatt et al.<sup>5</sup>  $\text{RuCl}_2(\text{PPh}_3)_3$ ,<sup>27</sup>  $\text{RuCl}_2(\text{DMSO})_4$ ,<sup>28</sup>  $[\text{Os}(\text{C}_5\text{H}_5)(\text{H})_2(\text{PPh}_3)_2]\text{BF}_4$ ,<sup>29</sup> and the acids of Table 1<sup>10,11</sup> were prepared according to literature methods.

Infrared spectra were recorded as Nujol mulls on NaCl plates using a Nicolet SDX FTIR spectrometer. NMR spectra were obtained on a Varian XL-400, operating at 400.00 MHz for  $^1\text{H}$ , 161.98 MHz for  $^{31}\text{P}$ , or on a Varian XL-200 operating at 200.00 MHz for  $^1\text{H}$  and 80.98 MHz for  $^{31}\text{P}$ . Reported chemical shifts refer to room temperature conditions (19 °C) unless specified otherwise. All  $^{31}\text{P}$  NMR were proton decoupled, unless stated otherwise.  $^{31}\text{P}$  NMR chemical shifts were measured relative to ~1%  $\text{P}(\text{OMe})_3$  in  $\text{C}_6\text{D}_6$  sealed in coaxial capillaries and are reported relative to  $\text{H}_3\text{PO}_4$  by use of  $\delta(\text{P}(\text{OMe})_3) = 140.4$  ppm.  $^1\text{H}$  chemical shifts were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. In all cases, high-frequency shifts are reported as positive.  $T_1$  measurements were made at 400 or 200 MHz, as specified, using the inversion recovery method.

Fast atom bombardment mass spectrometry (FAB MS) was carried out with a VG 70-250S mass spectrometer using a 3-nitrobenzylalcohol (NBA) matrix. All FAB MS samples were dissolved in acetone and placed in the matrix under a blanket of nitrogen. Microanalyses were performed by the Canadian Microanalytical Service Ltd., Delta, B.C.

A PAR Model 273 potentiostat was used for cyclic voltammetry studies. The electrochemical cell contained a Pt working electrode, W secondary electrode, and Ag wire reference electrode in a Luggin capillary. The cyclic voltammograms were collected in THF containing 0.2 M *n*-Bu<sub>4</sub>-NPF<sub>6</sub> as the supporting electrolyte. Reported potentials are referenced to ferrocene which was added to these solutions.

**Preparation of 1,2-Bis[bis(*p*-trifluoromethylphenyl)phosphino]ethane, dtfpe.** The preparation of this ligand was reported by Chatt et al.<sup>5</sup> Their method involved reacting *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>Br with *n*-butyllithium followed by

(21) Smith et al. (ref 22) used eq 2 with  $C = 58.3$  kcal mol<sup>-1</sup> for  $\text{p}K_a$  and  $E_{1/2}$  values in  $\text{CH}_3\text{CN}$  to calculate  $\Delta\text{BDE}(\text{Ru}-\text{H}) = 74-77$  kcal mol<sup>-1</sup> for some complexes  $[\text{Ru}(\text{C}_5\text{H}_5)(\text{PR}_3)_2(\text{H}_2)]^+$ . They assumed that the difference in  $\text{p}K_a$  between the aqueous scale and the  $\text{CH}_3\text{CN}$  scale is 7.8 units as determined by Coetzee for amines (see reference 23) to convert  $\text{p}K_a$  values (pseudoaqueous scale) for the Ru complexes obtained by us (ref 11) using protonated phosphines. We have recently determined the  $\text{p}K_a$  of protonated phosphines in  $\text{CD}_3\text{CN}$  by use of protonated amines of known  $\text{p}K_a$  in this solvent (ref 24). The difference between  $\text{p}K_a$  values of protonated phosphines on the  $\text{CH}_3\text{CN}$  scale and those on the aqueous scale is  $5.4 \pm 0.3$ , not the value of 7.8. Therefore the  $\Delta\text{BDE}$  values for Ru hydride complexes calculated by Smith et al. (ref 22) have to be reduced by 3 to 71-74 kcal mol<sup>-1</sup>.

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Table 1. Acids of Known pK<sub>a</sub> Used in the pK<sub>a</sub> Determinations

base form	acid form	pK <sub>a</sub>
PCy <sub>3</sub>	HPCy <sub>3</sub> <sup>+</sup>	9.7 <sup>39,40</sup>
P <sup>t</sup> Bu <sub>3</sub>	HP <sup>t</sup> Bu <sub>3</sub> <sup>+</sup>	11.4 <sup>39,40</sup>
RuH(C <sub>5</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (1)	[Ru(H) <sub>2</sub> (C <sub>5</sub> H <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]BF <sub>4</sub> (1H <sup>+</sup> )	8.0 ± 0.2 <sup>10</sup>
RuH(C <sub>5</sub> Me <sub>5</sub> )(dppm) (2)	[RuH <sub>2</sub> (C <sub>5</sub> Me <sub>5</sub> )(dppm)]BF <sub>4</sub> (2H <sup>+</sup> )	8.8 ± 0.2 <sup>11</sup>
RuH(C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> (3)	[Ru(H) <sub>2</sub> (C <sub>5</sub> Me <sub>5</sub> )(PPh <sub>3</sub> ) <sub>2</sub> ]BF <sub>4</sub> (3H <sup>+</sup> )	11.1 ± 0.2 <sup>11</sup>
RuH(C <sub>5</sub> Me <sub>5</sub> )(PMePh <sub>2</sub> ) <sub>2</sub> (4)	[Ru(H) <sub>2</sub> (C <sub>5</sub> Me <sub>5</sub> )(PMePh <sub>2</sub> ) <sub>2</sub> ]BPh <sub>4</sub> (4H <sup>+</sup> )	12.2 ± 0.4 <sup>11</sup>
RuH(C <sub>5</sub> Me <sub>5</sub> )(PMe <sub>2</sub> Ph) <sub>2</sub> (5)	[Ru(H) <sub>2</sub> (C <sub>5</sub> Me <sub>5</sub> )(PMe <sub>2</sub> Ph) <sub>2</sub> ]BPh <sub>4</sub> (5H <sup>+</sup> )	14.3 ± 0.4 <sup>11</sup>
RuH(C <sub>5</sub> Me <sub>5</sub> )(PMe <sub>3</sub> ) <sub>2</sub> (6)	[Ru(H) <sub>2</sub> (C <sub>5</sub> Me <sub>5</sub> )(PMe <sub>3</sub> ) <sub>2</sub> ]BPh <sub>4</sub> (6H <sup>+</sup> )	16.3 ± 0.6 <sup>11</sup>
proton sponge (7)	[proton sponge-H] <sup>+</sup> (7H <sup>+</sup> )	12.3 <sup>41</sup>
MeO <sup>-</sup>	MeOH	15.2 <sup>42</sup>
EtO <sup>-</sup>	EtOH	15.8 <sup>42</sup>
<sup>i</sup> PrO <sup>-</sup>	PrOH	16.5 <sup>42</sup>
<sup>t</sup> BuO <sup>-</sup>	<sup>t</sup> BuOH	16.6 <sup>42</sup>

the addition of Cl<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PCl<sub>2</sub>. The present procedure involves a Grignard reaction instead of the use of butyllithium.

In a pressure-equalizing addition funnel, 1-(trifluoromethyl)-4-bromobenzene (5 mL, 0.036 mol) was combined with diethyl ether (15 mL). This solution was added dropwise into a three-necked flask which was equipped with a reflux condenser and which contained magnesium turnings (2 g, excess) in 150 mL of diethyl ether. The addition caused the solution to reflux gently and turn green. The solution was cooled to -80 °C, and Cl<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PCl<sub>2</sub> (2.10 g, 0.009 mol) in 10 mL of diethyl ether was added dropwise to the stirring solution causing a white solid to form. After warming to room temperature, 100 mL of a saturated aqueous ammonium chloride solution was slowly added. The layers were separated, and the aqueous layer was washed four times with 15 mL of diethyl ether. The ether layers were combined and filtered to remove insoluble impurities. Under vacuum, all but 10 mL of the ether was removed. Addition of 20 mL of MeOH caused the precipitation of a cream-colored powder. The solid (3.9 g, 65%) was filtered off and washed with methanol: δ(<sup>31</sup>P, THF) -12.4 (s).

**Preparation of *trans*-FeH(Cl)(dtpe)<sub>2</sub>.** 1,2-Bis[di(*p*-tolyl)phosphino]ethane, dtpe, (0.12 g, 0.56 mmol) was dissolved in 30 mL of THF, and FeCl<sub>2</sub> (0.035 g, 0.28 mmol) was added. To the resulting tan-colored solution was added NaBH<sub>4</sub> (0.01 g, 0.28 mmol) along with 5 mL of ethanol. The solution was stirred for 1 h. This dark red solution was filtered through Celite, the volume was reduced to about 2 mL, and 5 mL of hexanes was added. A red precipitate (54% yield) was filtered off and washed with a small amount of diethyl ether: δ(<sup>31</sup>P, C<sub>6</sub>H<sub>6</sub>) 79.9 (s); δ(<sup>1</sup>H, C<sub>6</sub>D<sub>6</sub>) -29.1 (quint, <sup>2</sup>J<sub>HP</sub> = 48.0 Hz); FAB MS calcd for C<sub>60</sub>H<sub>65</sub><sup>35</sup>-Cl<sup>56</sup>FeP<sub>4</sub> 1001, found 1001 (M<sup>+</sup>).

**Preparation of *trans*-FeH(Cl)(dtfpe)<sub>2</sub>.** This compound was prepared in 49% yield by the above method except that a crop of the bright yellow *cis*-Fe(H)<sub>2</sub>(dtfpe)<sub>2</sub> was isolated prior to crystallization of the red *trans*-FeH(Cl)(dtfpe)<sub>2</sub>. The dihydride was filtered off after the first addition of hexanes. The dark red solution was left at room temperature overnight, while dark red needles formed. The solution was cooled for 2 h, and the dark red needles were filtered off and washed with hexanes: yield 49%; δ(<sup>31</sup>P, C<sub>6</sub>H<sub>6</sub>) 81.6 (s); δ(<sup>1</sup>H, C<sub>6</sub>D<sub>6</sub>) -29.2 (quint, <sup>2</sup>J<sub>HP</sub> = 52.2 Hz); FAB MS. Calcd for C<sub>60</sub>H<sub>41</sub><sup>35</sup>ClF<sub>24</sub><sup>56</sup>FeP<sub>4</sub>: 1432; Found: 1432 (M<sup>+</sup>). Anal. Calcd for C<sub>60</sub>H<sub>41</sub>ClF<sub>24</sub>FeP<sub>4</sub>: C, 50.28; H, 2.88; Found: C, 50.05; H, 2.98.

**Preparation of *cis*-FeH<sub>2</sub>(dtpe)<sub>2</sub>.** Under dinitrogen, dtpe (0.5 g, 1.1 mmol) was dissolved in 50 mL of THF, and FeCl<sub>2</sub> (0.07 g, 0.55 mmol) was added along with 5 mL of EtOH. NaBH<sub>4</sub> (0.07 g, excess) was added to the stirring solution. The solution was left stirring for about 20 h. After 1 h the solution turned dark red and after 20 h it had a brown-yellow color. The mixture was filtered through THF saturated Celite. The volume was reduced to 3 mL, and 10 mL of hexanes was added to give a bright yellow precipitate. The solid (0.24 g, 46%) was filtered and recrystallized from THF/ether: δ(<sup>31</sup>P, C<sub>6</sub>H<sub>6</sub>) 102.1 (br), 89.8 (br); δ(<sup>1</sup>H, C<sub>6</sub>D<sub>6</sub>) -12.82 (m); FAB MS calcd for C<sub>60</sub>H<sub>66</sub><sup>56</sup>FeP<sub>4</sub> 965.9, found 965.8 (M<sup>+</sup>), 964.8 (M<sup>+</sup> - H), 963.8 (M<sup>+</sup> - 2H).

**Preparation of *cis*-FeH<sub>2</sub>(dtfpe)<sub>2</sub>.** This bright yellow compound was obtained in 50% yield by the above method: δ(<sup>31</sup>P, THF) 107.3 (br), 94.2 (br); δ(<sup>1</sup>H, C<sub>6</sub>D<sub>6</sub>) -13.49 (m); FAB MS calcd for C<sub>60</sub>H<sub>42</sub>F<sub>24</sub><sup>56</sup>FeP<sub>4</sub> 1398.2, observed 1398.2 (M<sup>+</sup>), 1397.2 (M<sup>+</sup> - H), 1396.2 (M<sup>+</sup> - 2H). Anal. Calcd for C<sub>60</sub>H<sub>42</sub>F<sub>24</sub>FeP<sub>4</sub>: C, 51.55; H, 3.03. Found: C, 52.31; H, 3.63 (this sample was found to contain some free dtfpe which is difficult to remove; this would explain the high C analysis).

**Preparation of *trans*-[FeH(H<sub>2</sub>)L<sub>2</sub>]BF<sub>4</sub> where L = dtfpe and dtpe.** These pale yellow complexes were prepared in 80% yield by protonation of the

*cis*-dihydride species with excess HBF<sub>4</sub>·Et<sub>2</sub>O in diethyl ether. FeH<sub>2</sub>L<sub>2</sub> (0.13 mmol) was suspended in 10 mL of diethyl ether. Under dihydrogen, 0.3 mL of HBF<sub>4</sub>·Et<sub>2</sub>O (excess) was added dropwise with stirring. A yellow precipitate formed immediately. The product was filtered off and washed several times with diethyl ether: yield, ca. 80%; [FeH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup> δ(<sup>31</sup>P, acetone) 94.7 (s); δ(<sup>1</sup>H, acetone-*d*<sub>6</sub>) -7.62 (br, Fe-(H<sub>2</sub>)), -12.55 (quint, Fe-H, J<sub>HP</sub> = 44.7 Hz). FAB MS calcd for C<sub>60</sub>H<sub>43</sub>F<sub>24</sub><sup>56</sup>FeP<sub>4</sub> 1398.8, found 1396.4 (M<sup>+</sup> - 2H), 1395.4 (M<sup>+</sup> - 3H). Anal. Calcd for C<sub>60</sub>H<sub>43</sub>BF<sub>28</sub>FeP<sub>4</sub>: C, 48.47; H, 2.92. Found: C, 47.91; H, 2.89. [FeH(H<sub>2</sub>)(dtpe)<sub>2</sub>]<sup>+</sup> δ(<sup>31</sup>P, acetone) 90.7 (s); δ(<sup>1</sup>H, acetone-*d*<sub>6</sub>) -8.20 (br, Fe-(H<sub>2</sub>)), -12.50 (br m, Fe-H); FAB MS calcd for C<sub>60</sub>H<sub>67</sub><sup>56</sup>-FeP<sub>4</sub> 967.5, found 967.0 (M<sup>+</sup>), 965.0 (M<sup>+</sup> - 2H), 964.0 (M<sup>+</sup> - 3H).

**Preparation of *trans*-[FeH(HD)(dtfpe)<sub>2</sub>]BF<sub>4</sub>.** To prepare a solution of DBF<sub>4</sub>, 1 mL of D<sub>2</sub>O was added dropwise to an equal volume of HBF<sub>4</sub>·Et<sub>2</sub>O until the effervescence ceased. Addition of this mixture to an ether slurry of Fe(H)<sub>2</sub>(dtfpe)<sub>2</sub> proceeded as described above for the preparation of [FeH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]BF<sub>4</sub>: δ(<sup>1</sup>H, acetone-*d*<sub>6</sub>, 293 K, 200 MHz) -7.7 (1:1:1 t, <sup>1</sup>J<sub>HD</sub> = 32 ± 1 Hz), -12.6 (quint, <sup>2</sup>J<sub>HP</sub> = 46 Hz).

**Solid-State Reaction of *trans*-[FeH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]BF<sub>4</sub>.** The solid dihydrogen complex (yellow) was heated to ~170 °C under vacuum. The resulting blue solid was placed (while still hot) under 1 atm of D<sub>2</sub>, causing it to become pale yellow. This yellow solid was cooled to -80 °C and, to it was added cold (-80 °C) acetone-*d*<sub>6</sub>. The solution was stirred at -80 °C for 30 min, and a <sup>1</sup>H NMR spectrum of the solution at -55 °C was recorded: δ(<sup>1</sup>H, 218 K) -7.6 (1:1:1 t, <sup>1</sup>J<sub>HD</sub> = 32 ± 1 Hz), -12.5 (quint). These resonances correspond to *trans*-[FeD(HD)(dtfpe)<sub>2</sub>]BF<sub>4</sub>.

**Preparation of *trans*-RuCl<sub>2</sub>(dape)<sub>2</sub>.** A mixture of 0.20 g of dape (0.44 mmol) and 0.19 g of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (0.20 mmol) in 10 mL of acetone was stirred at room temperature to give a yellow precipitate. The precipitate was collected by filtration, washed with acetone, and dried under vacuum: yield, 0.13 g, 60%; δ(<sup>31</sup>P, CH<sub>2</sub>Cl<sub>2</sub>) 41.1 (s).

**Preparation of *cis*- and *trans*-RuCl<sub>2</sub>(dape)<sub>2</sub>.** A mixture of 0.20 g of dape (0.44 mmol) and 0.10 g of RuCl<sub>2</sub>(DMSO)<sub>4</sub> (0.21 mmol) in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> was stirred at room temperature overnight to give a yellow solution. The solvent was then removed completely. Addition of 10 mL of Et<sub>2</sub>O to the residue produced a yellow powder. The powder was collected by filtration, washed with Et<sub>2</sub>O, and dried under vacuum: yield, 0.14 g, 62%. The <sup>31</sup>P NMR spectrum shows that the product contains ca. 10% *trans*-RuCl<sub>2</sub>(dape)<sub>2</sub> and 90% of *cis*-RuCl<sub>2</sub>(dape)<sub>2</sub>: *cis*-RuCl<sub>2</sub>(dape)<sub>2</sub> δ(<sup>31</sup>P, C<sub>6</sub>H<sub>6</sub>) 48.8 (t), 33.5 (t, <sup>2</sup>J<sub>PP</sub> = 20.7 Hz).

**Preparation of *trans*-RuCl<sub>2</sub>(dtfpe)<sub>2</sub>.** A mixture of 0.30 g of dtfpe (0.45 mmol) and 0.20 g of RuCl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub> (0.20 mmol) in 20 mL of acetone was stirred at room temperature for 1 h to give a yellow solution. The solvent was then removed completely, and then 10 mL of hexane was added to the reaction flask to give a yellow precipitate. The precipitate was collected by filtration, washed with hexane, and dried under vacuum overnight: yield, 0.26 g, 86%; δ(<sup>31</sup>P, C<sub>6</sub>H<sub>6</sub>) 44.2 (s). Anal. Calcd for C<sub>60</sub>H<sub>40</sub>Cl<sub>2</sub>F<sub>24</sub>P<sub>4</sub>Ru: C, 47.63; H, 2.67; Cl, 4.69. Found: C, 47.33; H, 2.71; Cl, 5.12.

**Preparation of *cis*-RuCl<sub>2</sub>(dtfpe)<sub>2</sub>.** A mixture of 0.50 g of dtfpe (0.75 mmol) and 0.15 g of RuCl<sub>2</sub>(DMSO)<sub>4</sub> (0.31 mmol) in 10 mL of CH<sub>2</sub>Cl<sub>2</sub> reacted at room temperature overnight without stirring to give some crystalline solid and a yellow-orange solution. The CH<sub>2</sub>Cl<sub>2</sub> was then removed completely, and to the residue was added 3 mL of Et<sub>2</sub>O and 7 mL of hexane to give a yellow powder. The powder was collected by filtration, washed with hexane, and dried under vacuum: yield, 0.30 g, 64%; δ(<sup>31</sup>P, THF) 56.4 (t), 39.8 (t, <sup>2</sup>J<sub>PP</sub> = 18.8 Hz). Anal. Calcd for C<sub>60</sub>H<sub>40</sub>Cl<sub>2</sub>F<sub>24</sub>P<sub>4</sub>Ru: C, 47.63; H, 2.67; Cl, 4.69. Found: C, 47.76; H, 2.75; Cl, 5.22.

**Preparation of *cis*- and *trans*-RuH<sub>2</sub>(dape)<sub>2</sub>.** A mixture of 0.50 g of RuCl<sub>2</sub>(dape)<sub>2</sub> (0.41 mmol, both *cis* and *trans* isomers present) and 0.20 g of NaOMe (3.7 mmol) in 30 mL of MeOH was refluxed for 5 h to give a colorless solution. The MeOH was then removed completely under vacuum. To the residue was then added 30 mL of THF and 0.20 g of NaBH<sub>4</sub> (5.7 mmol). The resulting mixture was then refluxed for 5 h to give a colorless solution. The solvent was then removed completely, and the residue was extracted with benzene. The benzene was removed again. The residue was washed with a small amount of MeOH briefly to give a white solid. The solid was then collected by filtration, washed with MeOH, and dried under vacuum: yield, 0.30 g, 62%. <sup>31</sup>P NMR integration of the product in THF shows that it consists of *ca.* 87% of *cis*-RuH<sub>2</sub>(dape)<sub>2</sub> and 13% of *trans*-RuH<sub>2</sub>(dape)<sub>2</sub>: *cis*-RuH<sub>2</sub>(dape)<sub>2</sub> δ (<sup>31</sup>P, C<sub>6</sub>H<sub>6</sub>) 76.1 (t), 62.5 (br, <sup>2</sup>J<sub>PP</sub> = 15.7 Hz); δ (<sup>1</sup>H, C<sub>6</sub>D<sub>6</sub>) -8.40 (m); *trans*-RuH<sub>2</sub>(dape)<sub>2</sub> δ (<sup>31</sup>P, C<sub>6</sub>H<sub>6</sub>) 80.4 (s); δ (<sup>1</sup>H, C<sub>6</sub>D<sub>6</sub>) -8.28 (quint, <sup>2</sup>J<sub>PH</sub> = 19 Hz). Anal. Calcd for C<sub>60</sub>H<sub>66</sub>P<sub>4</sub>O<sub>8</sub>Ru·MeOH: C, 62.51; H, 6.02. Found: C, 62.20; H, 5.66.

**Preparation of *cis*- and *trans*-RuH<sub>2</sub>(dtfpe)<sub>2</sub>.** A mixture of 1.0 g of *cis*-RuCl<sub>2</sub>(dtfpe)<sub>2</sub> (0.66 mmol) and 0.30 g of NaOMe (5.5 mmol) in 30 mL of MeOH and 30 mL of benzene was refluxed overnight to give a clear yellow solution. The solvent of the reaction mixture was removed completely, and the residue was extracted with 40 mL of CH<sub>2</sub>Cl<sub>2</sub>. The CH<sub>2</sub>Cl<sub>2</sub> was removed again. Addition of 30 mL of MeOH to the residue gives a pale yellow solid. The solid was collected by filtration, washed with MeOH, and dried under vacuum: yield, 0.65 g, 68%. A <sup>31</sup>P NMR spectrum in THF of the product indicates that it consists of *ca.* 91% of *cis*-RuH<sub>2</sub>(dtfpe)<sub>2</sub> and *ca.* 9% of *trans*-RuH<sub>2</sub>(dtfpe)<sub>2</sub>: *cis*-RuH<sub>2</sub>(dtfpe)<sub>2</sub> δ (<sup>31</sup>P, C<sub>6</sub>H<sub>6</sub>) 82.6 (t), 67.8 (br, <sup>2</sup>J<sub>PP</sub> = 13.3 Hz); δ (<sup>1</sup>H, CD<sub>2</sub>Cl<sub>2</sub>) -8.98 (m); *trans*-RuH<sub>2</sub>(dtfpe)<sub>2</sub> δ (<sup>31</sup>P, C<sub>6</sub>H<sub>6</sub>) 84.8 (s); δ (<sup>1</sup>H, CD<sub>2</sub>Cl<sub>2</sub>) -8.76 (quint, <sup>2</sup>J<sub>PH</sub> = 19 Hz). Anal. Calcd. for C<sub>60</sub>H<sub>42</sub>F<sub>24</sub>P<sub>4</sub>Ru: C, 49.91; H, 2.93. Found: C, 49.53; H, 2.87.

**Preparation of [RuH(dtfpe)<sub>2</sub>]BF<sub>4</sub>.** A solution of 1.0 g of RuH<sub>2</sub>(dtfpe)<sub>2</sub> (0.69 mmol) in 30 mL of Et<sub>2</sub>O was titrated with HBF<sub>4</sub>·Et<sub>2</sub>O to give a white solid under an atmosphere of dihydrogen. The white solid was collected by filtration, washed with Et<sub>2</sub>O, and dried under vacuum to give a yellow solid: yield 0.98 g, 93%; δ (<sup>31</sup>P, THF) 64.5 (s); δ (<sup>1</sup>H, CD<sub>2</sub>Cl<sub>2</sub>) no hydride resonance observed.

**Preparation of *trans*-[RuH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]BF<sub>4</sub>.** The yellow solid [RuH(dtfpe)<sub>2</sub>]BF<sub>4</sub> was stored under a dihydrogen atmosphere for a few minutes to give a white solid. NMR data for the solid show that all the product is [Ru(H)(H<sub>2</sub>)(dtfpe)<sub>2</sub>]BF<sub>4</sub>. δ (<sup>31</sup>P, THF) 71.4 (s); δ (<sup>1</sup>H, acetone-*d*<sub>6</sub>, 293 K) -4.11 (br, Ru(H<sub>2</sub>)), -9.85 (quint, <sup>2</sup>J<sub>PH</sub> = 17.8 Hz, RuH). Anal. Calcd for C<sub>60</sub>H<sub>43</sub>BF<sub>28</sub>P<sub>4</sub>Ru: C, 47.05; H, 2.83. Found: C, 46.94; H, 2.87.

**Observation of *trans*-[RuH(HD)(dtfpe)<sub>2</sub>]BF<sub>4</sub>.** A <sup>1</sup>H NMR sample of [RuH(dtfpe)<sub>2</sub>]BF<sub>4</sub> in acetone-*d*<sub>6</sub> was stored under an HD atmosphere generated by slowly dropping D<sub>2</sub>O into a flask containing NaH for 30 min: δ (<sup>1</sup>H, 293 K) -4.16 (1:1:1 t, <sup>1</sup>J<sub>HD</sub> = 33.1, Ru(HD)), -9.78 (quint, <sup>2</sup>J<sub>PH</sub> = 17.7 Hz, RuH); [RuD(HD)(dtfpe)<sub>2</sub>]<sup>+</sup> was also present -4.28 (1:1:1 t, <sup>1</sup>J<sub>HD</sub> = 33.1, Ru(HD)).

**Observation of *trans*-[RuH(H<sub>2</sub>)(dape)<sub>2</sub>]BF<sub>4</sub>.** Method 1. To a solution of 0.20 g of the mixture of *cis*- and *trans*-RuH<sub>2</sub>(dape)<sub>2</sub> in 10 mL of THF was added HBF<sub>4</sub>·Et<sub>2</sub>O, drop by drop, to give a clear colorless solution. A <sup>31</sup>P NMR spectrum for the solution indicates that there is only [RuH(H<sub>2</sub>)(dape)<sub>2</sub>]BF<sub>4</sub> (δ = 66.3). The THF was removed under vacuum. The residue was redissolved in THF, and a <sup>31</sup>P NMR at this stage showed that extensive decomposition had occurred.

**Method 2.** To a suspension of 0.20 g of RuH<sub>2</sub>(dape)<sub>2</sub> in 20 mL of Et<sub>2</sub>O was added a slight excess of HBF<sub>4</sub>·Et<sub>2</sub>O to give a white solid. The solid was then collected by filtration, washed with Et<sub>2</sub>O, and dried under vacuum. The <sup>31</sup>P NMR spectrum for the solid dissolved in THF indicates that a complicated mixture formed.

**Method 3.** The compounds RuH<sub>2</sub>(dape)<sub>2</sub> and [HPCy<sub>3</sub>]BPh<sub>4</sub><sup>10</sup> were loaded into an NMR tube. Acetone-*d*<sub>6</sub> was then added, and <sup>31</sup>P NMR spectra were collected. The products were [RuH(H<sub>2</sub>)(dape)<sub>2</sub>]<sup>+</sup> and free PCy<sub>3</sub>: δ (<sup>1</sup>H, acetone-*d*<sub>6</sub>) -5.0 (br, Ru(H<sub>2</sub>)), -10.30 (quint, <sup>2</sup>J<sub>PH</sub> = 18.0 Hz, RuH). δ (<sup>31</sup>P) 66.3 (s), 9.0 (s).

**Observation of *trans*-[RuH(HD)(dape)<sub>2</sub>]<sup>+</sup>.** The acid [DPCy<sub>3</sub>]BF<sub>4</sub> was prepared as a white solid by titrating a solution of PCy<sub>3</sub> in diethyl ether with D<sub>2</sub>O acidified with HBF<sub>4</sub> in a fashion similar to the preparation of [HPtol<sub>3</sub>]BF<sub>4</sub><sup>10</sup>. The compounds RuH<sub>2</sub>(dape)<sub>2</sub> and [DPCy<sub>3</sub>]BF<sub>4</sub> were loaded into a <sup>1</sup>H NMR tube. Acetone-*d*<sub>6</sub> was then added: δ (<sup>1</sup>H) -4.8 (br 1:1:1 t, <sup>1</sup>J<sub>HD</sub> = 31, Ru(HD)), -10.2 (quint, <sup>2</sup>J<sub>PH</sub> = 17.8 Hz, RuH).

**Preparation of *cis*-OsCl<sub>2</sub>(dtfpe)<sub>2</sub>.** [Os<sub>2</sub>Cl<sub>3</sub>(PPh<sub>2</sub>Et)<sub>6</sub>]Cl (0.64 g, 0.36 mmol) and dtfpe (1.00 g, 1.5 mmol) were heated with stirring to 200 °C

**Table 2.** Reagents and Products of Low-Temperature Deprotonation Reactions Observed by <sup>1</sup>H NMR Spectroscopy at -80 °C

reagent	observed product
<i>trans</i> -[FeH(H <sub>2</sub> )(dtfpe) <sub>2</sub> ]BF <sub>4</sub>	<i>cis</i> -Fe(H) <sub>2</sub> (dtfpe) <sub>2</sub>
<i>trans</i> -[FeH(H <sub>2</sub> )(dppe) <sub>2</sub> ]BF <sub>4</sub>	<i>cis</i> -Fe(H) <sub>2</sub> (dppe) <sub>2</sub>
<i>trans</i> -[RuH(H <sub>2</sub> )(dppe) <sub>2</sub> ]BF <sub>4</sub>	<i>trans</i> -Ru(H) <sub>2</sub> (dppe) <sub>2</sub>
<i>trans</i> -[OsH(H <sub>2</sub> )(dppe) <sub>2</sub> ]BF <sub>4</sub>	<i>trans</i> -Os(H) <sub>2</sub> (dppe) <sub>2</sub> <sup>a</sup>

<sup>a</sup> After the sample was left at room temperature for 5 min, the *cis* isomer was the major product observed by use of room-temperature <sup>1</sup>H NMR spectroscopy.

in the absence of solvent to give a dark brown oil. The flask was cooled to 80 °C and evacuated for 1 h. Cold hexanes were added to the residue, and the resulting pale yellow precipitate (0.995 g, 86%) was filtered off and washed several times with cold hexanes. The *trans* isomer was not present: δ (<sup>31</sup>P, THF) 10.3 (br), 8.1 (br).

**Preparation of *cis*- and *trans*-OsH<sub>2</sub>(dtfpe)<sub>2</sub>.** A slurry of LiAlH<sub>4</sub> (0.062 g, 1.63 mmol) in 5 mL of THF was added to a stirred solution of *cis*-OsCl<sub>2</sub>(dtfpe)<sub>2</sub> (0.48 g, 0.30 mmol) in 25 mL of THF. The mixture was refluxed for 1 h and cooled, and then 10 mL of EtOH was added. After solvent evaporation, 20 mL of THF was added to the residue. This mixture was filtered through THF saturated Celite. The solvent was removed under vacuum, and 20 mL of acetone along with 0.06 g (1.2 mmol) of NaCl was added to the pale yellow residue. The mixture was refluxed for 1.5 h. The acetone was removed under vacuum, and 20 mL of THF was added to the remaining solid. The suspension was filtered through THF-saturated Celite, and NaBH<sub>4</sub> (0.34 g, 0.90 mmol) in 10 mL of EtOH was added to the filtrate. After stirring for 30 min the solvent was removed under vacuum, and the residue was treated with benzene and filtered through Celite. Concentration of the product to 2 mL and addition of hexanes (8 mL) caused precipitation of the pale yellow product. The solid (0.30 g, 65%), a mixture of the *cis* and *trans* isomers, was filtered off and washed with a small amount of methanol followed by hexanes: FAB MS calcd for C<sub>60</sub>H<sub>42</sub>F<sub>24</sub><sup>192</sup>OsP<sub>4</sub> 1534.3, observed 1534.6 (M<sup>+</sup>), 1533.3 (M<sup>+</sup> - H), 1532.3 (M<sup>+</sup> - 2H); *trans*-OsH<sub>2</sub>(dtfpe)<sub>2</sub> δ (<sup>31</sup>P, THF) 52.2 (s); δ (<sup>1</sup>H, acetone-*d*<sub>6</sub>) -11.10 (quint, <sup>2</sup>J<sub>HP</sub> = 15.2 Hz); *cis*-OsH<sub>2</sub>(dtfpe)<sub>2</sub> δ (<sup>31</sup>P, THF) 49.8 (br), 39.8 (br); δ (<sup>1</sup>H, acetone-*d*<sub>6</sub>) -10.47 (m). Anal. Calcd. for C<sub>60</sub>H<sub>42</sub>F<sub>24</sub>OsP<sub>4</sub>: C, 47.01; H, 2.76. Found: C, 46.73; H, 2.66.

**Preparation of *trans*-[OsH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]BF<sub>4</sub>.** *cis*- and *trans*-OsH<sub>2</sub>(dtfpe)<sub>2</sub> (0.20 g, 0.13 mmol) was suspended in 10 mL of diethyl ether. Under dihydrogen, 0.3 mL of HBF<sub>4</sub>·Et<sub>2</sub>O (excess) was added dropwise with stirring. A white precipitate formed immediately. The product (0.18 g, 85%) was filtered off and washed several times with diethyl ether: FAB MS calcd for C<sub>60</sub>H<sub>43</sub><sup>192</sup>OsP<sub>4</sub>F<sub>24</sub> 1535.1, found 1534.7 (M<sup>+</sup>), 1532.7 (M<sup>+</sup> - 2H), 1531.7 (M<sup>+</sup> - 3H); δ (<sup>31</sup>P, THF) 39.9 (s); δ (<sup>1</sup>H, acetone-*d*<sub>6</sub>, 293 K) -5.97 (br, Os(H<sub>2</sub>)), -8.95 (br, Os-H). Anal. Calcd for C<sub>60</sub>H<sub>43</sub>BF<sub>28</sub>OsP<sub>4</sub>: C, 44.46; H, 2.67. Found: C, 44.06; H, 2.60.

**Synthesis of *trans*-[OsD(HD)(dtfpe)<sub>2</sub>]BF<sub>4</sub>.** A slurry of LiAlD<sub>4</sub> (0.1 g) in 5 mL of THF was added to a stirred solution of *cis*-OsCl<sub>2</sub>(dtfpe)<sub>2</sub> (0.5 g) in 25 mL of THF. The mixture was refluxed for 1 h, cooled, and stirred overnight at room temperature. A 5-mL portion of MeOD was added to the stirring solution. This mixture was filtered through THF saturated Celite. Concentration of the solution to 2 mL and addition of hexanes (8 mL) caused precipitation of a pale yellow precipitate. The solid was filtered off and washed with hexanes. Under argon, the yellow solid was suspended in 10 mL of diethyl ether. A solution of HBF<sub>4</sub>·Et<sub>2</sub>O (0.2 mL, excess) was added dropwise with stirring. A white precipitate formed immediately. The product was filtered off and washed several times with diethyl ether: δ (<sup>1</sup>H, acetone-*d*<sub>6</sub>, 223 K) -5.97 (1:1:1 t, <sup>1</sup>J<sub>HD</sub> = 28.3 Hz, Os(HD)), -9.18 (quint, <sup>2</sup>J<sub>HP</sub> = 14 Hz, OsH).

**Low-Temperature Deprotonation of *trans*-[MH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup> Complexes, M = Fe, Ru, Os, L = dppe, M = Fe, L = dtfpe.** Under argon gas, a known amount of [MH(H<sub>2</sub>)L<sub>2</sub>]BF<sub>4</sub> was dissolved in acetone-*d*<sub>6</sub> at -80 °C. To the stirring solution was added an equivalent amount of *n*-BuLi (as a 1.0 M solution in hexanes). The mixture was stirred for 30 min at -80 °C. Table 2 lists the products observed.

**Preparation of Protonated "Proton Sponge", 7H<sup>+</sup>.** Excess HBF<sub>4</sub>·Et<sub>2</sub>O was added to proton sponge (1,8-bis(dimethylamino)naphthalene, ~30 mg) dissolved in 15 mL of diethyl ether. The white solid produced was filtered off, washed with diethyl ether, and redissolved in MeOH. A solution of NaBPh<sub>4</sub> in MeOH was added, and immediately a white solid precipitated out. The crude [proton sponge-H]BPh<sub>4</sub> was collected by filtration, washed with cold MeOH, and recrystallized as white needles

**Table 3.** Acid/Base Equilibria for Complexes [MH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup>/MH<sub>2</sub>L<sub>2</sub> (L = dtfpe at 20 °C under 1 atm of H<sub>2</sub>)  
B<sub>1</sub> + B<sub>2</sub>H<sup>+</sup> ⇌ B<sub>2</sub> + B<sub>1</sub>H<sup>+</sup>

no.	B <sub>1</sub>	B <sub>2</sub> H <sup>+</sup>	reaction conditions <sup>a</sup>	B <sub>2</sub>	B <sub>1</sub> H <sup>+</sup>	K <sup>b</sup>	pK <sub>a</sub> <sup>cis</sup> of	
							[MH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	M
1.	OsH <sub>2</sub> L <sub>2</sub>	1H <sup>+</sup>	THF-d <sub>8</sub> ; 0.3 h	1	[OsH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	2 ± 1 (8)	8.3 ± 0.2	Os
2.	1	[OsH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	THF-d <sub>8</sub> ; 24 h	OsH <sub>2</sub> L <sub>2</sub>	1H <sup>+</sup>	0.3 ± 0.1 (0.1)	8.5 ± 0.2	Os
3.	PCy <sub>3</sub>	[OsH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	THF; 20 h	OsH <sub>2</sub> L <sub>2</sub>	HPCy <sub>3</sub> <sup>+</sup>	>20 <sup>c</sup>	<9.7	Os
4.	RuH <sub>2</sub> L <sub>2</sub>	1H <sup>+</sup>	THF-d <sub>8</sub> ; 18 h	1	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	7 ± 4	8.8 ± 0.3	Ru
5.	RuH <sub>2</sub> L <sub>2</sub>	1H <sup>+</sup>	THF; 3 h	1	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	13 ± 6 (111)	9.1 ± 0.3	Ru
6.	RuH <sub>2</sub> L <sub>2</sub>	[OsH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	THF; 0.2 h	OsH <sub>2</sub> L <sub>2</sub>	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	5 ± 1 (35)	9.1 ± 0.2	Ru
7.	RuH <sub>2</sub> L <sub>2</sub>	1H <sup>+</sup>	ac-d <sub>6</sub> ; 3 h	1	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	8 ± 4	9.1 ± 0.3	Ru
8.	1	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	ac-d <sub>6</sub> ; 3 h	RuH <sub>2</sub> L <sub>2</sub>	1H <sup>+</sup>	0.2 ± 0.1	8.7 ± 0.3	Ru
9.	FeH <sub>2</sub> L <sub>2</sub>	[OsH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	THF; 24 h	OsH <sub>2</sub> L <sub>2</sub>	[FeH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	0.2 ± 0.1	7.7 ± 0.3	Fe
10.	OsH <sub>2</sub> L <sub>2</sub>	[FeH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	THF-d <sub>8</sub> ; 0.2 h	FeH <sub>2</sub> L <sub>2</sub>	[OsH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	4 ± 2	7.8 ± 0.3	Fe

<sup>a</sup> Reactions in deuterated solvents were monitored by <sup>1</sup>H NMR; those in nondeuterated by <sup>31</sup>P NMR. <sup>b</sup> K<sup>cis</sup> (K<sup>trans</sup> in brackets). Refer to eqs 8 and 9 for the definitions of K. <sup>c</sup> Impurity with <sup>31</sup>P resonance at 45.8 ppm(s) is also produced.

**Table 4.** Acid/Base Equilibria for the Complexes [MH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup>/MH<sub>2</sub>L<sub>2</sub> (L = dppe under 1 atm of H<sub>2</sub>)  
B<sub>1</sub> + B<sub>2</sub>H<sup>+</sup> ⇌ B<sub>2</sub> + B<sub>1</sub>H<sup>+</sup>

no.	B <sub>1</sub>	B <sub>2</sub> H <sup>+</sup>	reaction conditions <sup>a</sup>	B <sub>2</sub>	B <sub>1</sub> H <sup>+</sup>	K <sup>b</sup>	pK <sub>a</sub> <sup>cis</sup> of	
							[MH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	M
1.	OsH <sub>2</sub> L <sub>2</sub>	4H <sup>+</sup>	THF-d <sub>8</sub> ; 14 h	4	[OsH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	3 ± 1 (25)	12.7 ± 0.1	Os
2.	OsH <sub>2</sub> L <sub>2</sub>	4H <sup>+</sup>	ac-d <sub>6</sub> ; 18 h	4	[OsH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	2 ± 1 <sup>c</sup>	12.5 ± 0.1	Os
3.	OsH <sub>2</sub> L <sub>2</sub>	5H <sup>+</sup>	ac-d <sub>6</sub> ; 3 h	d	d	<0.05	<13	Os
4.	OsH <sub>2</sub> L <sub>2</sub>	MeOH	THF/ac; 3 h	d	d	e	<15	Os
5.	5	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	THF-d <sub>8</sub> ; 13 h	RuH <sub>2</sub> L <sub>2</sub>	5H <sup>+</sup>	2 ± 1	14 ± 0.4	Ru
6.	RuH <sub>2</sub> L <sub>2</sub>	5H <sup>+</sup>	ac-d <sub>6</sub> ; 16 h	5	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	0.2 ± 0.1	13.6 ± 0.4	Ru
7.	5	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	ac-d <sub>6</sub> ; 16 h	RuH <sub>2</sub> L <sub>2</sub>	5H <sup>+</sup>	5 ± 2	13.6 ± 0.4	Ru
8.	RuH <sub>2</sub> L <sub>2</sub>	MeOH	MeOH; 3 h	MeO <sup>-</sup>	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	f	~15	Ru
9.	RuH <sub>2</sub> L <sub>2</sub>	3H <sup>+</sup>	ac-d <sub>6</sub> ; 3 h	3	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	>50	>12.5	Ru
10.	FeH <sub>2</sub> L <sub>2</sub>	[OsH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	THF; 0.2 h	OsH <sub>2</sub> L <sub>2</sub>	[FeH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	0.10 ± 0.05	11.8 ± 0.4	Fe
11.	FeH <sub>2</sub> L <sub>2</sub>	4H <sup>+</sup>	THF; 12 h	4	[FeH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	~1 <sup>g</sup>	12.2 ± 0.5	Fe
12.	FeH <sub>2</sub> L <sub>2</sub>	7H <sup>+</sup>	THF; 5 h	7	[FeH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	~1 <sup>g</sup>	12.1 ± 0.5	Fe
13.	FeH <sub>2</sub> L <sub>2</sub>	5H <sup>+</sup>	THF; 1 h	d	d	<0.05	<13	Fe

<sup>a</sup> Deuterated solvents indicate that <sup>1</sup>H NMR was used; nondeuterated solvents indicate that <sup>31</sup>P NMR was used; ac = acetone. <sup>b</sup> K<sup>cis</sup> (K<sup>trans</sup> in brackets). Refer to eqs 8 and 9 for the definitions of K. <sup>c</sup> Average of two values. <sup>d</sup> Reactants observed, but not products. <sup>e</sup> No [OsH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup> observed but traces of side products produced; <sup>31</sup>P NMR: 23.6 (s), 8.9 (s). <sup>f</sup> [RuH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup> observed but not RuH<sub>2</sub>L<sub>2</sub> (too insoluble). <sup>g</sup> Some free dppe observed <sup>31</sup>P NMR: -13.4 ppm.

**Table 5.** Acid/Base Equilibria for the Complexes [FeH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup>/FeH<sub>2</sub>L<sub>2</sub> (L = dtpe)<sup>a</sup>  
B<sub>1</sub> + B<sub>2</sub>H<sup>+</sup> ⇌ B<sub>2</sub> + B<sub>1</sub>H<sup>+</sup>

no.	B <sub>1</sub>	B <sub>2</sub> H <sup>+</sup>	reaction conditions	B <sub>2</sub>	B <sub>1</sub> H <sup>+</sup>	K <sup>a</sup>	pK <sub>a</sub> <sup>cis</sup> of [FeH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>
1.	FeH <sub>2</sub> L <sub>2</sub>	4H <sup>+</sup>	THF	4	[FeH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	3 ± 1	12.7
2.	4	[FeH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	THF	FeH <sub>2</sub> L <sub>2</sub>	4H <sup>+</sup>	0.5 ± 0.2	12.5
3.	FeH <sub>2</sub> L <sub>2</sub>	5H <sup>+</sup>	THF	b	b	<0.05	<13

<sup>a</sup> Reactions monitored by <sup>31</sup>P NMR. <sup>b</sup> No products observed.

**Table 6.** Acid/Base Equilibria for the Complexes [RuH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup>/RuH<sub>2</sub>L<sub>2</sub> (L = dape)  
B<sub>1</sub> + B<sub>2</sub>H<sup>+</sup> ⇌ B<sub>2</sub> + B<sub>1</sub>H<sup>+</sup>

no.	B <sub>1</sub>	B <sub>2</sub> H <sup>+</sup>	reaction conditions	B <sub>2</sub>	B <sub>1</sub> H <sup>+</sup>	K <sup>a</sup>	pK <sub>a</sub> <sup>cis</sup> of [RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>
1.	RuH <sub>2</sub> L <sub>2</sub>	6H <sup>+</sup>	THF-d <sub>8</sub> ; 3 h, 12 h	6	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	3 ± 1 <sup>b</sup> (20)	16.8 ± 0.7
2.	RuH <sub>2</sub> L <sub>2</sub>	6H <sup>+</sup>	ac-d <sub>6</sub> ; 3 h, 12 h	6	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	0.4 ± 0.2	15.9 ± 0.7
3.	RuH <sub>2</sub> L <sub>2</sub>	5H <sup>+</sup>	ac-d <sub>6</sub> ; 3 h	5	[RuH(H <sub>2</sub> )L <sub>2</sub> ] <sup>+</sup>	>20	>15.5

<sup>a</sup> K<sup>cis</sup> (K<sup>trans</sup> in brackets). Refer to eqs 8 and 9 for the definitions of K. <sup>b</sup> Average of four values.

from CH<sub>2</sub>Cl<sub>2</sub> and MeOH: δ (<sup>1</sup>H, CD<sub>2</sub>Cl<sub>2</sub>) 18.7 (br s, 1H), 6.8–8.0 (m, 26H), 2.8 (d, 12H).

**Equilibrium Constant Measurements.** Appropriate amounts of an acid (hydride complex, [HPCy<sub>3</sub>]<sup>+</sup>, 7H<sup>+</sup>, or alcohol) were mixed with a base (dihydride complex) in THF-d<sub>8</sub> or acetone-d<sub>6</sub>. The resulting mixture was stirred at 20 °C under a dihydrogen atmosphere for a period from 3 to 18 h before <sup>1</sup>H and/or <sup>31</sup>P NMR spectra were collected. The relative concentrations of species involved in the equilibrium were determined by integration. When <sup>31</sup>P NMR was employed, data were collected with gated proton decoupling and a delay time of 10 s between pulses. Further experimental details are found in Tables 3–7.

Some <sup>31</sup>P NMR chemical shifts of complexes in THF at equilibrium not listed above: 1 67.9 (s); 1H<sup>+</sup> 58.4 (s); 4 46.1 (s); 4H<sup>+</sup> 40.9 (s); 5 26.4 (s); 5H<sup>+</sup> 25.4 (s); *cis*-Fe(H<sub>2</sub>)(dtfpe)<sub>2</sub> 107.3 (br), 94.2 (br); [FeH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup> 94.3 (s); *cis*-Fe(H<sub>2</sub>)(dppe)<sub>2</sub> 103.2 (br), 90.8 (br); [FeH(H<sub>2</sub>)(dppe)<sub>2</sub>]<sup>+</sup> 92.0; *cis*-FeH<sub>2</sub>(dtpe)<sub>2</sub> 102.2 (br), 89.9 (br); [FeH(H<sub>2</sub>)(dtpe)<sub>2</sub>]<sup>+</sup> 90.2 (s); *cis*-Ru(H<sub>2</sub>)(dtfpe)<sub>2</sub> 82.6 (t), 67.8 (t); *trans*-Ru(H<sub>2</sub>)(dtfpe)<sub>2</sub> 84.8 (s); [RuH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup> 71.5 (s); *trans*-RuH<sub>2</sub>(depe)<sub>2</sub> 84.4 (s); *cis*-RuH<sub>2</sub>(depe)<sub>2</sub> 76.0 (m), 63.0 (m); [Ru(η<sup>2</sup>-H<sub>2</sub>)H(depe)<sub>2</sub>]<sup>+</sup> 68.5 (s); *cis*-Os(H<sub>2</sub>)(dtfpe)<sub>2</sub> 50.4 (m), 40.4 (m); *trans*-Os(H<sub>2</sub>)(dtfpe)<sub>2</sub> 52.1 (s); [OsH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup> 40.4 (s); *cis*-Os(H<sub>2</sub>)(dppe)<sub>2</sub> 45.7 (t), 35.7 (t); *trans*-Os(H<sub>2</sub>)(dppe)<sub>2</sub> 49.8 (s); [OsH(H<sub>2</sub>)(dppe)<sub>2</sub>]<sup>+</sup> 37.6 (s); *trans*-OsH<sub>2</sub>(depe)<sub>2</sub> 49.2 (s); *cis*-OsH<sub>2</sub>(depe)<sub>2</sub> 39.2 (m), 30.2 (m); [Os(η<sup>2</sup>-H<sub>2</sub>)H(depe)<sub>2</sub>]<sup>+</sup> 36.4 (s); PCy<sub>3</sub> 9.0 (s); [HPCy<sub>3</sub>]BPh<sub>4</sub> 31.6 (s); P<sup>t</sup>Bu<sub>3</sub> 62.7 (s); [HP<sup>t</sup>Bu<sub>3</sub>]<sup>+</sup> 56.6 (s); dtfpe -12.6 (s); dppe -13.4 (s); dtpe -14.8 (s); dape -15.7; depe -19.3.

Some <sup>1</sup>H NMR chemical shifts of complexes in equilibria solution in THF-d<sub>8</sub> at equilibrium not listed above: 1 -12.3 (t); 1H<sup>+</sup> -7.3 (t); 5H<sup>+</sup> -9.5 (t); 6 -14.3 (t); 6H<sup>+</sup> -10.4 (t); *cis*-FeH<sub>2</sub>(dtpe)<sub>2</sub> -13.3 (m); *cis*-RuH<sub>2</sub>(dape)<sub>2</sub> -8.8 (m); *trans*-RuH<sub>2</sub>(dape)<sub>2</sub> -8.5 (quint); [RuH(H<sub>2</sub>)(dape)<sub>2</sub>]<sup>+</sup>

Table 7. Acid/Base Equilibria for Complexes  $[MH(H_2)L_2]^+/MH_2L_2$ , L = depe (Reaction Time 1 h)

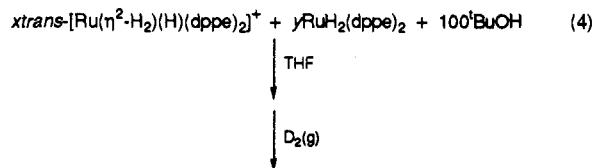
no.	B <sub>1</sub>	+	B <sub>2</sub> H <sup>+</sup>	reaction conditions	B <sub>2</sub>	+	B <sub>1</sub> H <sup>+</sup>	pK <sub>a</sub> <sup>cia</sup> of $[MH(H_2)L_2]^+$
1.	OsH <sub>2</sub> L <sub>2</sub>	+	EtOH	EtOH →	EtO <sup>-</sup>	+	$[OsH(H_2)L_2]^+$	>16
2.	OsH <sub>2</sub> L <sub>2</sub>	+	<sup>i</sup> PrOH	<sup>i</sup> PrOH ←				<16.5
3.	RuH <sub>2</sub> L <sub>2</sub>	+	EtOH	EtOH →	EtO <sup>-</sup>	+	$[RuH(H_2)L_2]^+$	>16
4.	RuH <sub>2</sub> L <sub>2</sub>	+	<sup>i</sup> PrOH	<sup>i</sup> PrOH ⇌	<sup>i</sup> PrO <sup>-</sup>	+	$[RuH(H_2)L_2]^+$	~16.5
5.	FeH <sub>2</sub> L <sub>2</sub>	+	EtOH	EtOH ⇌	EtO <sup>-</sup>	+	$[FeH(H_2)L_2]^+$	~16 <sup>a</sup>

<sup>a</sup> Some decomposition; free ligand observed.

(dape)<sub>2</sub><sup>+</sup> -5.0 (br), -10.4 (quint); *cis*-Os(H)<sub>2</sub>(dtfpe)<sub>2</sub> -11.0 (m); *trans*-Os(H)<sub>2</sub>(dtfpe)<sub>2</sub> -11.8 (quint);  $[OsH(H_2)(dtfpe)_2]^+$  -5.9 (br), -9.4 (br).

**Reactions of Ru(C<sub>5</sub>H<sub>5</sub>) and Os(C<sub>5</sub>H<sub>5</sub>) Hydride Complexes.** Complexes Os(C<sub>5</sub>H<sub>5</sub>)H(PPh<sub>3</sub>)<sub>2</sub> (10 mg) and  $[Ru(C_5H_5)(H)_2(PPh_3)_2]BF_4$  (10 mg) were dissolved in CD<sub>2</sub>Cl<sub>2</sub>, and the <sup>1</sup>H NMR spectrum was recorded immediately. All of the ruthenium dihydride (-7.3 (t), *J*(P,P) 24 Hz) was converted to Ru(C<sub>5</sub>H<sub>5</sub>)H(PPh<sub>3</sub>)<sub>2</sub> (δ -11.6 (t), *J*(P,P) 29.5 Hz) as the osmium monohydride (δ -14.6 (t) *J*(P,P) 27.9 Hz) was protonated to give  $[Os(C_5H_5)(H)_2(PPh_3)_2]BF_4$  (δ -11.8 (t) *J*(P,P) 33.9 Hz). When the ruthenium monohydride and osmium dihydride were mixed there was no reaction after 9 h.

**Catalysis of H/D Exchange between <sup>1</sup>BuOH and D<sub>2</sub>.** A series of reactions (4) were performed with *x* and *y* varying between 0 and 1.



The reactants, 0.01 mmol in Ru complex(es) and 1 mmol in <sup>1</sup>BuOH, were dissolved in 1 mL of THF, containing 2 μL of C<sub>6</sub>D<sub>6</sub> as a standard, and transferred to a 5-mm NMR tube. D<sub>2</sub> was bubbled through the solution for approximately 2 min after which time the sample was put into the NMR probe. <sup>2</sup>H NMR spectra were collected every 5 min over a 1-h period with the samples being shaken every other run. The amount of deuterated alcohol formed was determined by integration of the <sup>2</sup>H signal at δ 3.3 ppm against the standard C<sub>6</sub>D<sub>6</sub> in the <sup>2</sup>H NMR spectrum. The high field region of the <sup>2</sup>H NMR spectra for reactions when *x* = *y* = 0.4 revealed the presence of *trans*- $[Ru(\eta^2-D_2)(D)(dppe)_2]BPh_4$  and RuD<sub>2</sub>(dppe)<sub>2</sub>. The initial reaction between D<sub>2</sub> and <sup>1</sup>BuOH was very fast. This implies that the D<sub>2</sub> in solution was used up very quickly, and the reaction between D<sub>2</sub> and <sup>1</sup>BuOH was then diffusion controlled. The rates could not be quantified but did increase when the concentration of the two complexes was increased together (*x* = 1, *y* = 1). By contrast, with *x* = 1, *y* = 0, there was no H/D exchange under the same conditions. When CH<sub>2</sub>Cl<sub>2</sub> was used in place of THF, there was a maximum of 0.1 turnovers/min. However such rates were found to be unreliable because of problems with diffusion of gases into the solution in the NMR tube.

## Results

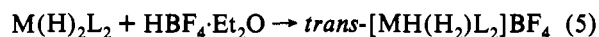
**Preparation and Properties of Dihydride Complexes.** The precursors to the dihydrogen complexes are dihydride complexes. The new iron dihydride complexes Fe(H)<sub>2</sub>L<sub>2</sub>, L = dtfpe, dtpe, were prepared by the reactions of mixtures of FeCl<sub>2</sub>, L, and NaBH<sub>4</sub> in THF. The corresponding complexes Ru(H)<sub>2</sub>L<sub>2</sub>, L = dtfpe, dape, and OsH<sub>2</sub>(dtfpe)<sub>2</sub> were prepared by reactions of the dichlorides *cis*-MCl<sub>2</sub>L<sub>2</sub> with NaOMe in MeOH (M = Ru) or LiAlH<sub>4</sub> in THF (M = Os). The dihydride complexes were characterized by FAB mass spectrometry in the case of the Fe and Os complexes. The FAB spectra showed the parent ion in all cases.

The <sup>31</sup>P NMR spectra of the dihydrides of iron consisted of two broad singlets of equal intensity. These spectra which are similar to that of FeH<sub>2</sub>(dppe)<sub>2</sub> are typical of *cis*-Fe(H)<sub>2</sub>L<sub>2</sub> complexes which are fluxional at 20 °C. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the Ru and Os dihydrides are consistent with mixtures

of *cis*-M(H)<sub>2</sub>L<sub>2</sub> and *trans*-M(H)<sub>2</sub>L<sub>2</sub> complexes with the *cis* complex in much higher concentration. These spectra contain two triplets (M<sub>2</sub>X<sub>2</sub> spin system) for the *cis* species and a singlet for the *trans* species. The <sup>2</sup>*J*(P,P) couplings for the *cis*-Ru(H)<sub>2</sub>L<sub>2</sub> complexes (13–16 Hz) were larger than those of the Os complexes (<5 Hz). The percentage of *trans* complex as observed in THF for the ruthenium complexes is 9, 5, 13, and 30% for L = dtfpe, dppe, dape, and depe, respectively.

<sup>1</sup>H NMR spectra of the Ru and Os dihydrides also indicate that *cis* and *trans* isomers are present. In the high field region of the <sup>1</sup>H NMR spectrum there is an intense AA' part of an AA'MM'X<sub>2</sub> pattern for the *cis* isomer and a small quintet for the *trans* isomer which is almost hidden in the peaks of the *cis* isomer.

**Preparation of the Dihydrogen Complexes.** The dihydrogen complexes *trans*- $[MH(H_2)L_2]^+$ , M = Fe, Ru, Os, L = dtfpe and M = Fe, L = dtpe, were prepared by protonation of the dihydrides (eq 5).



These new dihydrogen complexes were characterized by NMR spectroscopy and FAB mass spectrometry (see below). The complex  $[RuH(H_2)(dape)_2]BF_4$  was generated in solution as in eq 5 and was characterized by <sup>1</sup>H and <sup>31</sup>P NMR spectra but could not be isolated without decomposition to a mixture of products.

**NMR Spectra of the Dihydrogen Complexes.** The singlet in the <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of each of the dihydrogen complexes is consistent with a *trans*- $[MH(H_2)L_2]^+$  geometry. The high field <sup>1</sup>H NMR spectra are typical of such complexes in that they show a quintet for the terminal hydride and a broad peak of intensity two for the dihydrogen ligand at temperatures when there is no intramolecular H-atom exchange.<sup>6</sup>

Variable-temperature measurements of the *T*<sub>1</sub> values of the hydrogen ligands (Table 8) were used to positively identify the presence of an H–H bond in these new dihydrogen complexes. Calculated curves were fitted to the observed *T*<sub>1</sub> values for the dihydrogen and hydride ligands to obtain an accurate minimum *T*<sub>1</sub> time, *T*<sub>1</sub>(min), and dihydrogen bond length, *d*<sub>HH</sub>, as described previously.<sup>30</sup> A correction of *d*<sub>HH</sub> to account for relaxation of the H<sub>2</sub> nuclei by neighboring phenyl protons yields *d*<sub>HH</sub>(corr); this was done by subtracting the relaxation rate of the terminal hydride from the relaxation rate of the dihydrogen ligand by use of eq 4 of ref 6. It is assumed as before<sup>30</sup> that the H<sub>2</sub> ligand is spinning rapidly like a propeller.<sup>31</sup> This assumption is probably valid because the deuterated isotopomers of these complexes have large *J*(H,D) couplings.<sup>7</sup> The minimum *T*<sub>1</sub> and temperature data are listed in Table 9. As anticipated, the observed *T*<sub>1</sub> values for hydrides are much higher than those for dihydrogen ligands.

(30) Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Sella, A. *J. Am. Chem. Soc.* 1988, 110, 7031–7036.

(31) The rate of spinning of the dihydrogen ligand is relative to the Larmor precession frequency of a <sup>1</sup>H nucleus in the NMR spectrometer: rapid spinning refers to rates much greater than 400 MHz, while slow spinning refers to rates much less than 400 MHz.

Table 8. Observed (and Calculated) T<sub>1</sub> Values of the Dihydrogen and Hydride Ligands in the Complexes [MH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup>

[FeH(H <sub>2</sub> )(dtfpe) <sub>2</sub> ]BF <sub>4</sub> <sup>a</sup>					
T, K	293		253	233	213
T <sub>1</sub> of Fe(H <sub>2</sub> ), ms	20 (20 <sup>b</sup> )		15 (16)	17 (16)	20 (19)
T <sub>1</sub> of FeH, ms	83 (20 <sup>b</sup> )		275 (262)	287 (268)	289 (340)
[FeH(H <sub>2</sub> )(dtpe) <sub>2</sub> ]BF <sub>4</sub> <sup>a</sup>					
T, K			253	228	203
T <sub>1</sub> of Fe(H <sub>2</sub> ), ms			15 (16)	14 (14)	17 (17)
T <sub>1</sub> of FeH, ms			330 (240)	220 (221)	300 (290)
[RuH(H <sub>2</sub> )(dtfpe) <sub>2</sub> ]BF <sub>4</sub> <sup>c</sup>					
T, K	293	273	253	233	213
T <sub>1</sub> of Ru(H <sub>2</sub> ), ms	13 (20)	11 (15)	12 (13)	7 (10)	11 (10)
T <sub>1</sub> of RuH, ms	266 (271)	206 (210)	169 (175)	146 (146)	140 (141)
					203
					12 (11)
					150 (150)
[OsH(H <sub>2</sub> )(dtfpe) <sub>2</sub> ]BF <sub>4</sub> <sup>d</sup>					
T, K	293	273	243	228	213
T <sub>1</sub> of Os(H <sub>2</sub> ), ms	37 (36 <sup>b</sup> )	26 (28 <sup>b</sup> )	16 (16)	15 (15)	16 (17)
T <sub>1</sub> of OsH, ms	46 (36 <sup>b</sup> )	76 (28 <sup>b</sup> )	131 (135)		
					193
					22 (22)
[RuH(H <sub>2</sub> )(dape) <sub>2</sub> ]BPh <sub>4</sub> <sup>c</sup>					
T, K	293	273	253	233	213
T <sub>1</sub> of Ru(H <sub>2</sub> ), ms	16 (16)	13 (13)	12 (12)	11 (11)	12 (13)
T <sub>1</sub> of Ru(H), ms	212 (213)	169 (171)	150 (152)	145 (147)	166 (169)
					193
					20 (19)
					430 (250)

<sup>a</sup> In acetone-*d*<sub>6</sub> at 400 MHz; see Table 9 for parameters used in calculating T<sub>1</sub> values. <sup>b</sup> Rates of relaxation of M(H<sub>2</sub>) and MH averaged. <sup>c</sup> In CD<sub>2</sub>Cl<sub>2</sub> at 200 MHz. <sup>d</sup> In acetone-*d*<sub>6</sub> at 200 MHz.

Table 9. Observed T<sub>1</sub> (min) Values for H<sub>2</sub> and Terminal Hydride Ligands and Calculated H-H Distances

complex	T <sub>1</sub> <sup>min</sup> (H <sub>2</sub> ), ms	T, K	T <sub>1</sub> (H), ms	d <sub>HH</sub> , Å	d <sub>HH</sub> (corr), Å
[Fe(H <sub>2</sub> )(H)(dtfpe) <sub>2</sub> ] <sup>+</sup>	15.5 ± 0.6 <sup>a</sup>	247	275 ± 14 <sup>a</sup>	0.85 <sup>b</sup>	0.86 ± 0.02
[Fe(H <sub>2</sub> )(H)(dtpe) <sub>2</sub> ] <sup>+</sup>	14 ± 1 <sup>a</sup>	228	220 ± 15 <sup>a</sup>	0.83	0.84 ± 0.02
[Ru(H <sub>2</sub> )(H)(dtfpe) <sub>2</sub> ] <sup>+</sup>	10 ± 1 <sup>c</sup>	215	141 ± 5 <sup>c</sup>	0.89 <sup>d</sup>	0.90 ± 0.01
[Ru(H <sub>2</sub> )(H)(dape) <sub>2</sub> ] <sup>+</sup>	11.0 ± 0.5 <sup>c</sup>	235	145 ± 5 <sup>c</sup>	0.90 <sup>e</sup>	0.91 ± 0.01
[Os(H <sub>2</sub> )(H)(dtfpe) <sub>2</sub> ] <sup>+</sup>	15 ± 1 <sup>c</sup>	228	131 ± 9 <sup>c</sup>	0.95 <sup>f</sup>	0.97 ± 0.01

<sup>a</sup> 400 MHz. <sup>b</sup> τ<sub>0</sub> = 1.8 ps, E<sub>a</sub> = 2.4 kcal mol<sup>-1</sup>. <sup>c</sup> 200 MHz. <sup>d</sup> τ<sub>0</sub> = 2.9 ps, E<sub>a</sub> = 2.2 kcal mol<sup>-1</sup>. <sup>e</sup> τ<sub>0</sub> = 2.9 ps, E<sub>a</sub> = 2.4 kcal mol<sup>-1</sup>. <sup>f</sup> τ<sub>0</sub> = 2.5 ps, E<sub>a</sub> = 2.4 kcal mol<sup>-1</sup>.

Table 10. <sup>1</sup>J(H,D) Couplings for the HD Complexes

complex	<sup>1</sup> J(H,D) Hz	T, K	ν, MHz
[Fe(HD)(H)(dtfpe) <sub>2</sub> ] <sup>+</sup>	32 ± 1	293	200
[Ru(HD)(D)(dtfpe) <sub>2</sub> ] <sup>+</sup>	33.1 ± 0.5	293	200
[Ru(HD)(H)(dtfpe) <sub>2</sub> ] <sup>+</sup>	33.1 ± 0.5	293	200
[Ru(HD)(H)(dape) <sub>2</sub> ] <sup>+</sup>	31 ± 1	293	200
[Os(HD)(D)(dtfpe) <sub>2</sub> ] <sup>+</sup>	28.3 ± 0.5	233	200

The observation of a large <sup>1</sup>J(H,D) coupling constant proves the existence of an H-D bond. The HD ligand was introduced by a variety of methods. The iron complex [FeH(HD)(dtfpe)<sub>2</sub>]-BF<sub>4</sub> was prepared by reacting the dihydride complex with HBF<sub>4</sub>/D<sub>2</sub>O in a similar fashion to eq 5. The corresponding isotopomer [FeD(HD)(dtfpe)<sub>2</sub>]BF<sub>4</sub> was generated by reacting [FeH(dtpe)<sub>2</sub>]-BF<sub>4</sub> with D<sub>2</sub> gas in the solid state; this presumably generates [FeH(D<sub>2</sub>)(dtfpe)<sub>2</sub>]BF<sub>4</sub> which rearranges when dissolved, even at low temperature, to give the HD isotopomer as well. The corresponding Ru complex, [RuH(HD)(dtfpe)<sub>2</sub>]BF<sub>4</sub>, was prepared by reacting [RuH(dtpe)<sub>2</sub>]BF<sub>4</sub> with HD gas. Some [RuD(HD)(dtfpe)<sub>2</sub>]<sup>+</sup> isotopomer was also produced in this reaction. The complex [RuH(dape)<sub>2</sub>]<sup>+</sup> was unstable, and so the complex [RuH(HD)(dape)<sub>2</sub>]<sup>+</sup> was generated in solution by protonating RuH<sub>2</sub>(dape)<sub>2</sub> with [DPCy<sub>3</sub>]BF<sub>4</sub>. The Os complex [OsD(HD)(dape)<sub>2</sub>]BF<sub>4</sub> was prepared by protonating OsD<sub>2</sub>(dtfpe)<sub>2</sub> with HBF<sub>4</sub>·Et<sub>2</sub>O. Table 10 lists the <sup>1</sup>J(H,D) values for the complexes of this study. The relative population of isotopomers in the mixtures could not be determined accurately because of overlap of the resonances.

**Intramolecular H-Atom Exchange.** Approximate rate constants for the H-atom exchange processes between H<sub>2</sub> and hydride sites in the complexes *trans*-[MH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup> can be estimated from the T<sub>1</sub> data near relaxation coalescence (Table 11).<sup>2</sup> The H<sub>2</sub>

resonance (a broad singlet) and H resonance (a quintet) of the Fe complex are at relaxation coalescence at 293 K—the T<sub>1</sub> of both peaks is 21 ms at 400 MHz. The rate constant for H<sub>2</sub> → H exchange is about 1/T<sub>1</sub> or 50 s<sup>-1</sup>.<sup>2</sup> Data for the dppe complex are included for comparison in Table XI. The ΔG<sup>‡</sup> values refer to the temperature at which the rate constant is estimated. Clearly the exchange process is easier for the dppe complex than the dtfpe complex.

The hydride resonance of [RuH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup> is not broadened by exchange at 293 K, and the T<sub>1</sub> values are not averaged. A lower limit for the activation energy for the H<sub>2</sub> → H exchange is 17 kcal mol<sup>-1</sup> in this case.

The H<sub>2</sub> and H resonances of [OsH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup> are broadened by exchange at 293 K; the terminal hydride is a broad peak instead of the quintet observed for the corresponding Fe complex. This is consistent with the averaging of the T<sub>1</sub> for the resonances (both about 40 ms at 200 MHz, see Table 8) of the Os complex at 293 K. The ΔG<sup>‡</sup> value calculated for this process at 273 K is larger than that of the analogous dppe complex.

Line shape coalescence of the H<sub>2</sub> and H resonances for the dtfpe complexes would be expected to occur at temperatures greater than 293 K but this was not investigated.

**Loss of the Dihydrogen Ligand.** The ease of loss of the dihydrogen ligand in the series when L is dtfpe increases as Os < Fe < Ru just as it does in the dppe series. The behavior of the dihydrogen complexes under the conditions of FAB mass spectral analysis is consistent with this ordering. There was a peak for the parent ion of the Os complex in the FAB mass spectrum. The Fe complexes, on the other hand, readily lost H<sub>2</sub> so that the highest mass peak was attributed to [MHL<sub>2</sub>]<sup>+</sup> species. The Ru complexes were too unstable for mass spectral analysis.

The white complex [RuH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]BF<sub>4</sub> must be kept under 1 atm of H<sub>2</sub> in the solid state. Otherwise it loses H<sub>2</sub> to give a yellow complex [MHL<sub>2</sub>]<sup>+</sup> as in eq 6.



The yellow solid, [FeH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]BF<sub>4</sub>, was heated to about 170 °C under vacuum to give a navy blue solid. When the blue intermediate was placed under dihydrogen, the yellow complex [FeH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]BF<sub>4</sub> was obtained immediately as in eq 6. This blue solid turned pale yellow upon exposure to carbon monoxide to give [FeH(CO)(dtfpe)<sub>2</sub>]BF<sub>4</sub>.<sup>32</sup> The geometry of the blue complex is unknown. The complex [FeH(dppe)<sub>2</sub>]BPh<sub>4</sub> is also

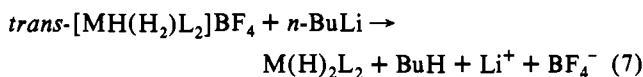
**Table 11.** Estimation of Rate Constants for H<sub>2</sub> to H Site Exchange from T<sub>1</sub> Data which Were Obtained Below the Region of Relaxation Coalescence

complex	MHz	T, K	H <sub>2</sub> T <sub>1</sub> (eff), <sup>a</sup> ms	H <sub>2</sub> T <sub>1</sub> , <sup>b</sup> ms	H T <sub>1</sub> (eff), <sup>a</sup> ms	H T <sub>1</sub> , <sup>b</sup> ms	k s <sup>-1</sup>	ΔG <sup>‡</sup> , kcal mol <sup>-1</sup>
[FeH(H <sub>2</sub> )(dtfpe) <sub>2</sub> ] <sup>+</sup>	400	293	21	20	21	287	50	14.9
[FeH(H <sub>2</sub> )(dppe) <sub>2</sub> ] <sup>+</sup>	200	244	11	12	116	169	5	13.4 <sup>6</sup>
	200	293					500 <sup>c</sup>	13.9 <sup>6</sup>
[RuH(H <sub>2</sub> )(dtfpe) <sub>2</sub> ] <sup>+</sup>	200	293	13		266		0	>17
[RuH(H <sub>2</sub> )(dppe) <sub>2</sub> ] <sup>+</sup>	200	285	29	26	294	357	2	16.3 <sup>2</sup>
[OsH(H <sub>2</sub> )(dtfpe) <sub>2</sub> ] <sup>+</sup>	200	273	26	21	78	168	30	14.1
[OsH(H <sub>2</sub> )(dppe) <sub>2</sub> ] <sup>+</sup>	200	245	29	28	69	211	30	12.6 <sup>7</sup>
	200	273					280 <sup>c</sup>	12.9 <sup>7</sup>

<sup>a</sup> T<sub>1</sub>(eff) refers to the observed value obtained by fitting the inversion recovery data to a single exponential decay (refer to ref 2 for further discussion on this). <sup>b</sup> T<sub>1</sub> is calculated from the parameters of Table 9 and refers to value expected if there were no exchange. <sup>c</sup> Obtained from line shape analysis.

blue.<sup>33</sup> The complex [OsH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]BF<sub>4</sub> turned from yellow to orange when heated above 100 °C; however hydride signals in the <sup>1</sup>H NMR spectrum of the product still indicated the presence of some starting complex.

**Deprotonation of Dihydrogen Complexes at Low Temperature.** Under normal conditions, complexes of the type Fe(H)<sub>2</sub>L<sub>2</sub> exist exclusively in the *cis* form. The analogous ruthenium and osmium dihydrides exist as an equilibrium between the *cis* and the *trans* forms. The *cis:trans* ratio is usually about 9:1. Thus, in all cases, the *cis* form is thermodynamically favored over the *trans*. Deprotonation of a *trans*-[MH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup> complex should give, initially, *trans*-M(H)<sub>2</sub>L<sub>2</sub> if the dihydrogen ligand is deprotonated in preference to the hydride ligand. The initial product would then convert to the more stable *cis* isomer. If the deprotonation is done at a low temperature, the rate of isomerization may be slow enough to allow observation of the initial *trans*-dihydride product by low temperature NMR spectroscopy. Table 2 lists the observed products for the following general reaction in acetone-*d*<sub>6</sub> at -80 °C:



When the *trans*-[OsH(H<sub>2</sub>)(dppe)<sub>2</sub>]BF<sub>4</sub> complex was deprotonated, only the *trans*-dihydride was observed at -80 °C. Isomerization to the equilibrium mixture where the *cis*-dihydride is the major isomer takes less than 5 min at room temperature. Deprotonation of the corresponding Ru complex at -80 °C also produced exclusively the *trans*-dihydride, which isomerized quickly at room temperature to the *cis/trans* equilibrium mixture. Thus, it seems that the deprotonation mechanism does indeed involve heterolytic cleavage of the dihydrogen ligand to give, initially, the *trans*-dihydride.

When the analogous iron complexes were deprotonated at -80 °C, only the *cis*-dihydride products were observed. It seems that even at -80 °C the *trans*-Fe(H)<sub>2</sub>L<sub>2</sub> complexes are very unstable and isomerize rapidly to the *cis*-dihydride.

**Acid/Base Equilibria and pK<sub>a</sub> Determinations.** The pK<sub>a</sub> values of the dihydrogen complexes were determined by finding a suitable acid of known pK<sub>a</sub> which is in equilibrium with the dihydrogen complex as in eq 1. The acids of known pK<sub>a</sub> are listed in Table 1. These are sterically hindered protonated phosphines and cationic metal hydride complexes. The pK<sub>a</sub> values of the latter which were determined in previous studies provide a suitable pK<sub>a</sub> range of 7–16 required for the present study. The conjugate bases of these acids cannot coordinate and displace the weakly bonded H<sub>2</sub> ligand. Although the equilibria are all in nonaqueous media, the pK<sub>a</sub> values are extrapolated to aqueous values as described previously.<sup>10</sup> The solvents of choice are THF and acetone. Acetonitrile is too strongly coordinating. Chlorinated solvents (CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>) are too reactive toward the metal-hydride complexes.

Tables 3–7 summarize the results of reactions attempted to observe equilibria between [MH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup>/M(H)<sub>2</sub>L<sub>2</sub> acid/base pairs at 20 °C. The reactions were usually equilibrated for hours to make sure the thermodynamically favored products were present; however later experiments suggested that the equilibria were established in less than 10 min. The pK<sub>a</sub> values were calculated from the equilibrium constant, K<sup>cis</sup>, for the reaction between a proton donor of known pK<sub>a</sub> and the dihydride complex under investigation (eq 8).



The K<sup>cis</sup> refers to the equilibrium between the *cis*-M(H)<sub>2</sub>L<sub>2</sub> isomer and the dihydrogen complex and not the *trans*-M(H)<sub>2</sub>L<sub>2</sub> species, which is present in a small amount (in about a 1:9 ratio with the *cis* isomer for M = Ru and Os). The constant for the equilibrium constant K<sup>trans</sup> for the *trans* isomer (eq 9) is about K<sup>cis</sup>/9 but it cannot be measured as accurately as K<sup>cis</sup>.



Therefore the pK<sub>a</sub><sup>trans</sup> (see below) for *trans*-[MH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup> calculated from the equilibrium data for eq 9 will be ≈1 unit greater than the pK<sub>a</sub><sup>cis</sup> derived from eq 8.

For the reaction mixtures described in Tables 3–7, THF (or THF-*d*<sub>8</sub>) was the chosen solvent since it is poorly coordinating and therefore does not displace H<sub>2</sub> from dihydrogen complexes. The dihydrogen complexes of dtpe and dppe were considerably less soluble in THF than the analogous dtfpe complexes, [MH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup>. Thus, the dtfpe complexes were most appropriate for this study since relatively large amounts of the reagents could be used for typical NMR samples, allowing well-resolved NMR spectra. Several reactions were attempted in acetone-*d*<sub>6</sub>. In certain reactions involving the Ru complexes, H/D exchange between the hydride species and the solvent occurred. Reactions were also attempted in CD<sub>2</sub>Cl<sub>2</sub>, but the Ru and Fe hydrides reacted with this solvent to give *trans*-MHCIL<sub>2</sub> complexes.

The integrals of NMR resonances (<sup>1</sup>H or <sup>31</sup>P), when carefully measured, for the different species of eq 8 can be converted to the relative concentrations of the species in solution, and these can be used to calculate K. A representative NMR spectrum obtained for the equilibrium mixture from the reaction of OsH<sub>2</sub>(dtfpe)<sub>2</sub> and [Ru(H)<sub>2</sub>(C<sub>3</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 1H<sup>+</sup>, in THF-*d*<sub>8</sub> is shown in Figure 1. All of the species are represented by resonances in the -5 to -15 ppm region which are well-resolved and fairly accurately integrated (apart from the *trans*-Os(H)<sub>2</sub>L<sub>2</sub> species); the equilibrium constant calculated from data from two spectra of this type is found in entry 1 of Table 3. The spectrum was almost identical when approached from the opposite direction: the reaction of 1 with [OsH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup> (entry 2 of Table 3). The pK<sub>a</sub> of 1H<sup>+</sup> has been determined to be 8.0 ± 0.2 (Table 1), and therefore the pK<sub>a</sub><sup>cis</sup> of [OsH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup> in THF-*d*<sub>8</sub> at 20 °C is calculated from the <sup>1</sup>H NMR intensities to be 8.3 ± 0.2 or 8.5 ± 0.2 for these two approaches to the same equilibrium.

(33) Aresta, M.; Giannoccaro, P.; Rossi, M.; Sacco, A. *Inorg. Chim. Acta* 1971, 5, 115.



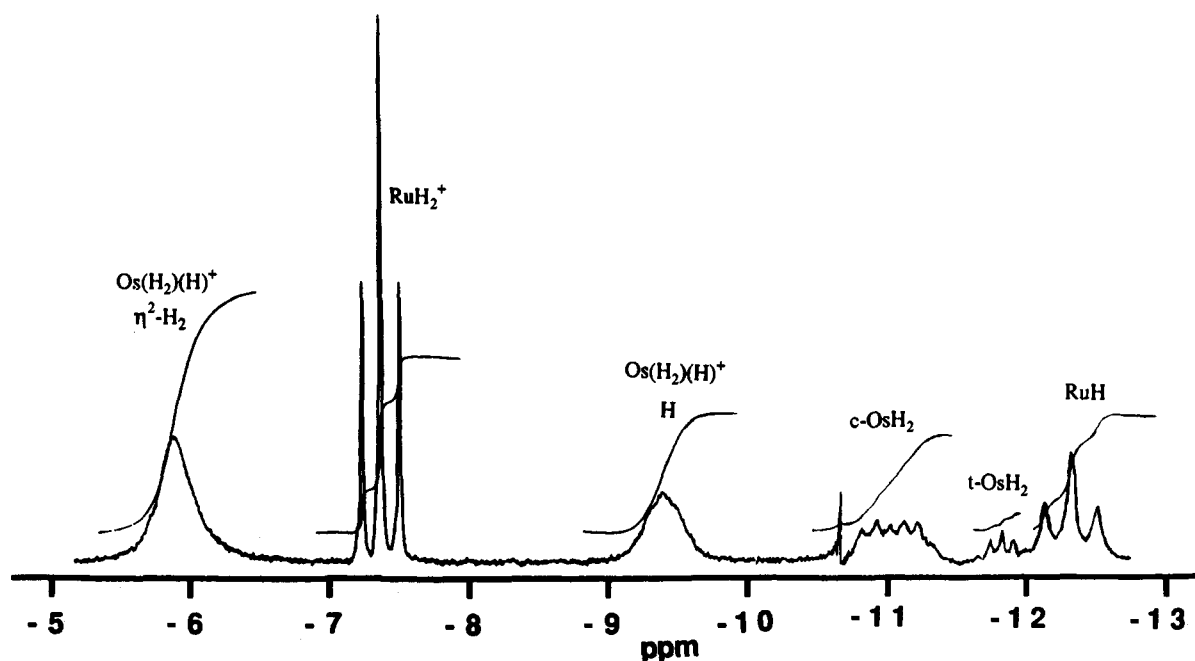
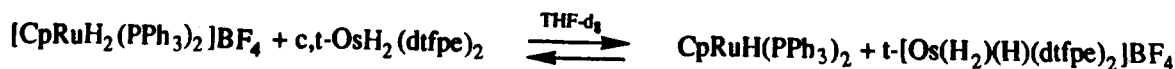


Figure 1. The hydride region of the <sup>1</sup>H NMR spectrum at 200 MHz for the reaction of [Ru(H)<sub>2</sub>(C<sub>5</sub>H<sub>5</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub> (pK<sub>a</sub> 8.0) with Os(H)<sub>2</sub>(dtfpe)<sub>2</sub> in THF-*d*<sub>6</sub>.  $K^{cis} = [\text{RuH}][\text{Os(H}_2\text{)(H)}^+]/([\text{RuH}_2^+][\text{cis-OsH}_2]) = 2.6 \pm 0.7$ .

The deprotonation of this dihydrogen complex by PCy<sub>3</sub> (entry 3, Table 3) is consistent with this result since HPCy<sub>3</sub><sup>+</sup> has pK<sub>a</sub> 9.7.

The pK<sub>a</sub><sup>cis</sup> of [RuH(H)<sub>2</sub>(dtfpe)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub> is determined to be about 9.0 in THF or acetone (entries 4–8). Both the reaction of Ru(H)<sub>2</sub>L<sub>2</sub> with 1H<sup>+</sup> or with [OsH(H)<sub>2</sub>(dtfpe)<sub>2</sub>]<sup>+</sup> leads to this conclusion. There was no sign of decomposition for these equilibria. The *cis* and *trans* forms of the M(H)<sub>2</sub>L<sub>2</sub> species were present in the usual 9:1 ratio. Thus the ruthenium–dihydrogen complex is considerably less acidic than the Os one, whether one considers the equilibria of eq 8 or 9.

It was difficult to find a reactant that gave a clean equilibrium with [Fe(H)<sub>2</sub>H(dtfepe)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub>. Os(H)<sub>2</sub>(dtfpe)<sub>2</sub> is the only compound to react without decomposition. This equilibrium was approached from both sides (entries 9 and 10) and examined by <sup>1</sup>H and <sup>31</sup>P NMR; a pK<sub>a</sub><sup>cis</sup> of 7.8 ± 0.3 can be calculated for [FeH(H)<sub>2</sub>(dtfpe)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub>. Thus [FeH(H)<sub>2</sub>(dtfpe)<sub>2</sub>]<sup>+</sup> is more acidic than the analogous osmium complex.

It is interesting that the similar reaction mixture of [FeH(H)<sub>2</sub>(dppe)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub> and Os(H)<sub>2</sub>(dppe)<sub>2</sub> involved some decomposition and side reactions. The dtfpe complexes appear to be more stable under the reaction conditions than the more electron rich dppe analogs.

The reaction of FeH<sub>2</sub>(dtfpe)<sub>2</sub> with 1H<sup>+</sup> (pK<sub>a</sub> 8.0) produced the expected species of eq 8 along with some free dtfpe ligand. The equilibrium could be approached from both directions with some decomposition, and thus an approximate pK<sub>a</sub><sup>cis</sup> value of 8 for [FeH(H)<sub>2</sub>(dtfpe)<sub>2</sub>]<sup>+</sup>BF<sub>4</sub> is suggested. This fits with the value of 7.8 mentioned above. The production of the free phosphine is thought to be due to the formation of a paramagnetic iron complex with only one dtfpe which would not be visible in the NMR spectrum.

Therefore, it is possible to conclude that the order of increasing acidity for [MH(H)<sub>2</sub>(dtfpe)<sub>2</sub>]<sup>+</sup> complexes is M = Ru < Os < Fe. The reaction between [RuH(H)<sub>2</sub>(dtfpe)<sub>2</sub>]<sup>+</sup> and Fe(H)<sub>2</sub>(dtfpe)<sub>2</sub> could not be used to confirm this order because decomposition and side reactions occurred.

Complex 4H<sup>+</sup> (pK<sub>a</sub> 12.2) has a comparable acidity to [OsH(H)<sub>2</sub>(dppe)<sub>2</sub>]<sup>+</sup>, and this was the key compound for determining

the value of 12.6 ± 0.1 for the pK<sub>a</sub><sup>cis</sup> of the osmium complex (entries 1 and 2 of Table 4). This value explains why OsH<sub>2</sub>(dppe)<sub>2</sub> is not protonated by 5H<sup>+</sup> (pK<sub>a</sub> 14.3) or MeOH (entries 3 and 4, Table 4).

Complex 5 reacted cleanly with [RuH(H)<sub>2</sub>(dppe)<sub>2</sub>]<sup>+</sup> to give an equilibrium mixture in THF or acetone-*d*<sub>6</sub> (entries 5–7); the pK<sub>a</sub><sup>cis</sup> values for the dihydrogen complex in the two solvents are 14.0 ± 0.4 and 13.6 ± 0.4, respectively. The former value is considered more reliable because we have found that this dihydrogen complex tends to exchange deuterium with acetone-*d*<sub>6</sub>, and this can influence the integrations of the hydride resonances. It is interesting that MeOH (pK<sub>a</sub> 15) does react with 5 to produce a low concentration of dihydrogen complex (entry 8) although this reaction may be driven by the greater solubility of this complex over that of RuH<sub>2</sub>(dppe)<sub>2</sub> in MeOH. Attempts to directly compare the acidity of [OsH(H)<sub>2</sub>(dppe)<sub>2</sub>]<sup>+</sup> with [RuH(H)<sub>2</sub>(dppe)<sub>2</sub>]<sup>+</sup> by reacting the former with RuH<sub>2</sub>(dppe)<sub>2</sub> or the latter with OsH<sub>2</sub>(dppe)<sub>2</sub> in acetone-*d*<sub>6</sub> or THF-*d*<sub>8</sub> were unsuccessful due to side reactions and the limited solubility of the dihydrides.

It was difficult to find an acid that gave an equilibrium with [FeH(H)<sub>2</sub>(dppe)<sub>2</sub>]<sup>+</sup> which was totally free of side reactions. The cleanest reaction was that of FeH<sub>2</sub>(dppe)<sub>2</sub> with [OsH(H)<sub>2</sub>(dppe)<sub>2</sub>]<sup>+</sup> (entry 10, Table 4) which occurs rapidly. The <sup>31</sup>P NMR spectrum gave the best integrations, but even here the resonance for the iron dihydride and dihydrogen species overlapped. This resulted in a large error in K. The reactions of 4H<sup>+</sup> or 7H<sup>+</sup> (protonated proton sponge) produced equilibrium mixtures, but some free dppe was present, indicating the presence of unknown side reactions, probably involving NMR inactive, paramagnetic iron complexes. Therefore the pK<sub>a</sub><sup>cis</sup> for the Fe complex is about 12. This seems correct because the acids [HPCy<sub>3</sub>]<sup>+</sup>BPh<sub>4</sub><sup>-</sup> (pK<sub>a</sub> 9.7) and [HP<sup>t</sup>Bu<sub>3</sub>]<sup>+</sup>BPh<sub>4</sub><sup>-</sup> (pK<sub>a</sub> 11.4) completely protonate FeH<sub>2</sub>(dppe)<sub>2</sub> to give [Fe(H)<sub>2</sub>H(dppe)<sub>2</sub>]<sup>+</sup> and free phosphine and some free dppe. Similarly 5H<sup>+</sup> (pK<sub>a</sub> 14.3) is not acidic enough to protonate the dihydride (entry 13, Table 4).

Therefore the acidity of the dppe complexes increases as Ru < Os < Fe as in the case of the dtfpe complexes. Other reactions

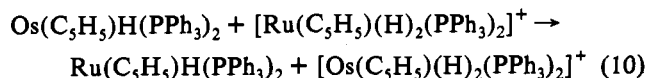
involving combinations of Ru and Os dppe complexes or Ru and Fe dppe complexes failed to produce clean equilibria and were not useful in verifying this ordering. The mixtures of dtfpe complexes, on the other hand, were much more stable with respect to decomposition (see above).

The acid/base mixtures with the iron complexes of dtpe (Table 5) always involved some decomposition to produce free dtpe. When  $\text{FeH}_2(\text{dtpe})_2$  is stirred with  $4\text{H}^+$  ( $\text{p}K_a$  12.2) for 2 h (entry 1), or when the reaction is approached from the other side, the four species of eq 8 are observed along with some free dtpe ligand. The fact that the equilibrium could be approached from both directions means that the  $\text{p}K_a$  value of 12.6 for  $[\text{FeH}(\text{H}_2)(\text{dtpe})_2]\text{BF}_4$  is probably reasonable. The table also indicates that the  $\text{p}K_a$  of  $[\text{FeH}(\text{H}_2)(\text{dtpe})_2]\text{BF}_4$  must be below 13 since  $\text{FeH}_2(\text{dtpe})_2$  is not protonated ( $K < 0.05$ ) by  $[\text{Ru}(\text{C}_5\text{Me}_5)\text{H}_2(\text{PPhMe}_2)_2]^+(\text{SH}^+, \text{p}K_a$  14.3).

The acidity determination of the weak acid  $[\text{RuH}(\text{H}_2)(\text{dape})_2]^+$  required the use of the weak acid  $[\text{Ru}(\text{C}_5\text{Me}_5)(\text{H})_2(\text{PMe}_3)_2]^+$  which has an approximate  $\text{p}K_a$  value of 16.3. The data of Table 6 suggest a  $\text{p}K_a$  of about 16.4 for this dape complex.

The weak acids  $[\text{MH}(\text{H}_2)(\text{depe})_2]^+$ ,  $\text{M} = \text{Fe, Ru, Os}$ , were studied by reacting their dihydride conjugate bases with alcohols (Table 7) in a similar fashion to that described by Baker et al.<sup>14</sup> Ethanol partially protonates the Fe complex and completely protonates the Ru and Os complexes according to  $^{31}\text{P}$  NMR studies. There is always some decomposition of the iron complexes as indicated by the formation of free depe. Of the series, only the Ru complex is protonated by  $^i\text{PrOH}$ , albeit partially. Therefore again the order of increasing acidity is  $\text{Ru} < \text{Os} < \text{Fe}$ . When  $[\text{Fe}(\eta^2\text{-H}_2)\text{H}(\text{depe})_2]\text{BPh}_4$  and  $\text{FeH}_2(\text{dppe})_2$  were mixed together, there was no visible reaction according to  $^{31}\text{P}$  NMR as expected. Other mixtures of depe complexes of Fe, Ru, and Os did not produce clean equilibria.

**Acidity of Dihydrides.** In view of the aperiodic ordering of the acidity of the dihydrogen complexes it was of interest to test the ordering of cationic dihydride complexes. A preliminary experiment (eq 10) revealed that  $[\text{Ru}(\text{C}_5\text{H}_5)(\text{H})_2(\text{PPh}_3)_2]^+$  is much more acidic than the corresponding osmium complex  $[\text{Os}(\text{C}_5\text{H}_5)(\text{H})_2(\text{PPh}_3)_2]^+$ . Thus eq 10 lies completely to the right.



**H/D Exchange Catalysis.** The  $^2\text{H}$  NMR spectra of reaction 4 revealed that when only *trans*- $[\text{Ru}(\text{H}_2)(\text{H})(\text{dppe})_2]\text{BPh}_4$  was used as catalyst in THF, no  $^i\text{BuOD}$  was produced over a 1-h period. It is interesting that when  $\text{CH}_2\text{Cl}_2$  was the solvent instead of THF, such a reaction caused some H/D exchange to occur;<sup>25</sup> we found that the dihydrogen complex in  $\text{CH}_2\text{Cl}_2$  had very low activity. When only  $\text{RuH}_2(\text{dppe})_2$  in THF was used, some H/D exchange occurred although less than when both *trans*- $[\text{RuH}(\text{H}_2)(\text{dppe})_2]\text{BPh}_4$  and  $\text{RuH}_2(\text{dppe})_2$  were present in equal amounts. It was impossible to determine the rate law for the reaction because of diffusion control problems; however, the rate did increase when the concentrations of both complexes were increased simultaneously.

## Discussion

**Effect of Ligand and Metal on NMR and Physical Properties of the  $\text{H}_2$  Ligand.** Some NMR properties of the complexes are organized in Table 12 by the metal and then by increasing electron density on the metal. The ordering by electron density is made on the basis of the data presented in Table 13 (see below). The  $^1J(\text{H},\text{D})$  values are in the usual range (20–35 Hz) for HD complexes. The greater  $^1J(\text{H},\text{D})$  value obtained for the dtfpe complex compared to the dape complex of Ru reflects a higher H–D bond order. One would expect that the more electron donating dape ligand would increase the amount of  $\pi$ -backbonding

**Table 12.** NMR Properties of the Complexes Arranged by Metal and Then by Increasing Electron Density on the Metal

	$\delta(^1\text{H}_2)$ , ppm	$d(\text{HH})$ , Å	$J(\text{HD})$ , <sup>a</sup> Hz	$\delta(^1\text{H})$ , ppm	$\Delta\delta^{31}\text{P}$ , <sup>b</sup> ppm
$[\text{FeH}(\text{H}_2)(\text{dtfpe})_2]^+$	-7.6	0.86	32	-12.6	107.3
$[\text{FeH}(\text{H}_2)(\text{dppe})_2]^+$	-7.9	0.87	30, 31	-12.6	105.9
$[\text{FeH}(\text{H}_2)(\text{dtpe})_2]^+$	-8.2	0.84		-12.5	105.5
$[\text{FeH}(\text{H}_2)(\text{depe})_2]^+$	-10.5	0.86	29.5	-14.6	117.1
$[\text{RuH}(\text{H}_2)(\text{dtfpe})_2]^+$	-4.1	0.90	33, 33	-9.9	84.0
$[\text{RuH}(\text{H}_2)(\text{dppe})_2]^+$	-4.6	0.90	32, 33	-10.0	82.0
$[\text{RuH}(\text{H}_2)(\text{dape})_2]^+$	-5.0	0.91	31	-10.3	82.0
$[\text{RuH}(\text{H}_2)(\text{depe})_2]^+$	-6.4	0.86	32, 32	-11.3	87.7 <sup>c</sup>
$[\text{OsH}(\text{H}_2)(\text{dtfpe})_2]^+$	-6.0	0.97	28	-9.0	52.5
$[\text{OsH}(\text{H}_2)(\text{dppe})_2]^+$	-6.8	1.02	25.5	-9.0	50.9
$[\text{OsH}(\text{H}_2)(\text{depe})_2]^+$	-10.0	1.1–1.5 <sup>d</sup>	11	-9.7	56.4 <sup>c</sup>

<sup>a</sup> When two values are given the first refers to the  $\text{M}(\text{HD})(\text{H})\text{L}_2^+$  isotopomer and the second refers to the  $\text{M}(\text{HD})(\text{D})\text{L}_2^+$  isotopomer. <sup>b</sup> Coordination chemical shift:  $\Delta\delta^{31}\text{P} = \delta(^{31}\text{P}$  in complex) –  $\delta(^{31}\text{P}$  in free L) in acetone- $d_6$ . <sup>c</sup> Reference 6 reported incorrect  $\delta$  for the Ru and Os depe compounds. The correct  $\delta$  are 68.7 ppm (Ru) and 37.1 ppm (Os). <sup>d</sup> See ref 7.

from the filled metal d orbitals into the HD  $\sigma^*$  orbital and decrease the H–D bond order as observed.

All the complexes of iron have very similar NMR properties despite the dramatic differences in electronic properties described below. The most sensitive parameter is the chemical shift of the  $\text{H}_2$  ligand—this shows that the  $\text{H}_2$  nuclei are more shielded on going from *p*- $\text{CF}_3$  (dtfpe) to *p*- $\text{CH}_3$  (dtpe) substituents on the ligands as might be expected on the basis of the acidity of the  $\text{H}_2$  (see below). It is notable that the hydride chemical shift remains constant within this series. The coordination chemical shift of the  $^{31}\text{P}$  nuclei decreases with this change of substituents and this is also a shielding effect. The change in chemical shift of the  $\text{H}_2$ ,  $^1\text{H}$ , and  $^{31}\text{P}$  donor atoms on going from the aryl-substituted ligands to the ethyl-substituted ligand (depe) is simply because the ring currents produced by the aryl-containing ligands are not present for the latter. The H–H distance calculated from the  $T_1$  data (*ca.* 0.86 Å) and the  $^1J(\text{H},\text{D})$  coupling constants (*ca.* 32 Hz) are quite insensitive to the electronics at the metal although the latter coupling does appear to decrease on going from the dtfpe ligand to the depe ligand.

The ruthenium complexes give the same trends as the iron complexes. Again  $\delta(\text{H}_2)$  is sensitive to the nature of the ligand L. All the  $\delta(\text{H}_2)$  data in Table 12 support the suggestion that a more positive chemical shift is associated with more H–H and less M–H character; in other words  $\delta(\text{H}_2)$  of the complex is closer to that of free  $\text{H}_2$  gas (+4.4 ppm). The distances  $d_{\text{HH}}$  for the Ru complexes are slightly longer than those of the Fe complexes which might argue for more activation of the H–H bond in the case of Ru than Fe. However the  $^1J(\text{H},\text{D})$  couplings are larger than those of Fe which suggest the opposite. Therefore it seems that the H–H bond order of the Fe and Ru complexes is similar. The Ru–H distances to the  $\text{H}_2$  ligand might be quite long, and the Ru–H bonds, quite weak, considering how labile the Ru dihydrogen complexes are relative to the Fe and Os ones; this has not yet been verified by neutron diffraction. The Ru–H distances would be expected to be at least 0.05 Å longer than corresponding Fe–H ones just because Ru(II) is larger than Fe(II).

The osmium–dihydrogen complexes show the greatest variation in  $\text{H}_2$  properties with a change in ligand. There is a significant lengthening of the H–H bond and decrease in the  $^1J(\text{H},\text{D})$  coupling constant on going from dtfpe to dppe. Again  $\delta(\text{H}_2)$  shows the same shielding trend.

The effect of the electron-withdrawing dtfpe ligand is to slow the intramolecular H-atom exchange process in the complex  $[\text{MH}(\text{H}_2)\text{L}_2]^+$  (refer to Table 11). This observation supports the proposal that the rate-determining step in the exchange mechanism is H–H bond cleavage to give a fluxional trihydride intermediate or transition state,  $[\text{M}(\text{H})_3\text{L}_2]^+$ .<sup>6</sup> For each metal, the more

Table 13. Approximate pK<sub>a</sub><sup>cis</sup> Values<sup>a</sup> for Some Dihydrogen Complexes in THF at 20 °C and Various Indicators of the Electron Density at the Metal

complex	pK <sub>a</sub> <sup>cis</sup> <sup>a</sup>	E <sub>1/2</sub> (MHClL <sub>2</sub> ), <sup>b</sup> V vs Fc <sup>+</sup> /Fc	E <sub>pa</sub> (MH <sub>2</sub> L <sub>2</sub> ), <sup>b,c</sup> V vs Fc <sup>+</sup> /Fc	ν(N <sub>2</sub> ), <sup>d</sup> cm <sup>-1</sup>	ν(CO), <sup>e</sup> cm <sup>-1</sup>
[FeH(H <sub>2</sub> )(dtfpe) <sub>2</sub> ] <sup>+</sup>	7.8 ± 0.3	0.25	0.01		1967
[FeH(H <sub>2</sub> )(dppe) <sub>2</sub> ] <sup>+</sup>	12.0 ± 0.4	-0.71	-0.54	2120	1950
[FeH(H <sub>2</sub> )(dtpe) <sub>2</sub> ] <sup>+</sup>	12.6 ± 0.4	-0.72	-0.77		1940
[FeH(H <sub>2</sub> )(depe) <sub>2</sub> ] <sup>+</sup>	≈ 16	-0.98		2090	1929
[RuH(H <sub>2</sub> )(dtfpe) <sub>2</sub> ] <sup>+</sup>	9.0 ± 0.3		0.50		
[RuH(H <sub>2</sub> )(dppe) <sub>2</sub> ] <sup>+</sup>	14.0 ± 0.4	-0.12	0.0	2194	1987
[RuH(H <sub>2</sub> )(dape) <sub>2</sub> ] <sup>+</sup>	16.4 ± 0.7		-0.1		
[RuH(H <sub>2</sub> )(depe) <sub>2</sub> ] <sup>+</sup>	≈ 16.5	-0.24		2163	1958
[OsH(H <sub>2</sub> )(dtfpe) <sub>2</sub> ] <sup>+</sup>	8.4 ± 0.2		0.21		
[OsH(H <sub>2</sub> )(dppe) <sub>2</sub> ] <sup>+</sup>	12.7 ± 0.1	-0.14	-0.17		2003
[OsH(H <sub>2</sub> )(depe) <sub>2</sub> ] <sup>+</sup>	≈ 16.3	-0.46		2136	1974

<sup>a</sup> Refer to eq 11 for the definition of K<sub>a</sub><sup>cis</sup>. <sup>b</sup> THF solvent, 0.2 M NBu<sub>4</sub>PF<sub>6</sub>, 0.2 V s<sup>-1</sup> scan rate.<sup>6,32</sup> <sup>c</sup> Anodic peak potential (irreversible) of *cis*-MH<sub>2</sub>L<sub>2</sub> in THF; the peak for the oxidation of *trans*-MH<sub>2</sub>L<sub>2</sub> (≈ 10%) for the Ru and Os complexes must be hidden in this peak.<sup>32,43</sup> <sup>d</sup> N<sub>2</sub> stretching frequency of the complex *trans*-[MH(N<sub>2</sub>)L<sub>2</sub>]<sup>+</sup> in Nujol mull.<sup>6</sup> <sup>e</sup> CO stretching frequency of the complex *trans*-[MH(CO)L<sub>2</sub>]<sup>+</sup> in Nujol mull.<sup>6,32</sup>

## Chart 1

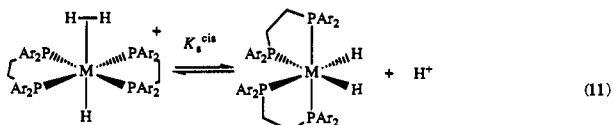


electron rich dppe complex stabilizes the trihydride intermediate by about 1 kcal mol<sup>-1</sup> (ΔΔG<sup>‡</sup>) relative to that of the analogous dtfpe complex. For the dppe, dtfpe, and depe triads, the ΔG<sup>‡</sup> values at a given temperature decrease as Ru > Fe > Os.

The relative labilities of the H<sub>2</sub> ligand in the dtfpe complexes parallels those of the dppe complexes: Ru > Fe > Os. Dihydrogen can be partially removed from the solid Ru complexes at 20 °C and readded. The same process occurs for [FeH(H<sub>2</sub>)(dtfpe)<sub>2</sub>]<sup>+</sup> above 100 °C. The Os complexes do not lose H<sub>2</sub> under these conditions in the solid state.

Overall we argue that the H–H bond of the dihydrogen ligand is activated toward homolytic cleavage the most in the osmium complexes and the least in the ruthenium complexes, with the iron complexes being intermediate in nature.

**Ligand Effects on the Acidity of the Dihydrogen Complexes.** The effect on the pK<sub>a</sub> of these complexes of changing the *para* substituent on the aryl of the diphosphine ligand is very dramatic (Table 13). On going from *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub><sup>-</sup> to *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub><sup>-</sup> substituents in the Fe complexes, the pK<sub>a</sub><sup>cis</sup> referring to eq 11 increases by 4.8 units. The change from *p*-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub><sup>-</sup> to *p*-CH<sub>3</sub>OC<sub>6</sub>H<sub>4</sub><sup>-</sup> substituents in the Ru complexes results in an even larger change of 7.4 units. The ethyl substituents give the least acidic complexes for each metal. These changes with L are about twice as large as those observed for the complexes [Ru(C<sub>5</sub>H<sub>5</sub>)(H<sub>2</sub>)L]<sup>+</sup> where [Ru(C<sub>5</sub>H<sub>5</sub>)(H<sub>2</sub>)(dtfpe)]<sup>+</sup> has a pK<sub>a</sub> of 4.7, while [Ru(C<sub>5</sub>H<sub>5</sub>)(H<sub>2</sub>)(dape)]<sup>+</sup> has a pK<sub>a</sub> of 8.6.<sup>10</sup> However in the later complexes there is only one bidentate phosphine ligand being altered compared to two in the present study. An increase of this magnitude is to be expected on the basis of additive ligand effects.<sup>15</sup>



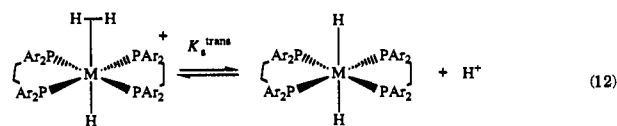
The deprotonation of [MH(H<sub>2</sub>)(dppe)<sub>2</sub>]<sup>+</sup>, M = Ru, Os, at -80 °C revealed that eq 12 is the kinetically favored pathway. This is consistent with the idea that proton transfer from the dihydrogen ligand to give the *trans*-dihydride is fast because there is little rearrangement at the metal center (it remains six-coordinate, in the d<sup>6</sup> configuration). As discussed above, the pK<sub>a</sub><sup>trans</sup> value is

Table 14. Approximate pK<sub>a</sub><sup>trans</sup>,<sup>a</sup> E<sub>1/2</sub>(*trans*-MH<sub>2</sub>L<sub>2</sub><sup>+</sup>/*trans*-MH<sub>2</sub>L<sub>2</sub>), and ΔH<sub>BDE</sub>{MH(H<sub>2</sub>)<sup>+</sup>} Values for the Dihydrogen Complexes [MH(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup>, M = Ru, Os, L = dtfpe, dppe, dape, depe as Well as the Values for Dihydride Complex [CpRu(H<sub>2</sub>)(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>

M, L	pK <sub>a</sub> <sup>trans</sup> <sup>a</sup>	E <sub>1/2</sub> <sup>b</sup> ± 0.1	ΔH <sub>BDE</sub> , <sup>c</sup> kcal mol <sup>-1</sup>
Ru, dtfpe	10.0 ± 0.3	0.4	89 ± 2
Ru, dppe	15.0 ± 0.5	-0.2	82 ± 2
Ru, depe	17.5 ± 1	-0.4	81 ± 2
Os, dtfpe	9.2 ± 0.3	0.1	81 ± 1
Os, dppe	13.6 ± 0.2	-0.2	80 ± 1
Os, depe	17.3 ± 1	-0.6	76 ± 2
CpRu(H <sub>2</sub> )(PPh <sub>3</sub> ) <sub>2</sub> <sup>+</sup>	8.0 ± 0.3 <sup>d</sup>	-0.3 <sup>e</sup>	72 ± 2 <sup>f</sup>

<sup>a</sup> Refer to eq 12 for the definition of K<sub>a</sub><sup>trans</sup>. <sup>b</sup> Values estimated as E<sub>1/2</sub> - 0.1 where E<sub>1/2</sub> values refer to either the corresponding *trans*-MH(CI)L<sub>2</sub> complexes or the *cis*-MH<sub>2</sub>L<sub>2</sub> complexes (see Discussion). <sup>c</sup> These values could all shift systematically if it is found that the constant (C = 66) of eq 17 needs further refinement. <sup>d</sup> See ref 11. <sup>e</sup> See ref 22. <sup>f</sup> See ref 21.

difficult to obtain accurately but is about one unit greater than pK<sub>a</sub><sup>cis</sup>, at least for the Ru and Os complexes. The pK<sub>a</sub><sup>trans</sup> values of Table 14 were calculated from K<sup>trans</sup> values of Table 3–6 or estimated from pK<sub>a</sub><sup>cis</sup>.



The pK<sub>a</sub><sup>trans</sup> values are most readily incorporated into a thermodynamic cycle (eqs 13–16, Chart 1, where all species are in solution) of the type used to derive eq 2. Tilset and Parker have shown how a similar cycle is applied in general to metal hydrides.<sup>17</sup> In their case they could determine an absolute value for the constant in an equation analogous to eq 15. In addition by making reasonable assumptions about the entropy change in the homolysis of the M–H bond they could convert ΔG<sub>BDE</sub>{M–H} into ΔH<sub>BDE</sub>{M–H} values. The same assumptions apply in converting ΔG<sub>BDE</sub>{MH(H<sub>2</sub>)<sup>+</sup>} values of eq 16 into the ΔH<sub>BDE</sub>{MH(H<sub>2</sub>)<sup>+</sup>} values of eq 17. Therefore the pK<sub>a</sub><sup>trans</sup> of the dihydrogen complexes should be a function of the *trans*-[M(H<sub>2</sub>)L<sub>2</sub>]<sup>+</sup>/*trans*-M(H<sub>2</sub>)L<sub>2</sub> electrochemical potential and of a bond dissociation energy involving the removal of a hydrogen atom from the dihydrogen complex

in solution:

$$\Delta H_{\text{BDE}}\{\text{MH}(\text{H}_2)^+\} = 1.37pK_a^{\text{trans}} + 23.1E^\circ(\text{MH}_2^+/\text{MH}_2) + 66 \quad (17)$$

Equation 17 is simply a rearranged form of eq 2 with the constant  $C$  which we have obtained empirically to be 66 when THF is the solvent (see Introduction). Therefore the ligand effect on the acidity should be explained in terms of the  $E^\circ$  and  $\Delta H$  parameters.

Unfortunately the  $E^\circ(\text{MH}_2^+/\text{MH}_2)$  value for *trans*- $\text{M}(\text{H})_2\text{L}_2$  of eq 13 cannot be directly measured because the small oxidation wave for the *trans* species is hidden under or is averaged with that of the predominant *cis*- $\text{M}(\text{H})_2\text{L}_2$  isomer. We have observed the redox wave of the related complex *trans*- $\text{Ru}(\text{H})_2(\text{meso-tet-1})$ , where the *trans* configuration is forced by the tetraphos ligand; this complex has  $E_{1/2}$  of  $-0.4$  V, while the related complex *trans*- $\text{Ru}(\text{H})\text{Cl}(\text{meso-tet-1})$  has  $E_{1/2}$  of  $-0.3$  V.<sup>34</sup> We have measured the  $\text{M}(\text{d}^5)/\text{M}(\text{d}^6)$  electrochemical potentials for other *trans*- $\text{MHClL}_2$  complexes (Table 13) which have  $E^\circ$  values that should be about 0.1 V more positive than  $E^\circ(\text{MH}_2^+/\text{MH}_2)$  for the corresponding *trans*-dihydride according to the tetraphos example and according to the additive effect of hydride versus chloride on electrochemical parameters ( $E_{\text{L}} = -0.4$  versus  $-0.24$ ).<sup>15,35</sup> We have also measured peak potentials for the oxidation of some *cis*- $\text{M}(\text{H})_2\text{L}_2$  complexes and find that they are close to the *trans*- $\text{MHClL}_2$  values.

The  $\Delta H_{\text{BDE}}\{\text{MH}(\text{H}_2)^+\}$  values for the complexes of Table 14 were calculated from the estimated  $E_{1/2}$  data by use of eq 17. If the  $\Delta H_{\text{BDE}}$  term of eq 17 were to stay constant over the range of ligands dtfpe, dppe, and depe for a given metal, then the slope of a plot of  $pK_a^{\text{trans}}$  vs  $E^\circ$  should be  $-16.9$  as it is for metal-hydride complexes.<sup>17</sup> The data of Table 14 can be used to show that this slope is actually about  $-6$  to  $-11$  depending on which pairs of data are chosen. Therefore changes in both the  $\Delta H$  term and the  $E^\circ$  term are responsible for the observed trend in  $pK_a^{\text{trans}}$  as a function of the ligand. Equation 2 shows that these two terms oppose each other in their contribution to  $pK_a$ .

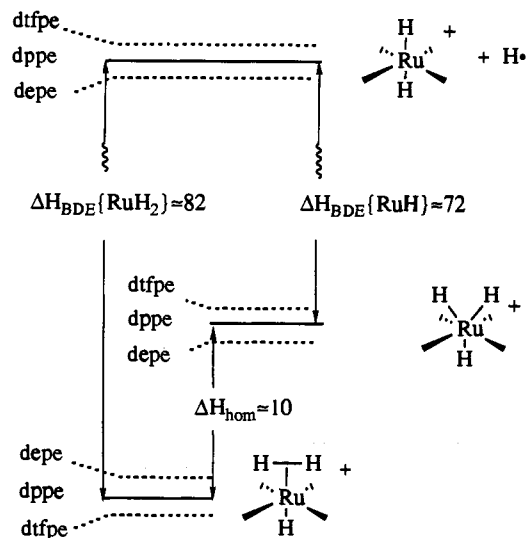
The electrochemical data demonstrate that the net donation of electrons to the metal increases as  $\text{dtfpe} < \text{dppe} < \text{dtpe} < \text{dape} < \text{depe}$ . The infrared data for the *trans* complexes  $[\text{MH}(\text{N}_2)\text{L}_2]^+$  and  $[\text{MH}(\text{CO})\text{L}_2]^+$  parallel this ligand ordering, in that the more electron donating ligand results in a lower NN or CO stretching frequency. This trend in  $E^\circ$  contributes strongly to an increase in  $pK_a^{\text{trans}}$  along this ligand series.

A change in ligand also affects the  $\Delta H_{\text{BDE}}$  term of eq 17 because it involves the energy of the H-H and M-H<sub>2</sub> interactions in  $[\text{M}(\text{H}_2)\text{H}(\text{L})_2]^+$  and the energy of the product of H atom abstraction, *trans*- $[\text{M}(\text{H})_2\text{L}_2]^+$ . This term makes a smaller, opposite contribution to  $pK_a^{\text{trans}}$ . A more electron donating ligand would weaken the strong H-H bond of the dihydrogen ligand through back-bonding and could possibly decrease  $\Delta H$  and therefore decrease  $pK_a^{\text{trans}}$ ; this assumes that an increase in  $\Delta H$  due to M-H bond strengthening does not occur during this change. However a change in ligand seems to have little influence on the H-H bond order of the present complexes as judged by the NMR data of Table 12, at least for the Fe and Ru complexes. The change to a more electron-donating ligand does move the dihydrogen complex closer in energy to its dihydride tautomer and could also stabilize the *trans*- $[\text{M}(\text{H})_2\text{L}_2]^+$  species (Figures 2 and 3 and see below).

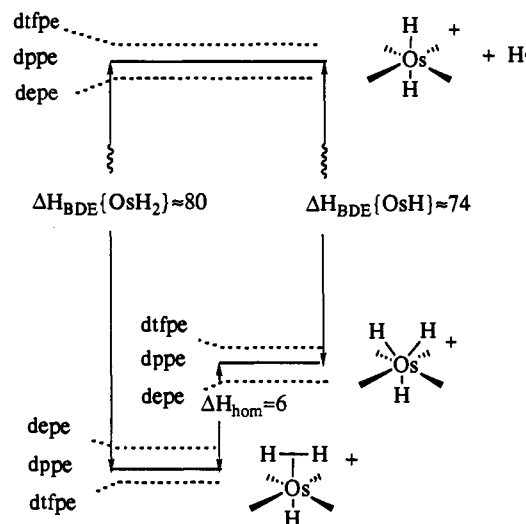
**Effect of the Metal on the Acidity of Dihydrogen Complexes.** Changing the metal produces a more subtle variation in  $pK_a$  than a change in ligand. Table 13 reveals a maximum change of about 2  $pK_a$  units from Fe to Ru for a given L. The ordering of  $pK_a^{\text{cis}}$

(34) *Meso-tet-1* is *R,S*- $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPhCH}_2\text{CH}_2\text{PPhCH}_2\text{CH}_2\text{PPh}_2$ ; Bautista, M. T.; Earl, K. A.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T. *Can. J. Chem.*, in press.

(35) Lever, A. B. P. *Inorg. Chem.* 1990, 29, 1271-1285.



**Figure 2.** Energy level diagram (in kcal mol<sup>-1</sup>) relating  $\Delta H_{\text{BDE}}\{\text{Ru}(\text{H}_2)^+\}$  to the energy of dihydrogen/dihydride tautomerism ( $\Delta H_{\text{hom}}$ ) and the Ru-H bond dissociation energy,  $\Delta H_{\text{BDE}}\{\text{RuH}\}$ , for the complexes  $[\text{Ru}(\text{H})_2\text{L}_2]^+$  as estimated from the energy for the complexes  $[\text{CpRu}(\text{H})_2\text{L}_2]^+$ . The solid levels are for L = dppe.



**Figure 3.** Energy level diagram (in kcal mol<sup>-1</sup>) relating  $\Delta H_{\text{BDE}}\{\text{Os}(\text{H}_2)^+\}$  to the energy of dihydrogen/dihydride tautomerism ( $\Delta H_{\text{hom}}$ ) and the estimated Os-H bond dissociation energy,  $\Delta H_{\text{BDE}}\{\text{OsH}\}$ , for the complexes  $[\text{Os}(\text{H})_2\text{L}_2]^+$ . The solid levels are for L = dppe.

values according to metal is  $\text{Ru(II)} > \text{Os(II)} > \text{Fe(II)}$ . The ordering of  $pK_a^{\text{trans}}$  values is also  $\text{Ru(II)} > \text{Os(II)}$  (Table 14). This trend in acidity of dihydrogen complexes contrasts with that observed for dihydride complexes. For example, for the complexes  $\text{M}(\text{H})_2(\text{CO})_4$ , the order of  $pK_a$  values is  $\text{Os(II)} > \text{Ru(II)} > \text{Fe(II)}$ .<sup>36</sup> Similarly the order according to our results from eq 10 is  $\text{Os(IV)} > \text{Ru(IV)}$ . The trend of decreasing acidity of metal hydrides when the metal is changed from the 3d to 4d to 5d congener is thought to be a general one<sup>16</sup> with the complexes  $[\text{MH}(\text{P}(\text{OR})_3)_4]^+$ ,  $\text{M} = \text{Ni, Pd, Pt}$ , and  $[\text{MH}(\text{CO})_2(\text{dppe})_2]^+$ ,  $\text{M} = \text{Mo, W}$ , providing the only exceptions.<sup>37</sup> The decrease in acidity of metal hydrides is associated with a stronger M-H bond going down the group. Thus the metal-related trend in the thermodynamic acidity of dihydrogen complexes is distinct from that of related dihydride complexes with no H-H interaction.

(36) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* 1986, 108, 2257;  $pK_1\{\text{FeH}_2(\text{CO})_4\} = 11.4 < pK_1\{\text{RuH}_2(\text{CO})_4\} = 18.7 < pK_1\{\text{OsH}_2(\text{CO})_4\} = 20.8$ ;  $pK_a\{\text{CrCpH}(\text{CO})_3\} = 13.3 < pK_a\{\text{MoCpH}(\text{CO})_3\} = 13.9 < pK_a\{\text{WCpH}(\text{CO})_3\} = 16.1$ .

(37) Sowa, J. R.; Bonanno, J. B.; Zanotti, V.; Angelici, R. *J. Inorg. Chem.* 1992, 31, 1370-1375.

Why is a ruthenium dihydrogen complex the least acidic? A possible answer might be that the ruthenium complexes are the most electron rich and thus make the dihydrogen ligand the least acidic by an inductive effect. However the evidence is against this. We have measured the M(d<sup>5</sup>)/M(d<sup>6</sup>) electrochemical potentials for a range of *trans*-MH(X)L<sub>2</sub> and *trans*-[MH(L')L<sub>2</sub>]<sup>+</sup> complexes and find that the ruthenium complex always has the most positive reversible potentials (*E*<sup>o</sup>) or irreversible peak potentials (*E*<sub>pa</sub>) of the Fe group triad. Table 13 shows that for a selection of *trans*-MH(Cl)L<sub>2</sub> and *cis*-M(H)<sub>2</sub>L<sub>2</sub> complexes the ruthenium complex has the more positive redox potential than Os or Fe for a given L. Lever's correlations show that this is true for a wide range of Ru and Os complexes.<sup>35</sup> We have also measured *E*<sub>1/2</sub>(M(C<sub>5</sub>H<sub>5</sub>)H(PPh<sub>3</sub>)<sub>2</sub><sup>+</sup>/M(C<sub>5</sub>H<sub>5</sub>)H(PPh<sub>3</sub>)<sub>2</sub>) vs Fc<sup>+</sup>/Fc and find a similar trend: -0.2 V for M = Ru and -0.36 V for M = Os. The infrared data for the dinitrogen complexes *trans*-[MH(N<sub>2</sub>)L<sub>2</sub>]<sup>+</sup> also show that the Ru complexes are the most electron deficient with regard to back-bonding to the N<sub>2</sub> ligand. The trend for the corresponding carbonyl complexes is different, with less net σ-withdrawal/π-back-donation for Os than Ru. Dihydrogen complexes are more like dinitrogen complexes than carbonyl complexes. Theoretical calculations on the ions MH<sup>+</sup> indicate that the 4d electrons of cationic Ru are particularly stable when compared to the energy of either 3d or 5d electrons,<sup>20</sup> and thus are less available for back-bonding to the H<sub>2</sub> ligand.

The reason that the Ru complexes are the least acidic is because of a large Δ*H*<sub>BDE</sub> term. This term can be estimated for the complexes of Ru and Os by use the data of Table 13, eq 17 (*E*<sup>o</sup> vs Fc<sup>+</sup>/Fc and Δ*H* in kcal mol<sup>-1</sup>) and the approximate p*K*<sub>a</sub><sup>trans</sup> values; see Table 14. The bond energy term for the ruthenium complexes is much larger than the ruthenium-hydride bond energies of about 72 kcal mol<sup>-1</sup> for complexes [Ru(C<sub>5</sub>R<sub>5</sub>)(H)<sub>2</sub>(L)]<sup>+</sup>.<sup>21</sup> The Δ*H*<sub>BDE}{Ru(H<sub>2</sub>)<sup>+</sup>} value of 83 kcal mol<sup>-1</sup> for [RuH(H<sub>2</sub>)(dppe)<sub>2</sub>]<sup>+</sup> is close to Δ*H*<sub>BDE}{Mn(H<sub>2</sub>)<sup>+</sup>} for the complex [Mn(H<sub>2</sub>)(CO)<sub>5</sub>]<sup>+</sup> (83.5 kcal mol<sup>-1</sup>) determined in the gas phase.<sup>20</sup> Like [RuH(H<sub>2</sub>)(dppe)<sub>2</sub>]<sup>+</sup>, the electron deficient manganese complex probably has a very labile H<sub>2</sub> ligand with a strong H-H bond.<sup>15</sup> Therefore probably the Δ*H*<sub>BDE</sub> value is so large because of the high H-H bond energy. Another possible reason is that the species *trans*-[Ru(H)<sub>2</sub>L<sub>2</sub>]<sup>+</sup> is of unusually high energy relative to *trans*-[Os(H)<sub>2</sub>L<sub>2</sub>]<sup>+</sup> and [Ru(C<sub>5</sub>R<sub>5</sub>)(H)(L)]<sup>+</sup> in their corresponding thermochemical cycles. There is much literature evidence that complexes with *trans*-hydrides are more unstable than those with *cis*-hydrides, but we note that our neutral complexes *trans*-MH<sub>2</sub>L<sub>2</sub> are close in energy to their *cis*-MH<sub>2</sub>L<sub>2</sub> isomers (see above).</sub></sub>

Figure 2 shows that the large Δ*H*<sub>BDE</sub> values for the [Ru(H<sub>2</sub>)-HL<sub>2</sub>]<sup>+</sup> complexes fit into a reasonable energy scheme when the energy of H-H homolytic splitting, Δ*H*<sub>hom</sub>, is also considered. The energy Δ*H*<sub>hom</sub> is thought to be related to the activation energy for H atom exchange (Δ*G*<sup>+</sup> of Table 11), a process which involves H-H homolysis to give a trihydride intermediate or transition state [Ru(H)<sub>3</sub>L<sub>2</sub>]<sup>+</sup>.<sup>6</sup> Figure 2 shows that a Ru-H bond dissociation energy for the trihydride could be about 72 kcal mol<sup>-1</sup> if the Δ*H*<sub>hom</sub> value is about 11 kcal mol<sup>-1</sup>, a quantity close to Δ*G*<sup>+</sup>. The ligand effect is also accounted for in this diagram; both Δ*H*<sub>BDE}{Ru(H<sub>2</sub>)<sup>+</sup>} (Table 14) and Δ*G*<sup>+</sup> ≈ Δ*H*<sub>hom</sub> (Table 11, ref 6) decrease on changing the ligand from dtfpe to dppe to depe. It is not clear whether, for example, the ligand dtfpe stabilizes the dihydrogen complex or destabilizes the hydride products in the diagram; both effects are shown in the diagram although the relative energies of the levels are qualitative. The insensitivity of the dihydrogen ligand parameters to changes in the phosphine ligand (Table 12) suggests that destabilization of the hydrides could be as or more important than stabilization of the dihydrogen complex. A future acidity determination of the one known trihydride complex of Ru</sub>

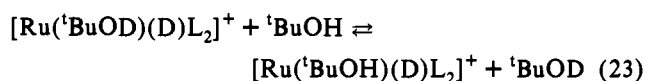
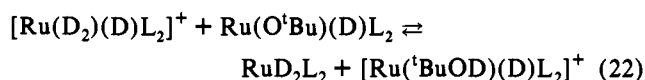
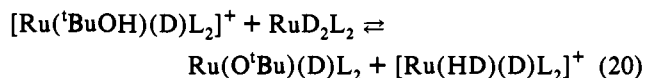
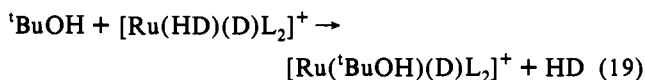
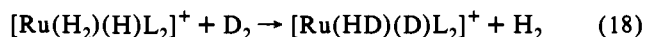
with bidentate ligands, [Ru(H)<sub>3</sub>L<sub>2</sub>]<sup>+</sup>, L = bis(diphenylphosphino)ferrocene,<sup>38</sup> might help to resolve this issue.

Elongated dihydrogen complexes which have more hydride character, such as the depe osmium complex of Table 13, would be expected to have Δ*H*<sub>BDE}{M(H<sub>2</sub>)<sup>+</sup>} values which are closer to metal-hydride bond energies (about 70–75 kcal mol<sup>-1</sup> for Os). Table 14 and Figure 3 show that this is true. However the value for Δ*G*<sup>+</sup> ≈ Δ*H*<sub>hom</sub> ≈ 6 expected on the basis of Figure 3 is too low when compared to actual Δ*G*<sup>+</sup> (Table 11) or Δ*H*<sup>+</sup> (ref 6) values for H atom exchange. This anomaly is explained, at least for the depe complex, by the demonstrated existence of a trihydride tautomer [Os(H)<sub>2</sub>H(depe)<sub>2</sub>]<sup>+</sup> that is close in energy to the [Os(H<sub>2</sub>)H(depe)<sub>2</sub>]<sup>+</sup> complex which is not associated with exchange between (H)<sub>2</sub> and terminal H atoms.<sup>7</sup> The dtfpe complex has the least hydride character in the Os(H<sub>2</sub>) unit and, as expected, has the largest Δ*H*<sub>BDE}{Os(H<sub>2</sub>)<sup>+</sup>} value.</sub></sub>

The high Δ*H*<sub>BDE}{Ru(H<sub>2</sub>)<sup>+</sup>} for these complexes contrasts with the lower value of about 72 kcal mol<sup>-1</sup> for the complexes [Ru(C<sub>5</sub>R'<sub>5</sub>)(H)<sub>2</sub>L]<sup>+</sup>. The latter complexes have elongated, slow-spinning dihydrogen ligands<sup>31</sup> which are more dihydride-like in character.<sup>11</sup> Therefore the distinctively low acidity of Ru(H<sub>2</sub>)L<sub>n</sub> complexes may only be observed when the dihydrogen is of the rapidly spinning variety with a short H-H bond (<1 Å) and when it is not close in energy to a dihydride tautomer.</sub>

**Isotope Exchange Reactions.** It was found that a catalyst system involving both *trans*-[Ru(H<sub>2</sub>)(H)L<sub>2</sub>]<sup>+</sup> and Ru(H)<sub>2</sub>L<sub>2</sub>, L = dppe, was more effective for H/D exchange between <sup>t</sup>BuOH and D<sub>2</sub> than *trans*-[Ru(H<sub>2</sub>)(H)L<sub>2</sub>]<sup>+</sup> alone, which was used by Albeniz et al.<sup>25</sup> We propose the following mechanism for this exchange process catalyzed by the dihydrogen/dihydride mixture.

This mechanism involves intermolecular H<sup>+</sup> transfer (eqs 20



and 22) and requires similar p*K*<sub>a</sub> values for coordinated H<sub>2</sub> (HD) and <sup>t</sup>BuOH (<sup>t</sup>BuOD). The H<sub>2</sub> complex has a p*K*<sub>a</sub> of about 14 (Table 13) while coordinated <sup>t</sup>BuOH should have a p*K*<sub>a</sub> less than that of the free alcohol (16.6, Table 1). The weakly coordinated dihydrogen (HD) ligand in the complex [Ru(H<sub>2</sub>)(H)L<sub>2</sub>]<sup>+</sup> would facilitate reactions 18 and 21. An intermolecular transfer mechanism looks more reasonable than the direct protonation of

(38) Saburi, M.; Aoyagi, K.; Kodama, T.; Takahashi, T.; Uchida, Y.; Kozawa, K.; Uchida, T. *Chem. Lett.* **1990**, 1909–1912.

(39) Streuli, C. A. *Anal. Chem.* **1960**, *32*, 985.

(40) Bush, R. C.; Angelici, R. J. *Inorg. Chem.* **1988**, *27*, 681–686.

(41) Alder, R. W.; Bowman, P. S.; Steele, W. R. S.; Winterman, D. R. J. *Chem. Soc., Chem. Commun.* **1968**, 723–724.

free alcohol because of the expected high acidity of  $t\text{BuOH}_2^+$  ( $pK_a \approx 0$ ). Finally, although from the data obtained to date we have not been able to prove it, the mechanism would have a second order rate law if intermolecular proton exchange were rate determining.

### Conclusions

The complexes  $\text{trans-}[M(\text{H}_2)\text{H}(\text{L})_2]^+$  are all thought to have rapidly spinning<sup>31</sup> dihydrogen ligands. For a given ligand L, the iron and ruthenium complexes have similar H–H bond lengths ( $\approx 0.9 \text{ \AA}$ ), while the osmium complexes have longer H–H distances ( $\approx 1.0 \text{ \AA}$ ). There is only a slight increase in H–H bond length as a function of R ( $\text{CF}_3$  to H to  $\text{OCH}_3$ ) for the complexes of Ru according to  $^1\text{H}$  NMR  $T_1$  and  $^1J(\text{HD})$  measurements, while there is a significant increase for the Os complexes. The Fe complexes show no significant change in H–H bond length. Despite the lack of structural changes the acidity of the complexes change dramatically with R. The  $pK_a$  values (reflecting a decrease in ease of heterolytic splitting) increase according to this order of R as do the rate constants for H atom exchange (reflecting the ease of homolytic splitting of  $\text{H}_2$ ).

Changing the phosphine ligand L in the complex  $\text{trans-}[M(\text{H}_2)\text{H}(\text{L})_2]^+$  has the expected inductive effect on the acidity of coordinated dihydrogen in that a more electron-withdrawing ligand L gives a more acidic complex. However the change in  $pK_a$  is not as large as might be expected on the basis of a change in electrochemical potential alone. Changes in the energy of H-atom abstraction from the dihydrogen complex to give  $\text{trans-}[\text{MH}_2\text{L}_2]^+$  ( $\Delta H_{\text{BDE}}\{\text{MH}_2\}$ ) appear to counteract this inductive effect in two possible ways. First, a more electron-withdrawing

L results in less back-bonding to the  $\text{H}_2$  ligand, a strengthening of the  $\text{H}_2$  bond and this could give a less acidic  $\text{H}_2$  ligand than might have been expected on the basis of inductive effects alone. Second, the more electron-withdrawing ligand could also destabilize the  $\text{trans-}[\text{MH}_2\text{L}_2]^+$  species. We believe the first effect is important and hope to find out in future studies whether  $\Delta H_{\text{BDE}}\{\text{MH}_2\}$  is a good indicator of H–H bond strength in dihydrogen complexes.

Changing the metal in these complexes from Ru to Os has the paradoxical effect of increasing the acidity of the dihydrogen complex even though the Os complex is more reducing than the Ru complex. This is probably because the Ru complex has a particularly high H–H bond dissociation energy which results in a large  $\Delta H_{\text{BDE}}\{\text{M}(\text{H}_2)\}$  for Ru versus Os. This is the first report of the distinctive contribution of the metal to the acidity of the  $\text{H}_2$  ligand. This should be studied further by calorimetry as done by Angelici and co-workers.<sup>29</sup>

A  $\text{RuH}_2\text{L}_2/[\text{RuH}(\text{H}_2)\text{L}_2]^+$  mixture, L = dppe, in THF was found to be more active at H/D exchange between  $\text{D}_2$  and  $\text{HO}^t\text{Bu}$  than the dihydrogen complex alone. This was predicted beforehand on the basis of matching the  $pK_a$  of the dihydrogen complex (14.0) and the  $pK_a$  of coordinated alcohol.

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