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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

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Abstract: The new dihydrogen complexes *trans*-$[MH(H_2)L_2]BF_4$, L = $P(C_6H_4\text{-}4\text{-}R)_2CH_2CH_2P(C_6H_4\text{-}4\text{-}R)_2$, 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 ^{1}H 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^{t}Bu than the dihydrogen complex alone.

Introduction

The reactions of transition metal dihydrogen complexes[1] is a growing field.[2] 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.[3] 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:

$$L = (4\text{-}RC_6H_4)_2PCH_2CH_2P(C_6H_4\text{-}4\text{-}R)_2$$

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,[4] W,[4] and Re.[5] 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 ($PEt_2CH_2CH_2PEt_2$),[6,7] 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,[6,7] while the latter involves the heterolytic splitting. Part of this work has been communicated.[8]

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.[9-11] 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).

$$MHL_5 + BH^+ \rightleftarrows [M(H_2)L_5]^+ + B \qquad (1)$$

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

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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[1] Kubas, G. J.; Burns, C. J.; Eckert, J.; Johnson, S. W.; Larson, A. C.; Vergamini, P. J.; Unkefer, C. J.; Khalsa, G. R. K.; Jackson, S. A.; Eisenstein, O. *J. Am. Chem. Soc.* **1993**, *115*, 569–581 and references therein.

[2] Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155–284.

[3] Jia, G.; Morris, R. H.; Schweitzer, C. T. *Inorg. Chem.* **1991**, *30*, 593–594.

[4] Hussain, W.; Leigh, G. J.; Mohd. Ali, H.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1703–1708.

[5] Chatt, J.; Hussain, W.; Leigh, G. J.; Mohd. Ali, H.; Pickett, C. J.; Rankin, D. A. *J. Chem. Soc., Dalton Trans.* **1985**, 1131.

[6] Bautista, M. T.; Cappellani, E. P.; Drouin, S. D.; Morris, R. H.; Schweitzer, C. T.; Sella, A.; Zubkowski, J. *J. Am. Chem. Soc.* **1991**, *113*, 4876–4887.

[7] Earl, K. A.; Jia, G.; Maltby, P. A.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 3027–3039.

[8] *Abstracts of Papers;* 4th Chemical Congress of North America, New York; American Chemical Society: Washington, DC, 1991; Inorganic Division, No. 380.

[9] Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1987**, *109*, 5865–5867.

[10] Jia, G.; Morris, R. H. *J. Am. Chem. Soc.* **1991**, *113*, 875–883.

[11] Jia, G.; Lough, A. J.; Morris, R. H. *Organometallics* **1992**, *11*, 161–171.

[12] Chinn, M. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1990**, *112*, 5166–5175.

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metal–hydride bond dissociation enthalpies ($\Delta H_{BDE}\{MH\}$) of transition-metal–hydride complexes in CH_3CN.[17,18] For example the complex $Mn(CO)_5H$ is reported to have a $\Delta H_{BDE}\{MnH\}$ of 68 kcal mol^{-1}, while complexes $M(C_5H_5)(CO)_2H$, M = Fe, Ru, have ΔH_{BDE} of 58 and 65 kcal mol^{-1}, respectively; the first value agrees fairly well with calorimetric determinations. A useful equation for understanding the acidity of dihydrogen complexes in THF or CH_2Cl_2 has been derived from an identical thermochemical cycle (eq 2).[11]

$$1.37\mathrm{p}K_a\{M(H_2)\} = \Delta H_{BDE}\{M(H_2)\} - 23.1E_{1/2}(MH/MH^-) - C \quad (2)$$

It relates the pK_a (pseudoaqueous scale[19]) of a dihydrogen complex $M(H_2)L'_5$ (all L′ not necessarily the same) to the electrochemical potential $E_{1/2}(MH/MH^-)$ for the oxidation of the hydride $[MHL'_5]^-$ in THF or CH_2Cl_2 (versus $Fe(C_5H_5)_2{}^+/Fe(C_5H_5)_2$ reference potential). The bond dissociation energy, $\Delta H_{BDE}\{M(H_2)\}$ is the energy required to take an H atom from the $M(H_2)$ unit in solution (eq 3).

$$\Delta H_{BDE}\{M(H_2)L'_5\} = \Delta H_f\{H^\bullet\} + \Delta H_f\{MHL'_5{}^\bullet\} - \Delta H_f\{M(H_2)L'_5\} \quad (3)$$

Such a ΔH_{BDE} energy has been measured in the gas phase to be 83.5 kcal mol^{-1} for the postulated species $[Mn(H_2)(CO)_5]^+$; this value should also apply approximately for the complex in nonpolar solvents.[20] The reason why this value is much higher than the $\Delta H_{BDE}\{MnH\}$ for $MnH(CO)_5$ mentioned above is probably because a strong H–H bond as well as the Mn–H interactions have to be broken in $[Mn(H_2)(CO)_5]^+$; presumably the coordinated H–H bond is weakened somewhat from the $\Delta H_{BDE}\{H_2(g)\}$ value of 104 kcal mol^{-1}. 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 $\Delta H_{BDE}\{M(H_2)\}$ values.

Initially C in eq (2) was evaluated as 59 kcal mol^{-1} on the assumption that the ΔH_{BDE}(Ru–H) values of the complexes $[Ru(C_5R_5)(H)_2L]^+$ in THF or CH_2Cl_2 were approximately 65 kcal mol^{-1}.[11,15] This gave $\Delta H_{BDE}\{M(H_2)\}$ values of about 65 kcal mol^{-1} for the dihydrogen complexes $[Ru(C_5R_5)(H_2)L]^+$ in solution which are close in energy to the dihydride tautomers just mentioned.[11] However recent work indicates that these ΔH_{BDE} values should be about 72 kcal mol^{-1},[21-24] and so a better value of C in eq 2 is 66 kcal mol^{-1}. Equation 2 with $C = 66$ should now provide ΔH_{BDE} values which can be compared to other ΔH_{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.[17] How the energy ΔH_{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 H_2 loss/coordination are known to catalyze H/D exchange between D_2 and alcohols.[25] Albeniz et al. found that *trans*-$[Ru(H_2)(H)(dppe)_2]BF_4$ was not as effective a catalyst as $[Ir(bq)(PPh_3)_2H(H_2O)]SbF_6$; the latter complex is known to react with H_2 to give $[Ir(bq)(PPh_3)_2H(H_2)]SbF_6$. Our acidity studies suggested that a mixture of *trans*-$[Ru(H_2)(H)(dppe)_2]BF_4$ and $RuH_2(dppe)_2$ might be a more efficient catalyst system than just *trans*-$[Ru(H_2)(H)(dppe)_2]BF_4$ 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 (Et_2O), 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 $PCl_2CH_2CH_2PCl_2$ 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[26] was used to prepare $[Os_2Cl_3(PEtPh_2)_6]Cl\cdot 2H_2O$. Complexes MH_2L_2 and *trans*-$[MH(H_2)L_2]BF_4$ were prepared by the method of Bautista et al.[6] (M = Fe, Ru, L = dppe, depe) or Earl et al.[7] (M = Os, L = dppe, depe). Ditertiaryphosphines $P(C_6H_4\text{-}4\text{-}R)_2CH_2CH_2P(C_6H_4\text{-}4\text{-}R)_2$, R = Me (dtpe) and R = MeO (dape), were prepared by the method of Chatt et al.[5] $RuCl_2(PPh_3)_3$,[27] $RuCl_2(DMSO)_4$,[28] $[Os(C_5H_5)(H)_2(PPh_3)_2]BF_4$,[29] and the acids of Table 1[10,11] were prepared according to literature methods.

Infrared spectra were recorded as Nujol mulls on NaCl plates using a Nicolet 5DX FTIR spectrometer. NMR spectra were obtained on a Varian XL-400, operating at 400.00 MHz for ^1H, 161.98 MHz for ^{31}P, or on a Varian XL-200 operating at 200.00 MHz for ^1H and 80.98 MHz for ^{31}P. Reported chemical shifts refer to room temperature conditions (19 °C) unless specified otherwise. All ^{31}P NMR were proton decoupled, unless stated otherwise. ^{31}P NMR chemical shifts were measured relative to ~1% $P(OMe)_3$ in C_6D_6 sealed in coaxial capillaries and are reported relative to H_3PO_4 by use of $\delta(P(OMe)_3) = 140.4$ ppm. ^1H 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_4NPF_6 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.[5] Their method involved reacting $p\text{-}CF_3C_6H_4Br$ with n-butyllithium followed by

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(13) Chinn, M. S.; Heinekey, D. M.; Payne, N. G.; Sofield, C. D. *Organometallics* **1989**, *8*, 1824–1826.

(14) Baker, M. V.; Field, L. D.; Young, D. J. *J. Chem. Soc., Chem. Commun.* **1988**, 546–548.

(15) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471–1478.

(16) Kristjansdottir, S. S.; Norton, J. R. In *Transition Metal Hydrides: Recent Advances in Theory and Experiment*; Dedieu, A., Ed.; VCH, New York, 1991; Chapter 10.

(17) Tilset, M.; Parker, V. D. *J. Am. Chem. Soc.* **1989**, *111*, 6711–6717.

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

(19) The pK_a values of some dihydrogen complexes and dihydrides were determined by use of protonated tertiaryphosphines whose pK_a values on the aqueous scale have been measured.

(20) Simões, J. A.; Beauchamp, J. L. *Chem. Rev.* **1990**, *90*, 629–688.

(21) Smith et al. (ref 22) used eq 2 with $C = 58.3$ kcal mol^{-1} for pK_a and $E_{1/2}$ values in CH_3CN to calculate ΔBDE(Ru–H) = 74–77 kcal mol^{-1} for some complexes $[Ru(C_5H_5)(PR_3)_2(H)_2]^+$. They assumed that the difference in pK_a between the aqueous scale and the CH_3CN scale is 7.8 units as determined by Coetzee for amines (see reference 23) to convert pK_a values (pseudoaqueous scale) for the Ru complexes obtained by us (ref 11) using protonated phosphines. We have recently determined the pK_a of protonated phosphines in CD_3CN by use of protonated amines of known pK_a in this solvent (ref 24). The difference between pK_a values of protonated phosphines on the CH_3CN scale and those on the aqueous scale is 5.4 ± 0.3, not the value of 7.8. Therefore the ΔBDE values for Ru hydride complexes calculated by Smith et al. (ref 22) have to be reduced by 3 to 71–74 kcal mol^{-1}.

(22) Smith, K.-T.; Rømming, C.; Tilset, M. *J. Am. Chem. Soc.* **1993**, *115*, 8681–8689.

(23) Coetzee, J. F. *Prog. Phys. Org. Chem.* **1967**, *4*, 45.

(24) Fong, T.; Greaves, B.; Morris, R. H. unpublished results.

(25) Albeniz, A. C.; Heinekey, D. M.; Crabtree, R. H. *Inorg. Chem.* **1991**, *30*, 3632.

(26) Chatt, J.; Hayter, R. G. *J. Chem. Soc.* **1961**, 896.

(27) Hallman, P. S.; Stephenson, T. A.; Wilkinson, G. *Inorg. Synth.* **1970**, *12*, 237.

(28) Evans, I. P.; Spenscer, A.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* **1973**, 204.

(29) Wilczewki, T. J. *J. Organomet. Chem.* **1986**, *317*, 307.

Table 1. Acids of Known pK_a Used in the pK_a Determinations

base form	acid form	pK_a
PCy_3	$HPCy_3^+$	9.7[39,40]
P^tBu_3	$HP^tBu_3^+$	11.4[39,40]
$RuH(C_5H_5)(PPh_3)_2$ (**1**)	$[Ru(H)_2(C_5H_5)(PPh_3)_2]BF_4$ (**1H$^+$**)	8.0 ± 0.2[10]
$RuH(C_5Me_5)$(dppm) (**2**)	$[RuH_2(C_5Me_5)(dppm)]BF_4$ (**2H$^+$**)	8.8 ± 0.2[11]
$RuH(C_5Me_5)(PPh_3)_2$ (**3**)	$[Ru(H)_2(C_5Me_5)(PPh_3)_2]BF_4$ (**3H$^+$**)	11.1 ± 0.2[11]
$RuH(C_5Me_5)(PMePh_2)_2$ (**4**)	$[Ru(H)_2(C_5Me_5)(PMePh_2)_2]BPh_4$ (**4H$^+$**)	12.2 ± 0.4[11]
$RuH(C_5Me_5)(PMe_2Ph)_2$ (**5**)	$[Ru(H)_2(C_5Me_5)(PMe_2Ph)_2]BPh_4$ (**5H$^+$**)	14.3 ± 0.4[11]
$RuH(C_5Me_5)(PMe_3)_2$ (**6**)	$[Ru(H)_2(C_5Me_5)(PMe_3)_2]BPh_4$ (**6H$^+$**)	16.3 ± 0.6[11]
proton sponge (**7**)	[proton sponge·H]$^+$ (**7H$^+$**)	12.3[41]
MeO^-	MeOH	15.2[42]
EtO^-	EtOH	15.8[42]
$^iPrO^-$	PrOH	16.5[42]
$^tBuO^-$	^tBuOH	16.6[42]

the addition of $Cl_2PCH_2CH_2PCl_2$. 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 $Cl_2PCH_2CH_2PCl_2$ (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: $\delta(^{31}P, THF)$ −12.4 (s).

Preparation of *trans*-FeH(Cl)(dtpe)$_2$. 1,2-Bis[di(*p*-tolyl)phosphino]ethane, dtpe, (0.12 g, 0.56 mmol) was dissolved in 30 mL of THF, and $FeCl_2$ (0.035 g, 0.28 mmol) was added. To the resulting tan-colored solution was added $NaBH_4$ (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: $\delta(^{31}P, C_6H_6)$ 79.9 (s); $\delta(^1H, C_6D_6)$ −29.1 (quint, $^2J_{HP} = 48.0$ Hz); FAB MS calcd for $C_{60}H_{65}{}^{35}Cl^{56}FeP_4$ 1001, found 1001 (M^+).

Preparation of *trans*-FeH(Cl)(dtfpe)$_2$. This compound was prepared in 49% yield by the above method except that a crop of the bright yellow *cis*-$Fe(H)_2(dtfpe)_2$ was isolated prior to crystallization of the red *trans*-$FeH(Cl)(dtfpe)_2$. 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%; $\delta(^{31}P, C_6H_6)$ 81.6 (s); $\delta(^1H, C_6D_6)$ −29.2 (quint, $^2J_{HP} = 52.2$ Hz); FAB MS. Calcd for $C_{60}H_{41}{}^{35}ClF_{24}{}^{56}FeP_4$: 1432; Found: 1432 ($M^+$). Anal. Calcd for $C_{60}H_{41}ClF_{24}FeP_4$: C, 50.28; H, 2.88; Found: C, 50.05; H, 2.98.

Preparation of *cis*-FeH$_2$(dtpe)$_2$. Under dinitrogen, dtpe (0.5 g, 1.1 mmol) was dissolved in 50 mL of THF, and $FeCl_2$ (0.07 g, 0.55 mmol) was added along with 5 mL of EtOH. $NaBH_4$ (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: $\delta(^{31}P, C_6H_6)$ 102.1 (br), 89.8 (br); $\delta(^1H, C_6D_6)$ −12.82 (m); FAB MS calcd for $C_{60}H_{66}{}^{56}FeP_4$ 965.9, found 965.8 (M^+), 964.8 ($M^+ - H$), 963.8 ($M^+ - 2H$).

Preparation of *cis*-FeH$_2$(dtfpe)$_2$. This bright yellow compound was obtained in 50% yield by the above method: $\delta(^{31}P, THF)$ 107.3 (br), 94.2 (br); $\delta(^1H, C_6D_6)$ −13.49 (m); FAB MS calcd for $C_{60}H_{42}F_{24}{}^{56}FeP_4$ 1398.2, observed 1398.2 (M^+), 1397.2 ($M^+ - H$), 1396.2 ($M^+ - 2H$). Anal. Calcd for $C_{60}H_{42}F_{24}FeP_4$: 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$_2$)L$_2$]BF$_4$ where L = dtfpe and dtpe. These pale yellow complexes were prepared in 80% yield by protonation of the *cis*-dihydride species with excess $HBF_4{\cdot}Et_2O$ in diethyl ether. FeH_2L_2 (0.13 mmol) was suspended in 10 mL of diethyl ether. Under dihydrogen, 0.3 mL of $HBF_4{\cdot}Et_2O$ (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%; $[FeH(H_2)(dtfpe)_2]^+$ $\delta(^{31}P$, acetone) 94.7 (s); $\delta(^1H$, acetone-d_6) −7.62 (br, $Fe(H_2)$), −12.55 (quint, Fe-H, J_{HP} = 44.7 Hz). FAB MS calcd for $C_{60}H_{43}F_{24}{}^{56}FeP_4$ 1398.8, found 1396.4 ($M^+ - 2H$), 1395.4 ($M^+ - 3H$). Anal. Calcd for $C_{60}H_{43}BF_{28}FeP_4$: C, 48.47; H, 2.92. Found: C, 47.91; H, 2.89. $[FeH(H_2)(dtpe)_2]^+$ $\delta(^{31}P$, acetone) 90.7 (s); $\delta(^1H$, acetone-d_6) −8.20 (br, $Fe(H_2)$), −12.50 (br m, Fe-H); FAB MS calcd for $C_{60}H_{67}{}^{56}FeP_4$ 967.5, found 967.0 (M^+), 965.0 ($M^+ - 2H$), 964.0 ($M^+ - 3H$).

Preparation of *trans*-[FeH(HD)(dtfpe)$_2$]BF$_4$. To prepare a solution of DBF_4, 1 mL of D_2O was added dropwise to an equal volume of $HBF_4{\cdot}Et_2O$ until the effervescence ceased. Addition of this mixture to an ether slurry of $Fe(H)_2(dtfpe)_2$ proceeded as described above for the preparation of $[FeH(H_2)(dtfpe)_2]BF_4$: $\delta(^1H$, acetone-d_6, 293 K, 200 MHz) −7.7 (1:1:1 t, $^1J_{HD}$ = 32 ± 1 Hz), −12.6 (quint, $^2J_{HP}$ = 46 Hz).

Solid-State Reaction of *trans*-[FeH(H$_2$)(dtfpe)$_2$]BF$_4$. 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_2, causing it to become pale yellow. This yellow solid was cooled to −80 °C and, to it was added cold (−80 °C) acetone-d_6. The solution was stirred at −80 °C for 30 min, and a ^1H NMR spectrum of the solution at −55 °C was recorded: $\delta(^1H$, 218 K) −7.6 (1:1:1 t, $^1J_{HD}$ = 32 ± 1 Hz), −12.5 (quint). These resonances correspond to *trans*-$[FeD(HD)(dtfpe)_2]BF_4$.

Preparation of *trans*-RuCl$_2$(dape)$_2$. A mixture of 0.20 g of dape (0.44 mmol) and 0.19 g of $RuCl_2(PPh_3)_3$ (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%; $\delta(^{31}P, CH_2Cl_2)$ 41.1 (s).

Preparation of *cis*- and *trans*-RuCl$_2$(dape)$_2$. A mixture of 0.20 g of dape (0.44 mmol) and 0.10 g of $RuCl_2(DMSO)_4$ (0.21 mmol) in 20 mL of CH_2Cl_2 was stirred at room temperature overnight to give a yellow solution. The solvent was then removed completely. Addition of 10 mL of Et_2O to the residue produced a yellow powder. The powder was collected by filtration, washed with Et_2O, and dried under vacuum: yield, 0.14 g, 62%. The ^{31}P NMR spectrum shows that the product contains *ca.* 10% *trans*-$RuCl_2(dape)_2$ and 90% of *cis*-$RuCl_2(dape)_2$: *cis*-$RuCl_2(dape)_2$ $\delta(^{31}P, C_6H_6)$ 48.8 (t), 33.5 (t, $^2J_{PP}$ = 20.7 Hz).

Preparation of *trans*-RuCl$_2$(dtfpe)$_2$. A mixture of 0.30 g of dtfpe (0.45 mmol) and 0.20 g of $RuCl_2(PPh_3)_3$ (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%; $\delta(^{31}P, C_6H_6)$ 44.2 (s). Anal. Calcd for $C_{60}H_{40}Cl_2F_{24}P_4Ru$: C, 47.63; H, 2.67; Cl, 4.69. Found: C, 47.33; H, 2.71; Cl, 5.12.

Preparation of *cis*-RuCl$_2$(dtfpe)$_2$. A mixture of 0.50 g of dtfpe (0.75 mmol) and 0.15 g of $RuCl_2(DMSO)_4$ (0.31 mmol) in 10 mL of CH_2Cl_2 reacted at room temperature overnight without stirring to give some crystalline solid and a yellow-orange solution. The CH_2Cl_2 was then removed completely, and to the residue was added 3 mL of Et_2O 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%; $\delta(^{31}P, THF)$ 56.4 (t), 39.8 (t, $^2J_{PP}$ = 18.8 Hz). Anal. Calcd for $C_{60}H_{40}Cl_2F_{24}P_4Ru$: C, 47.63; H, 2.67; Cl, 4.69. Found: C, 47.76; H, 2.75; Cl, 5.22.

Preparation of *cis*- and *trans*-$\mathrm{RuH_2(dape)_2}$. A mixture of 0.50 g of $\mathrm{RuCl_2(dape)_2}$ (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 $\mathrm{NaBH_4}$ (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%. ^{31}P NMR integration of the product in THF shows that it consists of *ca.* 87% of *cis*-$\mathrm{RuH_2(dape)_2}$ and 13% of *trans*-$\mathrm{RuH_2(dape)_2}$: *cis*-$\mathrm{RuH_2(dape)_2}$ δ (^{31}P, $\mathrm{C_6H_6}$) 76.1 (t), 62.5 (br, $^2J_{\mathrm{PP}} = 15.7$ Hz); δ (^{1}H, $\mathrm{C_6D_6}$) –8.40 (m); *trans*-$\mathrm{RuH_2(dape)_2}$ δ (^{31}P, $\mathrm{C_6H_6}$) 80.4 (s); δ (^{1}H, $\mathrm{C_6D_6}$) –8.28 (quint, $J_{\mathrm{PH}} = 19$ Hz). Anal. Calcd for $\mathrm{C_{60}H_{66}P_4O_8Ru{\cdot}MeOH}$: C, 62.51; H, 6.02. Found: C, 62.20; H, 5.66.

Preparation of *cis*- and *trans*-$\mathrm{RuH_2(dtfpe)_2}$. A mixture of 1.0 g of *cis*-$\mathrm{RuCl_2(dtfpe)_2}$ (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 $\mathrm{CH_2Cl_2}$. The $\mathrm{CH_2Cl_2}$ 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 ^{31}P NMR spectrum in THF of the product indicates that it consists of *ca.* 91% of *cis*-$\mathrm{RuH_2(dtfpe)_2}$ and *ca.* 9% of *trans*-$\mathrm{RuH_2(dtfpe)_2}$: *cis*-$\mathrm{RuH_2(dtfpe)_2}$ δ (^{31}P, $\mathrm{C_6H_6}$) 82.6 (t), 67.8 (br, $^2J_{\mathrm{PP}} = 13.3$ Hz); δ (^{1}H, $\mathrm{CD_2Cl_2}$) –8.98 (m); *trans*-$\mathrm{RuH_2(dtfpe)_2}$ δ (^{31}P, $\mathrm{C_6H_6}$) 84.8 (s); δ (^{1}H, $\mathrm{CD_2Cl_2}$) –8.76 (quint, $J_{\mathrm{PH}} = 19$ Hz). Anal. Calcd. for $\mathrm{C_{60}H_{42}F_{24}P_4Ru}$: C, 49.91; H, 2.93. Found: C, 49.53; H, 2.87.

Preparation of $\mathbf{[RuH(dtfpe)_2]BF_4}$. A solution of 1.0 g of $\mathrm{RuH_2(dtfpe)_2}$ (0.69 mmol) in 30 mL of $\mathrm{Et_2O}$ was titrated with $\mathrm{HBF_4{\cdot}Et_2O}$ to give a white solid under an atmosphere of dihydrogen. The white solid was collected by filtration, washed with $\mathrm{Et_2O}$, and dried under vacuum to give a yellow solid: yield 0.98 g, 93%; δ (^{31}P, THF) 64.5 (s); δ (^{1}H, $\mathrm{CD_2Cl_2}$) no hydride resonance observed.

Preparation of *trans*-$\mathbf{[RuH(H_2)(dtfpe)_2]BF_4}$. The yellow solid $\mathrm{[RuH(dtfpe)_2]BF_4}$ 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 $\mathrm{[Ru(H)(H_2)(dtfpe)_2]BF_4}$. δ (^{31}P, THF) 71.4 (s); δ (^{1}H, acetone-d_6, 293 K) –4.11 (br, $\mathrm{Ru(H_2)}$), –9.85 (quint, $^2J_{\mathrm{PH}} = 17.8$ Hz, RuH). Anal. Calcd for $\mathrm{C_{60}H_{43}BF_{28}P_4Ru}$: C, 47.05; H, 2.83. Found: C, 46.94; H, 2.87.

Observation of *trans*-$\mathbf{[RuH(HD)(dtfpe)_2]BF_4}$. A ^{1}H NMR sample of $\mathrm{[RuH(dtfpe)_2]BF_4}$ in acetone-d_6 was stored under an HD atmosphere generated by slowly dropping $\mathrm{D_2O}$ into a flask containing NaH for 30 min: δ (^{1}H, 293 K) –4.16 (1:1:1 t, $J_{\mathrm{HD}} = 33.1$, Ru(HD)), –9.78 (quint, $^2J_{\mathrm{PH}} = 17.7$ Hz, RuH); $\mathrm{[RuD(HD)(dtfpe)_2]^+}$ was also present –4.28 (1:1:1 t, $J_{\mathrm{HD}} = 33.1$, Ru(HD)).

Observation of *trans*-$\mathbf{[RuH(H_2)(dape)_2]BF_4}$. Method 1. To a solution of 0.20 g of the mixture of *cis*- and *trans*-$\mathrm{RuH_2(dape)_2}$ in 10 mL of THF was added $\mathrm{HBF_4{\cdot}Et_2O}$, drop by drop, to give a clear colorless solution. A ^{31}P NMR spectrum for the solution indicates that there is only $\mathrm{[RuH(H_2)(dape)_2]BF_4}$ ($\delta = 66.3$). The THF was removed under vacuum. The residue was redissolved in THF, and a ^{31}P NMR at this stage showed that extensive decomposition had occurred.

Method 2. To a suspension of 0.20 g of $\mathrm{RuH_2(dape)_2}$ in 20 mL of $\mathrm{Et_2O}$ was added a slight excess of $\mathrm{HBF_4{\cdot}Et_2O}$ to give a white solid. The solid was then collected by filtration, washed with $\mathrm{Et_2O}$, and dried under vacuum. The ^{31}P NMR spectrum for the solid dissolved in THF indicates that a complicated mixture formed.

Method 3. The compounds $\mathrm{RuH_2(dape)_2}$ and $\mathrm{[HPCy_3]BPh_4}$[10] were loaded into an NMR tube. Acetone-d_6 was then added, and ^{31}P NMR spectra were collected. The products were $\mathrm{[RuH(H_2)(dape)_2]^+}$ and free $\mathrm{PCy_3}$: δ (^{1}H, acetone-d_6) –5.0 (br, $\mathrm{Ru(H_2)}$), –10.30 (quint, $^2J_{\mathrm{PH}} = 18.0$ Hz, RuH). δ (^{31}P) 66.3 (s), 9.0 (s).

Observation of *trans*-$\mathbf{[RuH(HD)(dape)_2]^+}$. The acid $\mathrm{[DPCy_3]BF_4}$ was prepared as a white solid by titrating a solution of $\mathrm{PCy_3}$ in diethyl ether with $\mathrm{D_2O}$ acidified with $\mathrm{HBF_4}$ in a fashion similar to the preparation of $\mathrm{[HPtol_3]BF_4}$.[10] The compounds $\mathrm{RuH_2(dape)_2}$ and $\mathrm{[DPCy_3]BF_4}$ were loaded into a ^{1}H NMR tube. Acetone-d_6 was then added: δ (^{1}H) –4.8 (br 1:1:1 t, $J_{\mathrm{HD}} = 31$, Ru(HD)), –10.2 (quint, $^2J_{\mathrm{PH}} = 17.8$ Hz, RuH).

Preparation of *cis*-$\mathbf{OsCl_2(dtfpe)_2}$. $\mathrm{[Os_2Cl_3(PPh_2Et)_6]Cl}$ (0.64 g, 0.36 mmol) and dtfpe (1.00 g, 1.5 mmol) were heated with stirring to 200 °C 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 (^{31}P, THF) 10.3 (br), 8.1 (br).

Table 2. Reagents and Products of Low-Temperature Deprotonation Reactions Observed by ^{1}H NMR Spectroscopy at –80 °C

reagent	observed product
trans-$\mathrm{[FeH(H_2)(dtfpe)_2]BF_4}$	*cis*-$\mathrm{Fe(H)_2(dtfpe)_2}$
trans-$\mathrm{[FeH(H_2)(dppe)_2]BF_4}$	*cis*-$\mathrm{Fe(H)_2(dppe)_2}$
trans-$\mathrm{[RuH(H_2)(dppe)_2]BF_4}$	*trans*-$\mathrm{Ru(H)_2(dppe)_2}$
trans-$\mathrm{[OsH(H_2)(dppe)_2]BF_4}$	*trans*-$\mathrm{Os(H)_2(dppe)_2}$[a]

[a] After the sample was left at room temperature for 5 min, the cis isomer was the major product observed by use of room-temperature ^{1}H NMR spectroscopy.

Preparation of *cis*- and *trans*-$\mathbf{OsH_2(dtfpe)_2}$. A slurry of $\mathrm{LiAlH_4}$ (0.062 g, 1.63 mmol) in 5 mL of THF was added to a stirred solution of *cis*-$\mathrm{OsCl_2(dtfpe)_2}$ (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 $\mathrm{NaBH_4}$ (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 $\mathrm{C_{60}H_{42}F_{24}{}^{192}OsP_4}$ 1534.3, observed 1534.6 ($\mathrm{M^+}$), 1533.3 ($\mathrm{M^+ - H}$), 1532.3 ($\mathrm{M^+ - 2H}$); *trans*-$\mathrm{OsH_2(dtfpe)_2}$ δ (^{31}P, THF) 52.2 (s); δ (^{1}H, acetone-d_6) –11.10 (quint, $J_{\mathrm{HP}} = 15.2$ Hz); *cis*-$\mathrm{OsH_2(dtfpe)_2}$ δ (^{31}P, THF) 49.8 (br), 39.8 (br); δ (^{1}H, acetone-d_6) –10.47 (m). Anal. Calcd. for $\mathrm{C_{60}H_{42}F_{24}OsP_4}$: C, 47.01; H, 2.76. Found: C, 46.73; H, 2.66.

Preparation of *trans*-$\mathbf{[OsH(H_2)(dtfpe)_2]BF_4}$. *cis*- and *trans*-$\mathrm{OsH_2(dtfpe)_2}$ (0.20 g, 0.13 mmol) was suspended in 10 mL of diethyl ether. Under dihydrogen, 0.3 mL of $\mathrm{HBF_4{\cdot}Et_2O}$ (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 $\mathrm{C_{60}H_{43}{}^{192}OsP_4F_{24}}$ 1535.1, found 1534.7 ($\mathrm{M^+}$), 1532.7 ($\mathrm{M^+ - 2H}$), 1531.7 ($\mathrm{M^+ - 3H}$); δ (^{31}P, THF) 39.9 (s); δ (^{1}H, acetone-d_6, 293 K) –5.97 (br, $\mathrm{Os(H_2)}$), –8.95 (br, Os-H). Anal. Calcd for $\mathrm{C_{60}H_{43}BF_{28}OsP_4}$: C, 44.46; H, 2.67. Found: C, 44.06; H, 2.60.

Synthesis of *trans*-$\mathbf{[OsD(HD)(dtfpe)_2]BF_4}$. A slurry of $\mathrm{LiAlD_4}$ (0.1 g) in 5 mL of THF was added to a stirred solution of *cis*-$\mathrm{OsCl_2(dtfpe)_2}$ (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 $\mathrm{HBF_4{\cdot}Et_2O}$ (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 (^{1}H, acetone-d_6, 223 K) –5.97 (1:1:1 t, $J_{\mathrm{HD}} = 28.3$ Hz, Os(HD)), –9.18 (quint, $J_{\mathrm{HP}} = 14$ Hz, OsH).

Low-Temperature Deprotonation of *trans*-$\mathbf{[MH(H_2)L_2]^+}$ Complexes, M = Fe, Ru, Os, L = dppe, M = Fe, L = dtfpe. Under argon gas, a known amount of $\mathrm{[MH(H_2)L_2]BF_4}$ was dissolved in acetone-d_6 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$^+$. Excess $\mathrm{HBF_4{\cdot}Et_2O}$ was added to proton sponge (1,8-bis(dimethylamino)napthalene, ~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 $\mathrm{NaBPh_4}$ in MeOH was added, and immediately a white solid precipitated out. The crude [proton sponge·H]$\mathrm{BPh_4}$ was collected by filtration, washed with cold MeOH, and recrystallized as white needles

Table 3. Acid/Base Equilibria for Complexes $[\mathrm{MH(H_2)L_2}]^+/\mathrm{MH_2L_2}$ (L = dtfpe at 20 °C under 1 atm of $\mathrm{H_2}$)
$\mathrm{B_1 + B_2H^+ \rightleftarrows B_2 + B_1H^+}$

no.	$\mathrm{B_1}$	$\mathrm{B_2H^+}$	reaction conditions[a]	$\mathrm{B_2}$	$\mathrm{B_1H^+}$	K[b]	pK_a^{cis} of $[\mathrm{MH(H_2)L_2}]^+$	M
1.	$\mathrm{OsH_2L_2}$	$\mathbf{1}\mathrm{H^+}$	THF-d_8; 0.3 h	**1**	$[\mathrm{OsH(H_2)L_2}]^+$	2 ± 1 (8)	8.3 ± 0.2	Os
2.	**1**	$[\mathrm{OsH(H_2)L_2}^+$	THF-d_8; 24 h	$\mathrm{OsH_2L_2}$	$\mathbf{1}\mathrm{H^+}$	0.3 ± 0.1 (0.1)	8.5 ± 0.2	Os
3.	$\mathrm{PCy_3}$	$[\mathrm{OsH(H_2)L_2}]^+$	THF; 20 h	$\mathrm{OsH_2L_2}$	$\mathrm{HPCy_3^+}$	>20[c]	<9.7	Os
4.	$\mathrm{RuH_2L_2}$	$\mathbf{1}\mathrm{H^+}$	THF-d_8; 18 h	**1**	$[\mathrm{RuH(H_2)L_2}]^+$	7 ± 4	8.8 ± 0.3	Ru
5.	$\mathrm{RuH_2L_2}$	$\mathbf{1}\mathrm{H^+}$	THF; 3 h	**1**	$[\mathrm{RuH(H_2)L_2}]^+$	13 ± 6 (111)	9.1 ± 0.3	Ru
6.	$\mathrm{RuH_2L_2}$	$[\mathrm{OsH(H_2)L_2}]^+$	THF; 0.2 h	$\mathrm{OsH_2L_2}$	$[\mathrm{RuH(H_2)L_2}]^+$	5 ± 1 (35)	9.1 ± 0.2	Ru
7.	$\mathrm{RuH_2L_2}$	$\mathbf{1}\mathrm{H^+}$	ac-d_6; 3 h	**1**	$[\mathrm{RuH(H_2)L_2}]^+$	8 ± 4	9.1 ± 0.3	Ru
8.	**1**	$[\mathrm{RuH(H_2)L_2}]^+$	ac-d_6; 3 h	$\mathrm{RuH_2L_2}$	$\mathbf{1}\mathrm{H^+}$	0.2 ± 0.1	8.7 ± 0.3	Ru
9.	$\mathrm{FeH_2L_2}$	$[\mathrm{OsH(H_2)L_2}]^+$	THF; 24 h	$\mathrm{OsH_2L_2}$	$[\mathrm{FeH(H_2)L_2}]^+$	0.2 ± 0.1	7.7 ± 0.3	Fe
10.	$\mathrm{OsH_2L_2}$	$[\mathrm{FeH(H_2)L_2}]^+$	THF-d_8; 0.2 h	$\mathrm{FeH_2L_2}$	$[\mathrm{OsH(H_2)L_2}]^+$	4 ± 2	7.8 ± 0.3	Fe

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

Table 4. Acid/Base Equilibria for the Complexes $[\mathrm{MH(H_2)L_2}]^+/\mathrm{MH_2L_2}$ (L = dppe under 1 atm of $\mathrm{H_2}$)
$\mathrm{B_1 + B_2H^+ \rightleftarrows B_2 + B_1H^+}$

no.	$\mathrm{B_1}$	$\mathrm{B_2H^+}$	reaction conditions[a]	$\mathrm{B_2}$	$\mathrm{B_1H^+}$	K[b]	pK_a^{cis} of $[\mathrm{MH(H_2)L_2}]^+$	M
1.	$\mathrm{OsH_2L_2}$	$\mathbf{4}\mathrm{H^+}$	THF-d_8; 14 h	**4**	$[\mathrm{OsH(H_2)L_2}]^+$	3 ± 1 (25)	12.7 ± 0.1	Os
2.	$\mathrm{OsH_2L_2}$	$\mathbf{4}\mathrm{H^+}$	ac-d_6; 18 h	**4**	$[\mathrm{OsH(H_2)L_2}]^+$	2 ± 1[c]	12.5 ± 0.1	Os
3.	$\mathrm{OsH_2L_2}$	$\mathbf{5}\mathrm{H^+}$	ac-d_6; 3 h	*d*	*d*	<0.05	<13	Os
4.	$\mathrm{OsH_2L_2}$	MeOH	THF/ac; 3 h	*d*	*d*	*e*	<15	Os
5.	**5**	$[\mathrm{RuH(H_2)L_2}]^+$	THF-d_8; 13 h	$\mathrm{RuH_2L_2}$	$\mathbf{5}\mathrm{H^+}$	2 ± 1	14 ± 0.4	Ru
6.	$\mathrm{RuH_2L_2}$	$\mathbf{5}\mathrm{H^+}$	ac-d_6; 16 h	**5**	$[\mathrm{RuH(H_2)L_2}]^+$	0.2 ± 0.1	13.6 ± 0.4	Ru
7.	**5**	$[\mathrm{RuH(H_2)L_2}]^+$	ac-d_6; 16 h	$\mathrm{RuH_2L_2}$	$\mathbf{5}\mathrm{H^+}$	5 ± 2	13.6 ± 0.4	Ru
8.	$\mathrm{RuH_2L_2}$	MeOH	MeOH; 3 h	$\mathrm{MeO^-}$	$[\mathrm{RuH(H_2)L_2}]^+$	*f*	~15	Ru
9.	$\mathrm{RuH_2L_2}$	$\mathbf{3}\mathrm{H^+}$	ac-d_6; 3 h	**3**	$[\mathrm{RuH(H_2)L_2}]^+$	>50	>12.5	Ru
10.	$\mathrm{FeH_2L_2}$	$[\mathrm{OsH(H_2)L_2}]^+$	THF; 0.2 h	$\mathrm{OsH_2L_2}$	$[\mathrm{FeH(H_2)L_2}]^+$	0.10 ± 0.05	11.8 ± 0.4	Fe
11.	$\mathrm{FeH_2L_2}$	$\mathbf{4}\mathrm{H^+}$	THF; 12 h	**4**	$[\mathrm{FeH(H_2)L_2}]^+$	~1[g]	12.2 ± 0.5	Fe
12.	$\mathrm{FeH_2L_2}$	$\mathbf{7}\mathrm{H^+}$	THF; 5 h	**7**	$[\mathrm{FeH(H_2)L_2}]^+$	~1[g]	12.1 ± 0.5	Fe
13.	$\mathrm{FeH_2L_2}$	$\mathbf{5}\mathrm{H^+}$	THF; 1 h	*d*	*d*	<0.05	<13	Fe

[a] Deuterated solvents indicate that ^{1}H NMR was used; nondeuterated solvents indicate that ^{31}P NMR was used; ac = acetone. [b] K^{cis} (K^{trans} in brackets). Refer to eqs 8 and 9 for the definitions of K. [c] Average of two values. [d] Reactants observed, but not products. [e] No $[\mathrm{OsH(H_2)L_2}]^+$ observed but traces of side products produced; ^{31}P NMR: 23.6 (s), 8.9 (s). [f] $[\mathrm{RuH(H_2)L_2}]^+$ observed but not $\mathrm{RuH_2L_2}$ (too insoluble). [g] Some free dppe observed ^{31}P NMR: −13.4 ppm.

Table 5. Acid/Base Equilibria for the Complexes $[\mathrm{FeH(H_2)L_2}]^+/\mathrm{FeH_2L_2}$ (L = dtpe)[a]
$\mathrm{B_1 + B_2H^+ \rightleftarrows B_2 + B_1H^+}$

no.	$\mathrm{B_1}$	$\mathrm{B_2H^+}$	reaction conditions	$\mathrm{B_2}$	$\mathrm{B_1H^+}$	K[a]	pK_a^{cis} of $[\mathrm{FeH(H_2)L_2}]^+$
1.	$\mathrm{FeH_2L_2}$	$\mathbf{4}\mathrm{H^+}$	THF	**4**	$[\mathrm{FeH(H_2)L_2}]^+$	3 ± 1	12.7
2.	**4**	$[\mathrm{FeH(H_2)L_2}]^+$	THF	$\mathrm{FeH_2L_2}$	$\mathbf{4}\mathrm{H^+}$	0.5 ± 0.2	12.5
3.	$\mathrm{FeH_2L_2}$	$\mathbf{5}\mathrm{H^+}$	THF	*b*	*b*	<0.05	<13

[a] Reactions monitored by ^{31}P NMR. [b] No products observed.

Table 6. Acid/Base Equilibria for the Complexes $[\mathrm{RuH(H_2)L_2}]^+/\mathrm{RuH_2L_2}$ (L = dape)
$\mathrm{B_1 + B_2H^+ \rightleftarrows B_2 + B_1H^+}$

no.	$\mathrm{B_1}$	$\mathrm{B_2H^+}$	reaction conditions	$\mathrm{B_2}$	$\mathrm{B_1H^+}$	K[a]	pK_a^{cis} of $[\mathrm{RuH(H_2)L_2}]^+$
1.	$\mathrm{RuH_2L_2}$	$\mathbf{6}\mathrm{H^+}$	THF-d_8; 3 h, 12 h	**6**	$[\mathrm{RuH(H_2)L_2}]^+$	3 ± 1[b] (20)	16.8 ± 0.7
2.	$\mathrm{RuH_2L_2}$	$\mathbf{6}\mathrm{H^+}$	ac-d_6; 3 h, 12 h	**6**	$[\mathrm{RuH(H_2)L_2}]^+$	0.4 ± 0.2	15.9 ± 0.7
3.	$\mathrm{RuH_2L_2}$	$\mathbf{5}\mathrm{H^+}$	ac-d_6; 3 h	**5**	$[\mathrm{RuH(H_2)L_2}]^+$	>20	>15.5

[a] K^{cis} (K^{trans} in brackets). Refer to eqs 8 and 9 for the definitions of K. [b] Average of four values.

from $\mathrm{CH_2Cl_2}$ and MeOH: δ (^{1}H, $\mathrm{CD_2Cl_2}$) 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, $[\mathrm{HPCy_3}]^+$, $\mathbf{7}\mathrm{H^+}$, or alcohol) were mixed with a base (dihydride complex) in THF-d_8 or acetone-d_6. The resulting mixture was stirred at 20 °C under a dihydrogen atmosphere for a period from 3 to 18 h before ^{1}H and/or ^{31}P NMR spectra were collected. The relative concentrations of species involved in the equilibrium were determined by integration. When ^{31}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 ^{31}P NMR chemical shifts of complexes in THF at equilibrium not listed above: **1** 67.9 (s); $\mathbf{1}\mathrm{H^+}$ 58.4 (s); **4** 46.1 (s); $\mathbf{4}\mathrm{H^+}$ 40.9 (s); **5** 26.4 (s); $\mathbf{5}\mathrm{H^+}$ 25.4 (s); *cis*-$\mathrm{Fe(H)_2(dtfpe)_2}$ 107.3 (br), 94.2 (br); $[\mathrm{FeH(H_2)(dtfpe)_2}]^+$ 94.3 (s); *cis*-$\mathrm{Fe(H)_2(dppe)_2}$ 103.2 (br), 90.8 (br); $[\mathrm{FeH(H_2)(dppe)_2}]^+$ 92.0; *cis*-$\mathrm{FeH_2(dtpe)_2}$ 102.2 (br), 89.9 (br); $[\mathrm{FeH(H_2)(dtpe)_2}]^+$ 90.2 (s); *cis*-$\mathrm{Ru(H)_2(dtfpe)_2}$ 82.6 (t), 67.8 (t); *trans*-$\mathrm{Ru(H)_2(dtfpe)_2}$ 84.8 (s); $[\mathrm{RuH(H_2)(dtfpe)_2}]^+$ 71.5 (s); *trans*-$\mathrm{RuH_2(depe)_2}$ 84.4 (s); *cis*-$\mathrm{RuH_2(depe)_2}$ 76.0 (m), 63.0 (m); $[\mathrm{Ru(\eta^2\text{-}H_2)H(depe)_2}]^+$ 68.5 (s); *cis*-$\mathrm{Os(H)_2(dtfpe)_2}$ 50.4 (m), 40.4 (m); *trans*-$\mathrm{Os(H)_2(dtfpe)_2}$ 52.1 (s); $[\mathrm{OsH(H_2)(dtfpe)_2}]^+$ 40.4 (s); *cis*-$\mathrm{Os(H)_2(dppe)_2}$ 45.7 (t), 35.7 (t); *trans*-$\mathrm{Os(H)_2(dppe)_2}$ 49.8 (s); $[\mathrm{OsH(H_2)(dppe)_2}]^+$ 37.6 (s); *trans*-$\mathrm{OsH_2(depe)_2}$ 49.2 (s); *cis*-$\mathrm{OsH_2(depe)_2}$ 39.2 (m), 30.2 (m); $[\mathrm{Os(\eta^2\text{-}H_2)H(depe)_2}]^+$ 36.4 (s); $\mathrm{PCy_3}$ 9.0 (s); $[\mathrm{HPCy_3}]\mathrm{BPh_4}$ 31.6 (s); $\mathrm{P^tBu_3}$ 62.7 (s); $[\mathrm{HP^tBu_3}]^+$ 56.6 (s); dtfpe −12.6 (s); dppe −13.4 (s); dtpe −14.8 (s); dape −15.7; depe −19.3.

Some ^{1}H NMR chemical shifts of complexes in equilibria solution in THF-d_8 at equilibrium not listed above: **1** −12.3 (t); $\mathbf{1}\mathrm{H^+}$ −7.3 (t); $\mathbf{5}\mathrm{H^+}$ −9.5 (t); **6** −14.3 (t); $\mathbf{6}\mathrm{H^+}$ −10.4 (t); *cis*-$\mathrm{FeH_2(dtpe)_2}$ −13.3 (m); *cis*-$\mathrm{RuH_2(dape)_2}$ −8.8 (m); *trans*-$\mathrm{RuH_2(dape)_2}$ −8.5 (quint); $[\mathrm{RuH(H_2)}$-

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

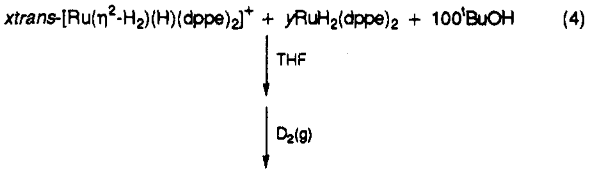
no.	B_1	+	B_2H^+	reaction conditions	B_2	+	B_1H^+	pK_a^{cis} of $[MH(H_2)L_2]^+$
1.	OsH_2L_2	+	EtOH	$\xrightarrow{EtOH}$	EtO^-	+	$[OsH(H_2)L_2]^+$	>16
2.	OsH_2L_2	+	^iPrOH	$\xleftarrow{iPrOH}$				<16.5
3.	RuH_2L_2	+	EtOH	$\xrightarrow{EtOH}$	EtO^-	+	$[RuH(H_2)L_2]^+$	>16
4.	RuH_2L_2	+	^iPrOH	$\overset{iPrOH}{\rightleftarrows}$	$^iPrO^-$	+	$[RuH(H_2)L_2]^+$	~16.5
5.	FeH_2L_2	+	EtOH	$\overset{EtOH}{\rightleftarrows}$	EtO^-	+	$[FeH(H_2)L_2]^+$	~16[a]

[a] Some decomposition; free ligand observed.

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

Reactions of $Ru(C_5H_5)$ and $Os(C_5H_5)$ Hydride Complexes. Complexes $Os(C_5H_5)H(PPh_3)_2$ (10 mg) and $[Ru(C_5H_5)(H)_2(PPh_3)_2]BF_4$ (10 mg) were dissolved in CD_2Cl_2, and the ^1H NMR spectrum was recorded immediately. All of the ruthenium dihydride (−7.3 (t), J(P,P) 24 Hz) was converted to $Ru(C_5H_5)H(PPh_3)_2$ (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 ^tBuOH and D_2. A series of reactions (4) were performed with x and y varying between 0 and 1.



$$x\,trans\text{-}[Ru(\eta^2\text{-}H_2)(H)(dppe)_2]^+ + y\,RuH_2(dppe)_2 + 100\,{}^tBuOH \quad (4)$$
$$\downarrow \text{THF}$$
$$\downarrow D_2(g)$$

The reactants, 0.01 mmol in Ru complex(es) and 1 mmol in ^tBuOH, were dissolved in 1 mL of THF, containing 2 μL of C_6D_6 as a standard, and transferred to a 5-mm NMR tube. D_2 was bubbled through the solution for approximately 2 min after which time the sample was put into the NMR probe. ^2H 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 ^2H signal at δ 3.3 ppm against the standard C_6D_6 in the ^2H NMR spectrum. The high field region of the ^2H NMR spectra for reactions when $x = y = 0.4$ revealed the presence of *trans*-$[Ru(\eta^2\text{-}D_2)(D)(dppe)_2]BPh_4$ and $RuD_2(dppe)_2$. The initial reaction between D_2 and ^tBuOH was very fast. This implies that the D_2 in solution was used up very quickly, and the reaction between D_2 and ^tBuOH 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_2Cl_2 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 $Fe(H)_2L_2$, L = dtfpe, dtpe, were prepared by the reactions of mixtures of $FeCl_2$, L, and $NaBH_4$ in THF. The corresponding complexes $Ru(H)_2L_2$, L = dtfpe, dape, and $OsH_2(dtfpe)_2$ were prepared by reactions of the dichlorides *cis*-MCl_2L_2 with NaOMe in MeOH (M = Ru) or $LiAlH_4$ 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 ^{31}P NMR spectra of the dihydrides of iron consisted of two broad singlets of equal intensity. These spectra which are similar to that of $FeH_2(dppe)_2$ are typical of *cis*-$Fe(H)_2L_2$ complexes which are fluxional at 20 °C. The $^{31}P\{^1H\}$ NMR spectra of the Ru and Os dihydrides are consistent with mixtures of *cis*-$M(H)_2L_2$ and *trans*-$M(H)_2L_2$ complexes with the *cis* complex in much higher concentration. These spectra contain two triplets (M_2X_2 spin system) for the *cis* species and a singlet for the *trans* species. The ^2J(P,P) couplings for the *cis*-$Ru(H)_2L_2$ 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.

^1H NMR spectra of the Ru and Os dihydrides also indicate that *cis* and *trans* isomers are present. In the high field region of the ^1H NMR spectrum there is an intense AA′ part of an $AA'MM'X_2$ 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).

$$M(H)_2L_2 + HBF_4{\cdot}Et_2O \rightarrow trans\text{-}[MH(H_2)L_2]BF_4 \quad (5)$$

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 ^1H and ^{31}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 $^{31}P\{^1H\}$ NMR spectrum of each of the dihydrogen complexes is consistent with a *trans*-$[MH(H_2)L_2]^+$ geometry. The high field ^1H 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.[6]

Variable-temperature measurements of the T_1 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_1 values for the dihydrogen and hydride ligands to obtain an accurate minimum T_1 time, T_1(min), and dihydrogen bond length, d_{HH}, as described previously.[30] A correction of d_{HH} to account for relaxation of the H_2 nuclei by neighboring phenyl protons yields d_{HH}(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[30] that the H_2 ligand is spinning rapidly like a propellor.[31] This assumption is probably valid because the deuterated isotopomers of these complexes have large J(H,D) couplings.[7] The minimum T_1 and temperature data are listed in Table 9. As anticipated, the observed T_1 values for hydrides are much higher than those for dihydrogen ligands.

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(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 ^1H 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_1 Values of the Dihydrogen and Hydride Ligands in the Complexes $[MH(H_2)L_2]^+$

$[FeH(H_2)(dtfpe)_2]BF_4$[a]						
T, K	293		253	233	213	
T_1 of $Fe(H_2)$, ms	20 (20[b])		15 (16)	17 (16)	20 (19)	
T_1 of FeH, ms	83 (20[b])		275 (262)	287 (268)	289 (340)	
$[FeH(H_2)(dtpe)_2]BF_4$[a]						
T, K			253	228		203
T_1 of $Fe(H_2)$, ms			15 (16)	14 (14)		17 (17)
T_1 of FeH, ms			330 (240)	220 (221)		300 (290)
$[RuH(H_2)(dtfpe)_2]BF_4$[c]						
T, K	293	273	253	233	213	203
T_1 of $Ru(H_2)$, ms	13 (20)	11 (15)	12 (13)	7 (10)	11 (10)	12 (11)
T_1 of RuH, ms	266 (271)	206 (210)	169 (175)	146 (146)	140 (141)	150 (150)
$[OsH(H_2)(dtfpe)_2]BF_4$[d]						
T, K	293	273	243	228	213	193
T_1 of $Os(H_2)$, ms	37 (36[b])	26 (28[b])	16 (16)	15 (15)	16 (17)	22 (22)
T_1 of OsH, ms	46 (36[b])	76 (28[b])	131 (135)			
$[RuH(H_2)(dape)_2]BPh_4$[c]						
T, K	293	273	253	233	213	193
T_1 of $Ru(H_2)$, ms	16 (16)	13 (13)	12 (12)	11 (11)	12 (13)	20 (19)
T_1 of Ru(H), ms	212 (213)	169 (171)	150 (152)	145 (147)	166 (169)	430 (250)

[a] In acetone-d_6 at 400 MHz; see Table 9 for parameters used in calculating T_1 values. [b] Rates of relaxation of $M(H_2)$ and MH averaged. [c] In CD_2Cl_2 at 200 MHz. [d] In acetone-d_6 at 200 MHz.

Table 9. Observed T_1 (min) Values for H_2 and Terminal Hydride Ligands and Calculated H–H Distances

complex	$T_1^{min}(H_2)$ ms	T, K	T_1(H), ms	d_{HH} Å	d_{HH}(corr) Å
$[Fe(H_2)(H)(dtfpe)_2]^+$	15.5 ± 0.6[a]	247	275 ± 14[a]	0.85[b]	0.86 ± 0.02
$[Fe(H_2)(H)(dtpe)_2]^+$	14 ± 1[a]	228	220 ± 15[a]	0.83	0.84 ± 0.02
$[Ru(H_2)(H)(dtfpe)_2]^+$	10 ± 1[c]	215	141 ± 5[c]	0.89[d]	0.90 ± 0.01
$[Ru(H_2)(H)(dape)_2]^+$	11.0 ± 0.5[c]	235	145 ± 5[c]	0.90[e]	0.91 ± 0.01
$[Os(H_2)(H)(dtfpe)_2]^+$	15 ± 1[c]	228	131 ± 9[c]	0.95[f]	0.97 ± 0.01

[a] 400 MHz. [b] $\tau_0 = 1.8$ ps, $E_a = 2.4$ kcal mol^{-1}. [c] 200 MHz. [d] $\tau_0 = 2.9$ ps, $E_a = 2.2$ kcal mol^{-1}. [e] $\tau_0 = 2.9$ ps, $E_a = 2.4$ kcal mol^{-1}. [f] $\tau_0 = 2.5$ ps, $E_a = 2.4$ kcal mol^{-1}.

Table 10. ^1J(H,D) Couplings for the HD Complexes

complex	^1J(H,D) Hz	T, K	ν, MHz
$[Fe(HD)(H)(dtfpe)_2]^+$	32 ± 1	293	200
$[Ru(HD)(D)(dtfpe)_2]^+$	33.1 ± 0.5	293	200
$[Ru(HD)(H)(dtfpe)_2]^+$	33.1 ± 0.5	293	200
$[Ru(HD)(H)(dape)_2]^+$	31 ± 1	293	200
$[Os(HD)(D)(dtfpe)_2]^+$	28.3 ± 0.5	233	200

The observation of a large ^1J(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 $[FeH(HD)(dtfpe)_2]BF_4$ was prepared by reacting the dihydride complex with HBF_4/D_2O in a similar fashion to eq 5. The corresponding isotopomer $[FeD(HD)(dtfpe)_2]BF_4$ was generated by reacting $[FeH(dtfpe)_2]BF_4$ with D_2 gas in the solid state; this presumably generates $[FeH(D_2)(dtfpe)_2]BF_4$ which rearranges when dissolved, even at low temperature, to give the HD isotopomer as well. The corresponding Ru complex, $[RuH(HD)(dtfpe)_2]BF_4$, was prepared by reacting $[RuH(dtfpe)_2]BF_4$ with HD gas. Some $[RuD(HD)(dtfpe)_2]^+$ isotopomer was also produced in this reaction. The complex $[RuH(dape)_2]^+$ was unstable, and so the complex $[RuH(HD)(dape)_2]^+$ was generated in solution by protonating $RuH_2(dape)_2$ with $[DPCy_3]BF_4$. The Os complex $[OsD(HD)(dape)_2]BF_4$ was prepared by protonating $OsD_2(dtfpe)_2$ with $HBF_4{\cdot}Et_2O$. Table 10 lists the ^1J(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_2 and hydride sites in the complexes *trans*-$[MH(H_2)(dtfpe)_2]^+$ can be estimated from the T_1 data near relaxation coalescence (Table 11).[2] The H_2 resonance (a broad singlet) and H resonance (a quintet) of the Fe complex are at relaxation coalescence at 293 K—the T_1 of both peaks is 21 ms at 400 MHz. The rate constant for $H_2 \rightarrow H$ exchange is about $1/T_1$ or 50 s^{-1}.[2] Data for the dppe complex are included for comparison in Table XI. The $\Delta G^{\ddagger}$ 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 $[RuH(H_2)(dtfpe)_2]^+$ is not broadened by exchange at 293 K, and the T_1 values are not averaged. A lower limit for the activation energy for the $H_2 \rightarrow H$ exchange is 17 kcal mol^{-1} in this case.

The H_2 and H resonances of $[OsH(H_2)(dtfpe)_2]^+$ 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_1 for the resonances (both about 40 ms at 200 MHz, see Table 8) of the Os complex at 293 K. The $\Delta G^{\ddagger}$ value calculated for this process at 273 K is larger than that of the analogous dppe complex.

Line shape coalescence of the H_2 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_2 so that the highest mass peak was attributed to $[MHL_2]^+$ species. The Ru complexes were too unstable for mass spectral analysis.

The white complex $[RuH(H_2)(dtfpe)_2]BF_4$ must be kept under 1 atm of H_2 in the solid state. Otherwise it loses H_2 to give a yellow complex $[MHL_2]^+$ as in eq 6.

$$[MH(H_2)L_2]BF_4 \rightleftarrows [MHL_2]BF_4 + H_2 \tag{6}$$

The yellow solid, $[FeH(H_2)(dtfpe)_2]BF_4$, 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 $[FeH(H_2)(dtfpe)_2]BF_4$ was obtained immediately as in eq 6. This blue solid turned pale yellow upon exposure to carbon monoxide to give $[FeH(CO)(dtfpe)_2]BF_4$.[32] The geometry of the blue complex is unknown. The complex $[FeH(dppe)_2]BPh_4$ is also

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(32) Drouin, S. D. **1991**, MSc. Thesis, University of Toronto.

Table 11. Estimation of Rate Constants for H_2 to H Site Exchange from T_1 Data which Were Obtained Below the Region of Relaxation Coalescence

complex	MHz	T, K	H_2 T_1(eff),[a] ms	H_2 T_1,[b] ms	H T_1(eff),[a] ms	H T_1,[b] ms	k s^{-1}	$\Delta G^{\ddagger}$, kcal mol^{-1}
$[FeH(H_2)(dtfpe)_2]^+$	400	293	21	20	21	287	50	14.9
$[FeH(H_2)(dppe)_2]^+$	200	244	11	12	116	169	5	13.4[6]
	200	293					500[c]	13.9[6]
$[RuH(H_2)(dtfpe)_2]^+$	200	293	13		266		0	>17
$[RuH(H_2)(dppe)_2]^+$	200	285	29	26	294	357	2	16.3[2]
$[OsH(H_2)(dtfpe)_2]^+$	200	273	26	21	78	168	30	14.1
$[OsH(H_2)(dppe)_2]^+$	200	245	29	28	69	211	30	12.6[7]
	200	273					280[c]	12.9[7]

[a] T_1(eff) refers to the observed value obtaining by fitting the inversion recovery data to a single exponential decay (refer to ref 2 for further discussion on this). [b] T_1 is calculated from the parameters of Table 9 and refers to value expected if there were no exchange. [c] Obtained from line shape analysis.

blue.[33] The complex $[OsH(H_2)(dtfpe)_2]BF_4$ turned from yellow to orange when heated above 100 °C; however hydride signals in the ^1H 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 $Fe(H)_2L_2$ 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*-$[MH(H_2)L_2]^+$ complex should give, initially, *trans*-$M(H)_2L_2$ 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_6 at -80 °C:

$$trans\text{-}[MH(H_2)L_2]BF_4 + n\text{-}BuLi \rightarrow M(H)_2L_2 + BuH + Li^+ + BF_4^- \quad (7)$$

When the *trans*-$[OsH(H_2)(dppe)_2]BF_4$ 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*-$Fe(H)_2L_2$ complexes are very unstable and isomerize rapidly to the *cis*-dihydride.

Acid/Base Equilibria and pK_a Determinations. The pK_a values of the dihydrogen complexes were determined by finding a suitable acid of known pK_a which is in equilibrium with the dihydrogen complex as in eq 1. The acids of known pK_a are listed in Table 1. These are sterically hindered protonated phosphines and cationic metal hydride complexes. The pK_a values of the latter which were determined in previous studies provide a suitable pK_a range of 7–16 required for the present study. The conjugate bases of these acids cannot coordinate and displace the weakly bonded H_2 ligand. Although the equilibria are all in nonaqueous media, the pK_a values are extrapolated to aqueous values as described previously.[10] The solvents of choice are THF and acetone. Acetonitrile is too strongly coordinating. Chlorinated solvents ($CHCl_3$, CH_2Cl_2) are too reactive toward the metal–hydride complexes.

Tables 3–7 summarize the results of reactions attempted to observe equilibria between $[MH(H_2)L_2]^+/M(H)_2L_2$ 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_a values were calculated from the equilibrium constant, K^{cis}, for the reaction between a proton donor of known pK_a and the dihydride complex under investigation (eq 8).

$$cis\text{-}M(H)_2L_2 + BH^+ \overset{K^{cis}}{\rightleftarrows} trans\text{-}[MH(H_2)L_2]^+ + B \quad (8)$$

The K^{cis} refers to the equilibrium between the *cis*-$M(H)_2L_2$ isomer and the dihydrogen complex and not the *trans*-$M(H)_2L_2$ 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^{trans} for the *trans* isomer (eq 9) is about $K^{cis}/9$ but it cannot be measured as accurately as K^{cis}.

$$trans\text{-}M(H)_2L_2 + BH^+ \overset{K^{trans}}{\rightleftarrows} trans\text{-}[MH(H_2)L_2]^+ + B \quad (9)$$

Therefore the pK_a^{trans} (see below) for *trans*-$[MH(H_2)L_2]^+$ calculated from the equilibrium data for eq 9 will be ≈1 unit greater than the pK_a^{cis} derived from eq 8.

For the reaction mixtures described in Tables 3–7, THF (or THF-d_8) was the chosen solvent since it is poorly coordinating and therefore does not displace H_2 from dihydrogen complexes. The dihydrogen complexes of dtpe and dppe were considerably less soluble in THF than the analogous dtfpe complexes, $[MH(H_2)(dtfpe)_2]^+$. 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_6. In certain reactions involving the Ru complexes, H/D exchange between the hydride species and the solvent occurred. Reactions were also attempted in CD_2Cl_2, but the Ru and Fe hydrides reacted with this solvent to give *trans*-$MHClL_2$ complexes.

The integrals of NMR resonances (^1H or ^{31}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 $OsH_2(dtfpe)_2$ and $[Ru(H)_2(C_5H_5)(PPh_3)_2]^+$, **1**$H^+$, in THF-$d_8$ 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*-$Os(H)_2L_2$ 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 $[OsH(H_2)(dtfpe)_2]^+$ (entry 2 of Table 3). The pK_a of **1**H^+ has been determined to be 8.0 ± 0.2 (Table 1), and therefore the pK_a^{cis} of $[OsH(H_2)(dtfpe)_2]^+$ in THF-d_8 at 20 °C is calculated from the ^1H NMR intensities to be 8.3 ± 0.2 or 8.5 ± 0.2 for these two approaches to the same equilibrium.

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

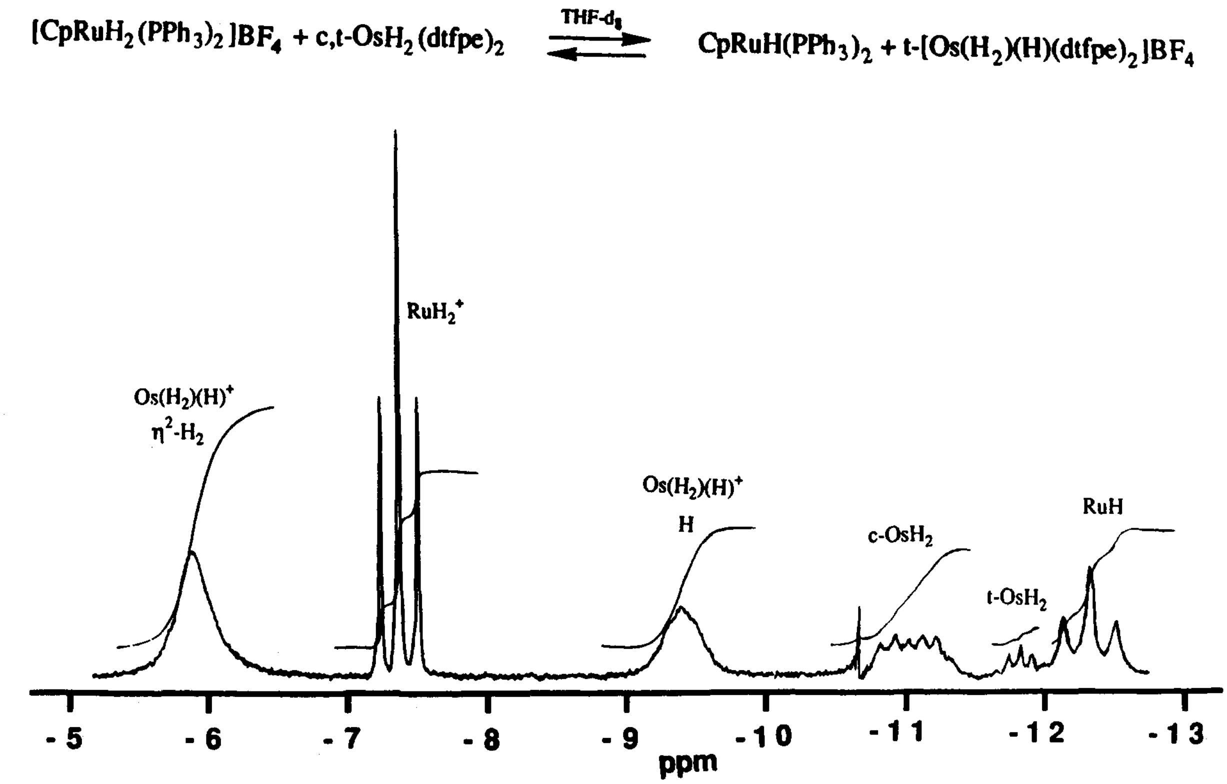


Figure 1. The hydride region of the ^1H NMR spectrum at 200 mHz for the reaction of $[Ru(H)_2(C_5H_5)(PPh_3)_2]BF_4$ (pK_a 8.0) with $Os(H)_2(dtfpe)_2$ in THF-d_8. K^{cis} = $[RuH][Os(H_2)H^+]/([RuH_2^+][cis\text{-}OsH_2])$ = 2.6 ± 0.7.

The deprotonation of this dihydrogen complex by PCy_3 (entry 3, Table 3) is consistent with this result since $HPCy_3^+$ has pK_a 9.7.

The pK_a^{cis} of $[RuH(H_2)(dtfpe)_2]BF_4$ is determined to be about 9.0 in THF or acetone (entries 4–8). Both the reaction of $Ru(H)_2L_2$ with $1H^+$ or with $[OsH(H_2)(dtfpe)_2]^+$ leads to this conclusion. There was no sign of decomposition for these equilibria. The *cis* and *trans* forms of the $M(H)_2L_2$ 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 $[Fe(H_2)H(dtfpe)_2]BF_4$. $Os(H)_2(dtfpe)_2$ is the only compound to react without decomposition. This equilibrium was approached from both sides (entries 9 and 10) and examined by ^1H and ^{31}P NMR; a pK_a^{cis} of 7.8 ± 0.3 can be calculated for $[FeH(H_2)(dtfpe)_2]BF_4$. Thus $[FeH(H_2)(dtfpe)_2]^+$ is more acidic than the analogous osmium complex.

It is interesting that the similar reaction mixture of $[FeH(H_2)(dppe)_2]BF_4$ and $Os(H)_2(dppe)_2$ 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 $FeH_2(dtfpe)_2$ with $1H^+$ (pK_a 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_a^{cis} value of 8 for $[FeH(H_2)(dtfpe)_2]BF_4$ 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 $[MH(H_2)(dtfpe)_2]^+$ complexes is M = Ru < Os < Fe. The reaction between $[RuH(H_2)(dtfpe)_2]^+$ and $Fe(H)_2(dtfpe)_2$ could not be used to confirm this order because decomposition and side reactions occurred.

Complex $4H^+$ (pK_a 12.2) has a comparable acidity to $[OsH(H_2)(dppe)_2]^+$, and this was the key compound for determining the value of 12.6 ± 0.1 for the pK_a^{cis} of the osmium complex (entries 1 and 2 of Table 4). This value explains why $OsH_2(dppe)_2$ is not protonated by $5H^+$ (pK_a 14.3) or MeOH (entries 3 and 4, Table 4).

Complex **5** reacted cleanly with $[RuH(H_2)(dppe)_2]^+$ to give an equilibrium mixture in THF or acetone-d_6 (entries 5–7); the pK_a^{cis} 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_6, and this can influence the integrations of the hydride resonances. It is interesting that MeOH (pK_a 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 $RuH_2(dppe)_2$ in MeOH. Attempts to directly compare the acidity of $[OsH(H_2)(dppe)_2]^+$ with $[RuH(H_2)(dppe)_2]^+$ by reacting the former with $RuH_2(dppe)_2$ or the latter with $OsH_2(dppe)_2$ in acetone-d_6 or THF-d_8 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 $[FeH(H_2)(dppe)_2]^+$ which was totally free of side reactions. The cleanest reaction was that of $FeH_2(dppe)_2$ with $[OsH(H_2)(dppe)_2]^+$ (entry 10, Table 4) which occurs rapidly. The ^{31}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 $4H^+$ or $7H^+$ (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_a^{cis} for the Fe complex is about 12. This seems correct because the acids $[HPCy_3]BPh_4$ (pK_a 9.7) and $[HP^tBu_3]BPh_4$ (pK_a 11.4) completely protonate $FeH_2(dppe)_2$ to give $[Fe(H_2)H(dppe)_2]^+$ and free phosphine and some free dppe. Similarly $5H^+$ (pK_a 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 $FeH_2(dtpe)_2$ is stirred with **4**H^+ (pK_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 pK_a value of 12.6 for $[FeH(H_2)(dtpe)_2]BF_4$ is probably reasonable. The table also indicates that the pK_a of $[FeH(H_2)(dtpe)_2]BF_4$ must be below 13 since $FeH_2(dtpe)_2$ is not protonated ($K < 0.05$) by $[Ru(C_5Me_5)H_2(PPhMe_2)_2]^+$ (**5**H^+, pK_a 14.3).

The acidity determination of the weak acid $[RuH(H_2)(dape)_2]^+$ required the use of the weak acid $[Ru(C_5Me_5)(H)_2(PMe_3)_2]^+$ which has an approximate pK_a value of 16.3. The data of Table 6 suggest a pK_a of about 16.4 for this dape complex.

The weak acids $[MH(H_2)(depe)_2]^+$, M = 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.[14] Ethanol partially protonates the Fe complex and completely protonates the Ru and Os complexes according to ^{31}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 ^iPrOH, albeit partially. Therefore again the order of increasing acidity is Ru < Os < Fe. When $[Fe(\eta^2\text{-}H_2)H(depe)_2]BPh_4$ and $FeH_2(dppe)_2$ were mixed together, there was no visible reaction according to ^{31}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 $[Ru(C_5H_5)(H)_2(PPh_3)_2]^+$ is much more acidic than the corresponding osmium complex $[Os(C_5H_5)(H)_2(PPh_3)_2]^+$. Thus eq 10 lies completely to the right.

$$Os(C_5H_5)H(PPh_3)_2 + [Ru(C_5H_5)(H)_2(PPh_3)_2]^+ \rightarrow Ru(C_5H_5)H(PPh_3)_2 + [Os(C_5H_5)(H)_2(PPh_3)_2]^+ \quad (10)$$

H/D Exchange Catalysis. The ^2H NMR spectra of reaction 4 revealed that when only *trans*-$[Ru(H_2)(H)(dppe)_2]BPh_4$ was used as catalyst in THF, no ^tBuOD was produced over a 1-h period. It is interesting that when CH_2Cl_2 was the solvent instead of THF, such a reaction caused some H/D exchange to occur;[25] we found that the dihydrogen complex in CH_2Cl_2 had very low activity. When only $RuH_2(dppe)_2$ in THF was used, some H/D exchange occurred although less than when both *trans*-$[RuH(H_2)(dppe)_2]BPh_4$ and $RuH_2(dppe)_2$ 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 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 $^1J(H,D)$ values are in the usual range (20–35 Hz) for HD complexes. The greater $^1J(H,D)$ 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 π-backbonding from the filled metal d orbitals into the HD σ* orbital and decrease the H–D bond order as observed.

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

	$\delta(^1H_2)$, ppm	d(HH), Å	J(HD),[a] Hz	$\delta(^1H)$, ppm	$\Delta\delta^{31}P$,[b] ppm
$[FeH(H_2)(dtfpe)_2]^+$	−7.6	0.86	32	−12.6	107.3
$[FeH(H_2)(dppe)_2]^+$	−7.9	0.87	30, 31	−12.6	105.9
$[FeH(H_2)(dtpe)_2]^+$	−8.2	0.84		−12.5	105.5
$[FeH(H_2)(depe)_2]^+$	−10.5	0.86	29.5	−14.6	117.1
$[RuH(H_2)(dtfpe)_2]^+$	−4.1	0.90	33, 33	−9.9	84.0
$[RuH(H_2)(dppe)_2]^+$	−4.6	0.90	32, 33	−10.0	82.0
$[RuH(H_2)(dape)_2]^+$	−5.0	0.91	31	−10.3	82.0
$[RuH(H_2)(depe)_2]^+$	−6.4	0.86	32, 32	−11.3	87.7[c]
$[OsH(H_2)(dtfpe)_2]^+$	−6.0	0.97	28	−9.0	52.5
$[OsH(H_2)(dppe)_2]^+$	−6.8	1.02	25.5	−9.0	50.9
$[OsH(H_2)(depe)_2]^+$	−10.0	1.1–1.5[d]	11	−9.7	56.4[c]

[a] When two values are given the first refers to the $M(HD)(H)L_2^+$ isotopomer and the second refers to the $M(HD)(D)L_2^+$ isotopomer. [b] Coordination chemical shift: $\Delta\delta^{31}P = \delta(^{31}P \text{ in complex}) - \delta(^{31}P \text{ in free L})$ in acetone-d_6. [c] Reference 6 reported incorrect δP for the Ru and Os depe compounds. The correct δ are 68.7 ppm (Ru) and 37.1 ppm (Os). [d] See ref 7.

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 H_2 ligand—this shows that the H_2 nuclei are more shielded on going from p-CF_3 (dtfpe) to p-CH_3 (dtpe) substituents on the ligands as might be expected on the basis of the acidity of the H_2 (see below). It is notable that the hydride chemical shift remains constant within this series. The coordination chemical shift of the ^{31}P nuclei decreases with this change of substituents and this is also a shielding effect. The change in chemical shift of the H_2, ^1H, and ^{31}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 $^1J(H,D)$ 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 δ (H_2) is sensitive to the nature of the ligand L. All the δ (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 δ (H_2) of the complex is closer to that of free H_2 gas (+4.4 ppm). The distances d_{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 $^1J(H,D)$ 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 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 H_2 properties with a change in ligand. There is a significant lengthening of the H–H bond and decrease in the $^1J(H,D)$ coupling constant on going from dtfpe to dppe. Again δ (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 $[MH(H_2)L_2]^+$ (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, $[M(H)_3L_2]^+$.[6] For each metal, the more

Table 13. Approximate pK_a^{cis} Values[a] for Some Dihydrogen Complexes in THF at 20 °C and Various Indicators of the Electron Density at the Metal

complex	$pK_a^{cis\ a}$	$E_{1/2}(MHClL_2)$,[b] V vs Fc^+/Fc	$E_{pa}(MH_2L_2)$,[b,c] V vs Fc^+/Fc	$\nu(N_2)$,[d] cm^{-1}	$\nu(CO)$,[e] cm^{-1}
$[FeH(H_2)(dtfpe)_2]^+$	7.8 ± 0.3	0.25	0.01		1967
$[FeH(H_2)(dppe)_2]^+$	12.0 ± 0.4	–0.71	–0.54	2120	1950
$[FeH(H_2)(dtpe)_2]^+$	12.6 ± 0.4	–0.72	–0.77		1940
$[FeH(H_2)(depe)_2]^+$	≈16	–0.98		2090	1929
$[RuH(H_2)(dtfpe)_2]^+$	9.0 ± 0.3		0.50		
$[RuH(H_2)(dppe)_2]^+$	14.0 ± 0.4	–0.12	0.0	2194	1987
$[RuH(H_2)(dape)_2]^+$	16.4 ± 0.7		–0.1		
$[RuH(H_2)(depe)_2]^+$	≈16.5	–0.24		2163	1958
$[OsH(H_2)(dtfpe)_2]^+$	8.4 ± 0.2		0.21		
$[OsH(H_2)(dppe)_2]^+$	12.7 ± 0.1	–0.14	–0.17		2003
$[OsH(H_2)(depe)_2]^+$	≈16.3	–0.46		2136	1974

[a] Refer to eq 11 for the definition of K_a^{cis}. [b] THF solvent, 0.2 M NBu_4PF_6, 0.2 V s^{-1} scan rate.[6,32] [c] Anodic peak potential (irreversible) of *cis*-MH_2L_2 in THF; the peak for the oxidation of *trans*-MH_2L_2 (≈10%) for the Ru and Os complexes must be hidden in this peak.[32,43] [d] N_2 stretching frequency of the complex *trans*-$[MH(N_2)L_2]^+$ in Nujol mull.[6] [e] CO stretching frequency of the complex *trans*-$[MH(CO)L_2]^+$ in Nujol mull.[6,32]

Chart 1

$$\text{trans-}[MH(H_2)L_2]^+ \rightleftarrows \text{trans-}M(H)_2L_2 + H^+ \qquad 2.301RTpK_a = 1.37\ pK_a^{trans} \qquad (13)$$

$$\text{trans-}M(H)_2L_2 \rightleftarrows \text{trans-}[M(H)_2L_2]^+ + e^- \qquad FE^\circ(MH_2{}^+) = 23.1E^\circ(MH_2{}^+/MH_2) \qquad (14)$$

$$e^- + H^+ \rightleftarrows H\cdot \qquad \text{constant} \qquad (15)$$

$$\text{trans-}[MH(H_2)L_2]^+ \rightleftarrows \text{trans-}[M(H)_2L_2]^+ + H\cdot \qquad \Delta G_{BDE}\{MH(H_2)^+\} = 1.37\ pK_a^{trans} + 23.1E^\circ(MH_2{}^+/MH_2) + \text{constant} \qquad (16)$$

Table 14. Approximate pK_a^{trans},[a] $E_{1/2}$(*trans*-$MH_2L_2^+$/*trans*-MH_2L_2), and $\Delta H_{BDE}\{MH(H_2)^+\}$ Values for the Dihydrogen Complexes $[MH(H_2)L_2]^+$, M = Ru, Os, L = dtfpe, dppe, dape, depe as Well as the Values for Dihydride Complex $[CpRu(H_2)(PPh_3)_2]^+$

M, L	$pK_a^{trans\ a}$	$E_{1/2}$[b] ± 0.1	ΔH_{BDE},[c] kcal mol^{-1}
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
$CpRu(H)_2(PPh_3)_2^+$	8.0 ± 0.3[d]	–0.3[e]	72 ± 2[f]

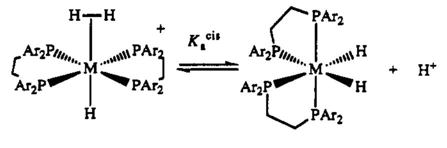
[a] Refer to eq 12 for the definition of K_a^{trans}. [b] Values estimated as $E_{1/2} - 0.1$ where $E_{1/2}$ values refer to either the corresponding *trans*-$MH(Cl)L_2$ complexes or the *cis*-MH_2L_2 complexes (see Discussion). [c] These values could all shift systematically if it is found that the constant ($C = 66$) of eq 17 needs further refinement. [d] See ref 11. [e] See ref 22. [f] See ref 21.

electron rich dppe complex stabilizes the trihydride intermediate by about 1 kcal mol^{-1} ($\Delta\Delta G^\ddagger$) relative to that of the analogous dtfpe complex. For the dppe, dtfpe, and depe triads, the $\Delta G^\ddagger$ values at a given temperature decrease as Ru > Fe > Os.

The relative labilities of the H_2 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 $[FeH(H_2)(dtfpe)_2]^+$ above 100 °C. The Os complexes do not lose H_2 under these conditions in the solid state.

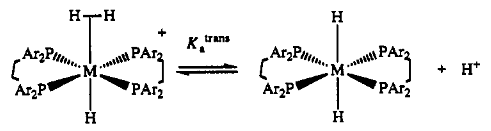
Overall we argue that the H–H bond of the dihydrogen ligand is activated toward homolytic cleavage the most in the osmium complexes and the least in the ruthenium complexes, with the iron complexes being intermediate in nature.

Ligand Effects on the Acidity of the Dihydrogen Complexes. The effect on the pK_a of these complexes of changing the *para* substituent on the aryl of the diphosphine ligand is very dramatic (Table 13). On going from p-$CF_3C_6H_4^-$ to p-$CH_3C_6H_4^-$ substituents in the Fe complexes, the pK_a^{cis} referring to eq 11 increases by 4.8 units. The change from p-$CF_3C_6H_4^-$ to p-$CH_3OC_6H_4^-$ 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 $[Ru(C_5H_5)(H_2)L]^+$ where $[Ru(C_5H_5)(H_2)(dtfpe)]^+$ has a pK_a of 4.7, while $[Ru(C_5H_5)(H_2)(dape)]^+$ has a pK_a of 8.6.[10] 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.[15]



(11)

The deprotonation of $[MH(H_2)(dppe)_2]^+$, 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^6 configuration). As discussed above, the pK_a^{trans} value is difficult to obtain accurately but is about one unit greater than pK_a^{cis}, at least for the Ru and Os complexes. The pK_a^{trans} values of Table 14 were calculated from K^{trans} values of Table 3–6 or estimated from pK_a^{cis}.



(12)

The pK_a^{trans} 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.[17] 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 $\Delta G_{BDE}\{M–H\}$ into $\Delta H_{BDE}\{M–H\}$ values. The same assumptions apply in converting $\Delta G_{BDE}\{MH(H_2)^+\}$ values of eq 16 into the $\Delta H_{BDE}\{MH(H_2)^+\}$ values of eq 17. Therefore the pK_a^{trans} of the dihydrogen complexes should be a function of the *trans*-$[M(H)_2L_2]^+$/*trans*-$M(H)_2L_2$ electrochemical potential and of a bond dissociation energy involving the removal of a hydrogen atom from the dihydrogen complex in solution:

$$\Delta H_{BDE}\{MH(H_2)^+\} = 1.37pK_a^{trans} + 23.1E^\circ(MH_2^+/MH_2) + 66 \quad (17)$$

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° and ΔH parameters.

Unfortunately the $E^\circ(MH_2^+/MH_2)$ value for *trans*-$M(H)_2L_2$ 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*-$M(H)_2L_2$ isomer. We have observed the redox wave of the related complex *trans*-$Ru(H)_2$(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*-Ru(H)Cl(meso-tet-1) has $E_{1/2}$ of -0.3 V.[34] We have measured the $M(d^5)/M(d^6)$ electrochemical potentials for other *trans*-$MHClL_2$ complexes (Table 13) which have E° values that should be about 0.1 V more positive than $E^\circ(MH_2^+/MH_2)$ for the corresponding *trans*-dihydride according to the tetraphos example and according to the additive effect of hydride versus chloride on electrochemical parameters ($E_L = -0.4$ versus -0.24).[15,35] We have also measured peak potentials for the oxidation of some *cis*-$M(H)_2L_2$ complexes and find that they are close to the *trans*-$MHClL_2$ values.

The $\Delta H_{BDE}\{MH(H_2)^+\}$ values for the complexes of Table 14 were calculated from the estimated $E_{1/2}$ data by use of eq 17. If the ΔH_{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^{trans} vs E° should be -16.9 as it is for metal–hydride complexes.[17] 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 ΔH term and the E° term are responsible for the observed trend in pK_a^{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 dtfpe < dppe < dtpe < dape < depe. The infrared data for the *trans* complexes $[MH(N_2)L_2]^+$ and $[MH(CO)L_2]^+$ parallel this ligand ordering, in that the more electron donating ligand results in a lower NN or CO stretching frequency. This trend in E° contributes strongly to an increase in pK_a^{trans} along this ligand series.

A change in ligand also affects the ΔH_{BDE} term of eq 17 because it involves the energy of the H–H and $M-H_2$ interactions in $[M(H_2)H(L)_2]^+$ and the energy of the product of H atom abstraction, *trans*-$[M(H)_2L_2]^+$. This term makes a smaller, opposite contribution to pK_a^{trans}. A more electron donating ligand would weaken the strong H–H bond of the dihydrogen ligand through back-bonding and could possibly decrease ΔH and therefore decrease pK_a^{trans}; this assumes that an increase in ΔH 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*-$[M(H)_2L_2]^+$ 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^{cis} values according to metal is Ru(II) > Os(II) > Fe(II). The ordering of pK_a^{trans} values is also Ru(II) > Os(II) (Table 14). This trend in acidity of dihydrogen complexes contrasts with that observed for dihydride complexes. For example, for the complexes $M(H)_2(CO)_4$, the order of pK_a values is Os(II) > Ru(II) > Fe(II).[36] Similarly the order according to our results from eq 10 is Os(IV) > 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[16] with the complexes $[MH(P(OR)_3)_4]^+$, M = Ni, Pd, Pt, and $[MH(CO)_2(dppe)_2]^+$, M = Mo, W, providing the only exceptions.[37] 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.

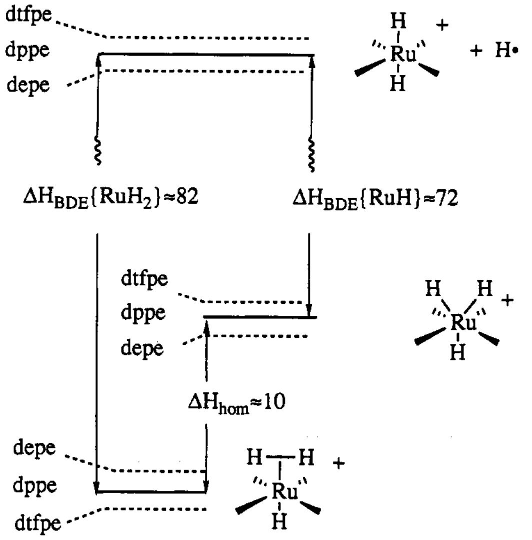


Figure 2. Energy level diagram (in kcal mol^{-1}) relating $\Delta H_{BDE}\{Ru(H_2)^+\}$ to the energy of dihydrogen/dihydride tautomerism (ΔH_{hom}) and the Ru–H bond dissociation energy, $\Delta H_{BDE}\{RuH\}$, for the complexes $[Ru(H)_3L_2]^+$ as estimated from the energy for the complexes $[CpRu(H)_2L]^+$. The solid levels are for L = dppe.

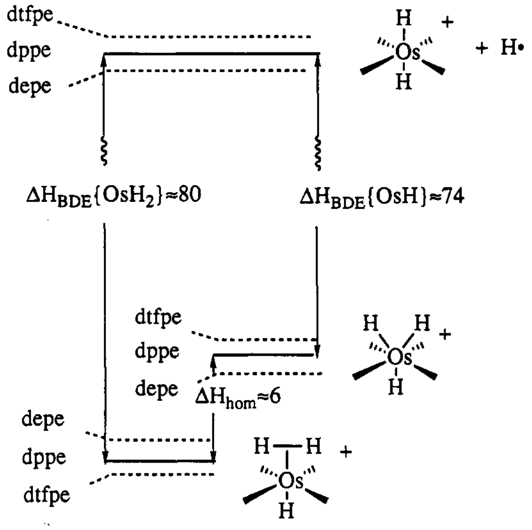


Figure 3. Energy level diagram (in kcal mol^{-1}) relating $\Delta H_{BDE}\{Os(H_2)^+\}$ to the energy of dihydrogen/dihydride tautomerism (ΔH_{hom}) and the estimated Os–H bond dissociation energy, $\Delta H_{BDE}\{OsH\}$, for the complexes $[Os(H)_3L_2]^+$. The solid levels are for L = dppe.

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(34) Meso-tet-1 is *R,S*-$Ph_2PCH_2CH_2PPhCH_2CH_2PPhCH_2CH_2PPh_2$; 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.

(36) Moore, E. J.; Sullivan, J. M.; Norton, J. R. *J. Am. Chem. Soc.* **1986**, *108*, 2257: $pK_1\{FeH_2(CO)_4\} = 11.4 < pK_1\{RuH_2(CO)_4\} = 18.7 < pK_1\{OsH_2(CO)_4\} = 20.8$; $pK_a\{CrCpH(CO)_3\} = 13.3 < pK_a\{MoCpH(CO)_3\} = 13.9 < pK_a\{WCpH(CO)_3\} = 16.1$.

(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 $M(d^5)/M(d^6)$ electrochemical potentials for a range of *trans*-$MH(X)L_2$ and *trans*-$[MH(L')L_2]^+$ complexes and find that the ruthenium complex always has the most positive reversible potentials (E°) or irreversible peak potentials (E_{pa}) of the Fe group triad. Table 13 shows that for a selection of *trans*-$MH(Cl)L_2$ and *cis*-$M(H)_2L_2$ 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.[35] We have also measured $E_{1/2}(M(C_5H_5)H(PPh_3)_2^+/M(C_5H_5)H(PPh_3)_2)$ vs Fc^+/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*-$[MH(N_2)L_2]^+$ also show that the Ru complexes are the most electron deficient with regard to back-bonding to the N_2 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^+ indicate that the 4d electrons of cationic Ru are particularly stable when compared to the energy of either 3d or 5d electrons,[20] and thus are less available for back-bonding to the H_2 ligand.

The reason that the Ru complexes are the least acidic is because of a large ΔH_{BDE} term. This term can be estimated for the complexes of Ru and Os by use the data of Table 13, eq 17 (E° vs Fc^+/Fc and ΔH in kcal mol^{-1}) and the approximate pK_a^{trans} 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^{-1} for complexes $[Ru(C_5R_5)(H)_2(L)]^+$.[21] The $\Delta H_{BDE}\{Ru(H_2)^+\}$ value of 83 kcal mol^{-1} for $[RuH(H_2)(dppe)_2]^+$ is close to $\Delta H_{BDE}\{Mn(H_2)^+\}$ for the complex $[Mn(H_2)(CO)_5]^+$ (83.5 kcal mol^{-1}) determined in the gas phase.[20] Like $[RuH(H_2)(dppe)_2]^+$, the electron deficient manganese complex probably has a very labile H_2 ligand with a strong H–H bond.[15] Therefore probably the ΔH_{BDE} value is so large because of the high H–H bond energy. Another possible reason is that the species *trans*-$[Ru(H)_2L_2]^+$ is of unusually high energy relative to *trans*-$[Os(H)_2L_2]^+$ and $[Ru(C_5R_5)(H)(L)]^+$ 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_2L_2 are close in energy to their *cis*-MH_2L_2 isomers (see above).

Figure 2 shows that the large ΔH_{BDE} values for the $[Ru(H_2)HL_2]^+$ complexes fit into a reasonable energy scheme when the energy of H–H homolytic splitting, ΔH_{hom}, is also considered. The energy ΔH_{hom} is thought to be related to the activation energy for H atom exchange ($\Delta G^\ddagger$ of Table 11), a process which involves H–H homolysis to give a trihydride intermediate or transition state $[Ru(H)_3L_2]^+$.[6] Figure 2 shows that a Ru–H bond dissociation energy for the trihydride could be about 72 kcal mol^{-1} if the ΔH_{hom} value is about 11 kcal mol^{-1}, a quantity close to $\Delta G^\ddagger$. The ligand effect is also accounted for in this diagram; both $\Delta H_{BDE}\{Ru(H_2)^+\}$ (Table 14) and $\Delta G^\ddagger \approx \Delta H_{hom}$ (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 with bidentate ligands, $[Ru(H)_3L_2]^+$, L = bis(diphenylphosphino)ferrocene,[38] 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 $\Delta H_{BDE}\{M(H_2)^+\}$ values which are closer to metal–hydride bond energies (about 70–75 kcal mol^{-1} for Os). Table 14 and Figure 3 show that this is true. However the value for $\Delta G^\ddagger \approx \Delta H_{hom} \approx 6$ expected on the basis of Figure 3 is too low when compared to actual $\Delta G^\ddagger$ (Table 11) or $\Delta H^\ddagger$ (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 $[Os(H)_2H(depe)_2]^+$ that is close in energy to the $[Os(H_2)H(depe)_2]^+$ complex which is not associated with exchange between $(H)_2$ and terminal H atoms.[7] The dtfpe complex has the least hydride character in the $Os(H_2)$ unit and, as expected, has the largest $\Delta H_{BDE}\{Os(H_2)^+\}$ value.

The high $\Delta H_{BDE}\{Ru(H_2)^+\}$ for these complexes contrasts with the lower value of about 72 kcal mol^{-1} for the complexes $[Ru(C_5R'_5)(H_2)L]^+$. The latter complexes have elongated, slow-spinning dihydrogen ligands[31] which are more dihydride-like in character.[11] Therefore the distinctively low acidity of $Ru(H_2)L_n$ 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.

Isotope Exchange Reactions. It was found that a catalyst system involving both *trans*-$[Ru(H_2)(H)L_2]^+$ and $Ru(H)_2L_2$, L = dppe, was more effective for H/D exchange between ^tBuOH and D_2 than *trans*-$[Ru(H_2)(H)L_2]^+$ alone, which was used by Albeniz et al.[25] We propose the following mechanism for this exchange process catalyzed by the dihydrogen/dihydride mixture.

This mechanism involves intermolecular H^+ transfer (eqs 20

$$[Ru(H_2)(H)L_2]^+ + D_2 \rightarrow [Ru(HD)(D)L_2]^+ + H_2 \qquad (18)$$

$$^tBuOH + [Ru(HD)(D)L_2]^+ \rightarrow [Ru(^tBuOH)(D)L_2]^+ + HD \qquad (19)$$

$$[Ru(^tBuOH)(D)L_2]^+ + RuD_2L_2 \rightleftarrows Ru(O^tBu)(D)L_2 + [Ru(HD)(D)L_2]^+ \qquad (20)$$

$$[Ru(HD)(D)L_2]^+ + D_2 \rightleftarrows [Ru(D_2)(D)L_2]^+ + HD \qquad (21)$$

$$[Ru(D_2)(D)L_2]^+ + Ru(O^tBu)(D)L_2 \rightleftarrows RuD_2L_2 + [Ru(^tBuOD)(D)L_2]^+ \qquad (22)$$

$$[Ru(^tBuOD)(D)L_2]^+ + {}^tBuOH \rightleftarrows [Ru(^tBuOH)(D)L_2]^+ + {}^tBuOD \qquad (23)$$

$$D_2 + {}^tBuOH \rightleftarrows {}^tBuOD + HD \qquad (24)$$

and 22) and requires similar pK_a values for coordinated H_2 (HD) and ^tBuOH (^tBuOD). The H_2 complex has a pK_a of about 14 (Table 13) while coordinated ^tBuOH should have a pK_a less than that of the free alcohol (16.6, Table 1). The weakly coordinated dihydrogen (HD) ligand in the complex $[Ru(H_2)(H)L_2]^+$ would facilitate reactions 18 and 21. An intermolecular transfer mechanism looks more reasonable than the direct protonation of

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(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 $^tBuOH_2^+$ ($pK_a \approx 0$). 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 *trans*-$[M(H_2)H(L)_2]^+$ are all thought to have rapidly spinning[31] dihydrogen ligands. For a given ligand L, the iron and ruthenium complexes have similar H–H bond lengths ($\approx$0.9 Å), while the osmium complexes have longer H–H distances ($\approx$1.0 Å). There is only a slight increase in H–H bond length as a function of R (CF_3 to H to OCH_3) for the complexes of Ru according to ^1H NMR T_1 and $^1J(HD)$ 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 H_2).

Changing the phosphine ligand L in the complex *trans*-$[M(H_2)H(L)_2]^+$ 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 *trans*-$[MH_2L_2]^+$ ($\Delta H_{BDE}\{MH_2\}$) appear to counteract this inductive effect in two possible ways. First, a more electron-withdrawing L results in less back-bonding to the H_2 ligand, a strengthening of the H_2 bond and this could give a less acidic H_2 ligand than might have been expected on the basis of inductive effects alone. Second, the more electron-withdrawing ligand could also destablize the *trans*-$[MH_2L_2]^+$ species. We believe the first effect is important and hope to find out in future studies whether ΔH_{BDE}-$\{MH_2\}$ 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 $\Delta H_{BDE}\{M(H_2)\}$ for Ru versus Os. This is the first report of the distinctive contribution of the metal to the acidity of the H_2 ligand. This should be studied further by calorimetry as done by Angelici and co-workers.[29]

A $RuH_2L_2/[RuH(H_2)L_2]^+$ mixture, L = dppe, in THF was found to be more active at H/D exchange between D_2 and HO^tBu 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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(42) Reeve, W.; Erikson, C. M.; Aluotto, P. F. *Can. J. Chem.* **1979**, *57*, 2747–2754.

(43) Jia, G.; Morris, R. H., unpublished results.