cooled to -40 °C, and photolyzed with Pyrex-filtered light at -40 °C for 40 min. The $^1H$ NMR of the resulting mixture ($CDCl_3$) showed the formation of Ph(*p*-Tol)C=NPh in 94% yield as well as nitrene complex **7** ($\delta$ 3.83, s, 6 H) in 66% yield. Complex **7** was found to persist for several hours in solution. Additional spectroscopic data for **7** (variable-temperature $^1H$ NMR, $^{13}C$ NMR, $^{15}N$ NMR, and IR) are reported and discussed in detail in ref 12. The original spectra for **7** are also available in the supplementary material of ref 12.

**Reaction of 7 with Benzaldehyde.** Carbene **19** (16 mg, 0.033 mmol) in 0.5 mL of toluene-$d_8$ was added to triazene **20** (25 mg, 0.17 mmol). The solution was transferred to an NMR tube and photolyzed at -40 °C with Pyrex-filtered light for 40 min. $^1H$ NMR of the resulting mixture showed the appearance of **7** ($\delta$ 2.77, s, 6 H). An excess of benzaldehyde (50 mg, 0.47 mmol) was added to this solution, and the mixture was allowed to stand in the dark at room temperature for 13 h. $^1H$ NMR spectra of the resulting solution showed the disappearance of **7**, and the formation of PhHC=NNMe$_2$ ($\delta$ 2.65, s, 6 H) in 85% yield.

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# Preparation and Spectroscopic Properties of the $\eta^2$-Dihydrogen Complexes $[MH(\eta^2\text{-}H_2)(PR_2CH_2CH_2PR_2)_2]^+$ (M = Fe, Ru; R = Ph, Et) and Trends in Properties down the Iron Group Triad

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**Abstract:** Complexes *trans*-$[M(H)(\eta^2\text{-}H_2)L_2]BF_4$ (L = $PPh_2CH_2CH_2PPh_2$ = dppe (**1Fe**, **1Ru**), $PEt_2CH_2CH_2PEt_2$ = depe (**2Ru**)) are prepared by reaction of *cis*-$M(H)_2L_2$ with 1 equiv of $HBF_4 \cdot Et_2O$. Deprotonation of **1Ru** by BuLi at 200 K, gives thermally unstable *trans*-$Ru(H)_2(dppe)_2$, which isomerizes to *cis*-$Ru(H)_2(dppe)_2$. Tetraphenylborate salts of the complexes **1Fe**, **2Fe**, and **2Ru** are prepared by reaction of *trans*-$M(Cl)(H)L_2$ with $NaBPh_4$ under 1 atm of $H_2$. **2Fe**, **1Ru**, and **2Ru** can also be made directly from the complexes *cis*-$MCl_2L_2$ by reaction with 1 atm of $H_2$, excess $NaBPh_4$, and 1 equiv of NaOEt (or NaO$^t$Bu) in THF. Some properties of the complexes $[Os(H)(H_2)(L)_2]^+$ (L = dppe (**1Os**), depe (**2Os**)) are included to reveal trends down the triad of metals; $ReH_3(dppe)_2$ also provides useful comparisons. The terminal hydride stretching mode, $\nu$(M-H), increases in frequency as Fe < Ru < Os, and the $^{31}P$ chemical shifts increase in the order Fe < Ru < Os as expected for isostructural complexes. However, indicators of dihydrogen vs dihydride character show that Ru is out of place in the periodic order. $^1H$ NMR spectra of isotopomers *trans*-$[M(H)(\eta^2\text{-}HD)L_2]^+$ and *trans*-$[M(D)(\eta^2\text{-}HD)L_2]^+$ give couplings $^1J$(H,D) that decrease as Ru > Fe > Os. The chemical shifts of the HD for these two isotopomers are quite different because of the higher trans influence of D than H. The chemical shift difference, $\delta$(dihydrogen) - $\delta$(terminal hydride), for complexes **1** and **2** also decreases as Ru > Fe > Os. The $T_1$ values of the dihydrogen nuclei, $T_1(H_2)$, and the hydride ligand, $T_1(H)$, were determined over the temperature range of 190-300 K for the complexes **2Fe** and **2Ru** in acetone-$d_6$. Analysis of these and other data suggests H-H distances for the rapidly spinning $H_2$ ligand of the Fe and Ru complexes are comparable at 0.87 ± 0.02 Å. An overall ordering of increasing distances is Ru ≈ Fe < Os. The lability of dihydrogen as judged by the qualitative $H_2/D_2$ rates of exchange increases as Os < Fe < Ru. The equilibrium constant for $H_2$ binding and hence the strength of the $H_2$-metal bond likely increases as Ru < Fe < Os. Thus, the Ru complexes have the strongest H-H interaction and weakest metal-dihydrogen interaction. The $[RuHL_2]^+$ unit is a poorer $\pi$-back-bonder than the corresponding complexes of either Fe or Os and forms weaker $\sigma$-bonds than Os. Electrochemical and infrared data both indicate that the ease of oxidation of the binding sites for $N_2$ and $Cl^-$ decreases as $ReH(dppe)_2 \gg [FeH(depe)_2]^+ > [FeH(dppe)_2]^+ > [MH(depe)_2]^+ > [MH(dppe)_2]^+$ (M = Ru, Os). H atom exchange between $H_2$ and hydride ligands is monitored by variable-temperature $^1H$ NMR, and spectra are simulated to give $\Delta G^\ddagger$ values that decrease as Ru > Fe > Os and dppe > depe. This exchange likely proceeds via the homolytic cleavage of the H-H bond.

## Introduction

Since the report of the first $\eta^2$-dihydrogen complexes,[1,2] many transition-metal complexes, both stable[3-21] and unstable[18,22,23] at room temperature, have been identified as containing hydrogen ligands with H-H bonding interactions. This is a study of how

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the physical and spectroscopic properties of the complexes *trans*-$[M(H)(dppe)_2(\eta^2\text{-}H_2)]BF_4$ (dppe = $PPh_2CH_2CH_2PPh_2$; M = Fe (**1Fe**), Ru (**1Ru**), Os (**1Os**)) and *trans*-$[M(H)(depe)_2(\eta^2\text{-}H_2)]BPh_4$ (depe = $PEt_2CH_2CH_2PEt_2$; **2Fe**, **2Ru**, **2Os**) depend on the nature of the iron group metal and on the diphosphine. Preliminary reports of the discovery of complexes **1Fe** and **1Ru**[24] and complexes **2**[6,13,25] as well as some of their NMR properties have already appeared. The X-ray and neutron diffraction studies of single crystals of the $BPh_4^-$ salt of **1Fe** show it to have a symmetrically coordinated $\eta^2$-$H_2$ ligand with a H–H separation of 0.82 (2) Å at 20 K (neutron) and 0.9 (1) Å at 293 K (X-ray).[10] This may be compared to the H–H distance of 0.74 Å in free $H_2$ and to 0.82 (1) Å (neutron) in $W(CO)_3(H_2)(P(i\text{-}Pr)_3)_2$,[26] 0.82 (1) Å (neutron) in $Fe(H)_2(H_2)(PEtPh_2)_3$,[4] and 0.82 (2) Å (X-ray) in $Fe(C_5H_5)\{C_5H_3CHMeNMe_2P(i\text{-}Pr)_2\}(H_2)(Ru)(\mu\text{-}H)(\mu\text{-}Cl)_2(Ru)(H)(PPh_3)_2$.[27] Thus, there is little variation in H–H distances revealed by diffraction methods so far, apart from a recent study of $[Re(H)_4(H_2)(Cyttp)]^+$ where the dihydrogen distance is 1.08 (5) Å.[3] The X-ray diffraction study of the $BF_4^-$ salt of **1Os** revealed that the $OsP_4$ structural unit is perfectly square planar and consistent with an octahedral *trans*-$[Os(H)(dppe)_2(H_2)]^+$ formulation.[28] The osmium-bonded hydrogens were not located accurately. Spectroscopic data indicate that **1Os** has a H–H bond length of about 1.0 Å, which is significantly longer than that of the Fe or Ru complexes.[29] Crystals of **2Os** have also been examined by X-ray diffraction, but disorder of the depe ligands prevented location of H atoms.[30] No distinction could be made between a distorted octahedral geometry expected for *trans*-$[Os(H)(H_2)L_2]^+$ versus a pentagonal bipyramidal geometry expected for $[Os(H)_3L_2]^+$ on the basis of the positions of the phosphorus atoms; a cocrystallized mixture of the two forms probably explains the disorder.[31]

Preliminary results based on $^1J(H,D)$ couplings and $T_1$ measurements at one temperature indicated that H–H bond length increased and the strength decreased as the M–$H_2$ interaction increased in the order **1Ru** < **2Ru** < **1Fe** < **2Fe** < **2Os**.[25] However, the present work suggests that the Ru and Fe complexes have similar H–H bond lengths. This is a full account of the studies of the iron and ruthenium complexes; the osmium complexes have been described elsewhere,[29] but some of their properties are included here to demonstrate the trends in properties down the triad of metals. Comparisons to the properties of the classical trihydride $ReH_3(dppe)_2$ (**3Re**) are illuminating as well.

Other studies of periodic trends have included groups 6, 8, and 9. The stability of the group 6 complexes $M(CO)_3(H_2)(PR_3)_2$ (R = *i*-Pr and Cy[32]) with respect to loss of the dihydrogen ligand increases as Cr < Mo < W. By contrast, the complexes $M(CO)_5(H_2)$, each with a very labile dihydrogen ligand, increase in stability as Mo < Cr < W; the stretching mode, $\nu(H_2)$, decrease in frequency (Mo > Cr > W) as the stability increases,[33] but this is a consequence of increasing withdrawal of $\sigma(H_2)$ electrons by the metal and to a lesser extent backdonation to $\sigma^*(H_2)$ from the metal. Group 8 dihydrogen complexes exist for Fe and Ru as *mer*-$M(H)_2(H_2)(PR_3)_3$, but the corresponding Os complexes $OsH_4(P(p\text{-}tol)_3)_3$ and $OsH_4(PMePh_2)_3$ have no H–H bonding.[19] Studies of the group 8 series of complexes $[M(H)(H_2)\{PPh(OEt)_2\}_4]^+$ revealed that the Os complex might have a longer H–H bond than corresponding Fe and Ru ones on the basis of the longer $T_1$ time of the dihydrogen ligand.[5] However, the minimum $T_1$ values were not observed, and this difference for Os could be due to a more rapid exchange of H atoms between $H_2$ and hydride sites or due to other factors including differences in rotational correlation times. In keeping with a more hydridic character of the $H_2$ ligand in the Os complex, it underwent substitution reactions more slowly than the Fe and Ru complexes. The complex $[OsH_3(PPh_3)_4]^+$ is a true trihydride with a nonoctahedral structure.[20] Of the group 9 complexes $[MH_2(PP_3)]^+$, the Co complex is an $\eta^2$-dihydrogen complex and the Ir complex is a dihydride, while the Rh complex is thought to have both forms in equilibrium.[15]

The study of dihydrogen complexes can assist the understanding of processes like hydrogen storage, hydrogen detection, hydride formation from dihydrogen, and catalytic hydrogenation reactions. Some complexes of $\eta^2$-dihydrogen are precursors to catalysts for the hydrogenation of olefins[8,9,17,27,34] and the dehydrogenation of alcohols.[35] Dihydrogen complexes may also exist in nature; metal centers in hydrogenase and nitrogenase are candidates.[36,37]

## Results

**Preparation of the Dihydrogen Complexes.** The dppe complexes **1** are readily prepared in high yields as the $BF_4^-$ salts by reaction of suspensions in ether of the corresponding dihydride complexes with 1 equiv of $HBF_4 \cdot Et_2O$ (eq 1). Pale yellow (**1Fe**) or white

$$M(H)_2(dppe)_2 + HBF_4 \rightarrow \underset{\textbf{1Fe, 1Ru, 1Os}}{\textit{trans}\text{-}[M(H)(dppe)_2(\eta^2\text{-}H_2)]BF_4} \quad (1)$$

(**1Ru**, **1Os**[29]) precipitates form immediately when the reaction is performed under 1 atm of $H_2$. Pure complexes **1Fe** and **1Os** but not **1Ru** are also obtained when an Ar atmosphere is used; solid **1Ru** is only stable under 1 atm of $H_2$. A $N_2$ atmosphere is suitable for the preparation of **1Os**, but not **1Fe** since *trans*-$[Fe(H)(dppe)_2(N_2)]BF_4$ also forms. The complex *trans*-$[Ru(H)(depe)_2(\eta^2\text{-}H_2)]BF_4$ has also been prepared by this method from *cis*-$RuH_2(depe)_2$ under 1 atm of Ar.

The complexes prepared from the reaction of $FeH_2(dppe)_2$ and $HClO_4$[38] or $H_2C(SO_2CF_3)_2$[20,39] are also $[Fe(H)(dppe)_2(H_2)]^+$ salts

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**Table I.** Hydride Stretching Frequencies (Nujol) and $^{31}P$ NMR Data (Acetone Solvent; versus $H_3PO_4$) for the Complexes That Show Periodic Trends

| | complex | $\nu$(M–H), cm$^{-1}$ | $\delta$($^{31}$P) |
|---|---|---|---|
| **1Fe** | $[Fe(H_2)(H)(dppe)_2]BF_4$ | 1919 | 92.5 |
| **1Ru** | $[Ru(H_2)(H)(dppe)_2]BF_4$ | 1961 | 68.6 |
| **1Os** | $[Os(H_2)(H)(dppe)_2]BF_4$ | 1997 | 37.5 |
| **2Fe** | $[Fe(H_2)(H)(depe)_2]BPh_4$ | 1887 | 97.9 |
| **2Ru** | $[Ru(H_2)(H)(depe)_2]BPh_4$ | 1964 | 60.8 |
| **2Os** | $[Os(H_2)(H)(depe)_2]BPh_4$ | 1983, 1937 | 41.3 |

and not the complexes previously reported as $[Fe(H)_3(dppe)_2]ClO_4$ or $[FeH(dppe)_2][HC(SO_2CF_3)_2]$, respectively. $[FeH(dppe)_2]^+$, when generated by protonating $FeH(C_6H_4PPhCH_2CH_2PPh_2)$-(dppe), immediately reacts with $H_2$ to give **1Fe**.

Significantly, the reverse of reaction 1, deprotonation of *trans*-$[Ru(H)(dppe)_2(\eta^2\text{-}H_2)]^+$ by BuLi at −80 °C, gives thermally unstable *trans*-$Ru(H)_2(dppe)_2$, which isomerizes to *cis*-$Ru(H)_2$-$(dppe)_2$ at room temperature. The acid–base properties of the other complexes are under investigation.

A convenient preparation of the $BPh_4^-$ salts of the complexes **1Ru**, **2Fe**, and **2Ru** involves the reactions of the dichloro complexes with 1 atm of $H_2$, excess $NaBPh_4$, and 1 equiv of NaOEt (or NaO$^t$Bu) in THF/EtOH (eq 2). Only *cis*-$RuCl_2(depe)_2$ reacts to produce **2Ru**; if some of the unreactive *trans*-dichloro isomer is also present, it is easily separated from the cationic product **2Ru**.

$$MCl_2(PR_2CH_2CH_2PR_2)_2 + NaOR' + 2H_2 \xrightarrow{\text{2–4 equiv } NaBPh_4} [M(H)(H_2)(PR_2CH_2CH_2PR_2)_2]BPh_4 + 2NaCl + HOR' \quad (2)$$

Reaction 2 is thought to proceed via the heterolytic cleavage of dihydrogen in the intermediate complexes $[M(Cl)(H_2)$-$(PR_2CH_2CH_2PR_2)_2]^+$.[6] Hydrogen uptake of 1.7 mol/mol Fe occurs in less than 5 min when $FeCl_2(depe)_2$ in EtOH at 13 °C is reacted as in eq 2 to give **2Fe** as a white precipitate. Corresponding preparations of the white ruthenium complexes **1Ru** and **2Ru** take about 4 h at 20 °C. The preparation of **1Ru** will proceed without the addition of NaOR′ if the reaction flask is continuously purged with $H_2$, presumably to remove the HCl that is produced.

The dihydrides $RuH_2(dppe)_2$, $OsH_2(dppe)_2$, and $OsH_2(depe)_2$ can be prepared by a modification of eq 2 where an additional 1 equiv of base ($OR^-$) is added to deprotonate the dihydrogen ligand;[6] a convenient preparation of $RuH_2(dppe)_2$, which just requires NaOEt, is included in the Experimental Section. $RuH_2(depe)_2$ has not yet been prepared cleanly by this method. It was prepared by the reaction of Ru(cod)(cot) with depe and $H_2$.

Equation 2 provides a more direct route to the depe complexes **2** than eq 3, the details of which were reported in a brief form previously.[25] The procedure for eq 3 was based on the preparation of the analogous dinitrogen complexes *trans*-$[M(H)(depe)_2$-$(N_2)]BPh_4$.[40] Complex **1Fe** can also be prepared from $FeClH$-$(dppe)_2$ in this fashion. In reaction 3, the heterolytic cleavage of the M–Cl bond is assisted by the high trans influence of the hydride.

$$\textit{trans}\text{-}M(Cl)(H)(depe)_2 + NaBPh_4 + H_2 \rightarrow \textit{trans}\text{-}[M(H)(depe)_2(H_2)]BPh_4 + NaCl \quad (3)$$

Complex **1Os** and complexes **2** are soluble and stable to loss of $H_2$ in THF, acetone, or $CH_2Cl_2$ (for at least 30 min) under Ar at 22 °C. Complex **1Fe** is stable under Ar in THF, acetone, and $CH_2Cl_2$ up to 50 °C. Complex **1Ru** must be kept under 1 atm of $H_2$ in all these solvents.

**Spectroscopic Properties.** A terminal hydride stretching mode, $\nu$(M–H), is detected by infrared spectroscopy for the complexes (Table I), but the weak $\nu$(H–H) absorption is not. The latter, which is expected below 2600 cm$^{-1}$,[2] may be obscured by overtones from the ditertiary phosphine ligand vibrations. The $\nu$(M–H) mode increases in frequency going from **Fe** to **Ru** to **Os**. This trend supports our suggestion that complexes **1** are isostructural $\eta^2$-dihydrogen complexes. Typically the frequency for isostructural neutral complexes increases by 60 ± 40 cm$^{-1}$ on going from Fe to Ru and 120 ± 40 from Ru to Os;[41] the order $\nu$(Fe–H) < $\nu$(Ru–H) < $\nu$(Os–H) is expected to be maintained in cationic complexes although no infrared studies of this type have been reported yet. The two-band pattern for **2Os** might be due to a cocrystallized mixture of distorted octahedral ($\eta^2$-$H_2$)(H) and pentagonal bipyramidal trihydride tautomers.[31] A study of inelastic neutron scattering off microcrystalline **1Fe** gave a rotational tunneling splitting of 2.1 cm$^{-1}$ and a barrier to rotational tunneling of ~1.7 kcal mol$^{-1}$.[42] In other words, the dihydrogen is rapidly spinning like a propeller in this complex, even in the solid state.

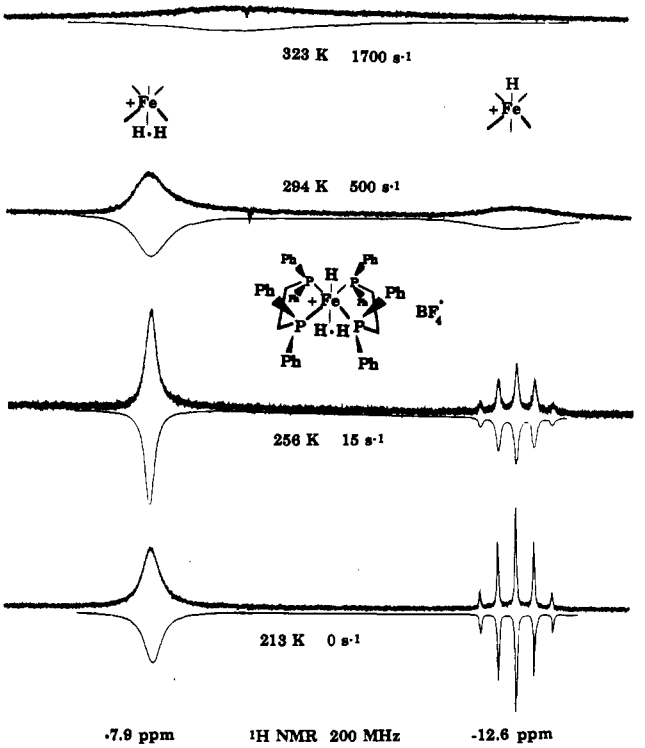


**Figure 1.** Observed 200-MHz $^1$H NMR spectra and simulated (inverted) spectra in the high-field region for the complex $[Fe(H)(dppe)_2(H_2)]BF_4$ (**1Fe**) in acetone-$d_6$.

Table I also lists the $^{31}$P NMR chemical shift of each complex. For each, the resonance is a singlet that broadens somewhat due primarily to the temperature dependence of $T_2$ as the temperature is lowered from 300 K to 200 K. The usual periodic trend in $\delta$($^{31}$P) for isostructural phosphine complexes is observed where the chemical shift decreases on going from the 3d to the 4d and then to the 5d metal.[43]

**Low-Temperature $^1$H NMR Spectra in the Hydride Region.** Complexes **2Fe**[25] and **1Os** give temperature-dependent $^1$H NMR spectra in the hydride region that are similar to those of **1Fe** shown in Figure 1. The temperature dependence is caused by an intramolecular hydrogen atom exchange process (see below). The spectra for **2Os** differ in that the $H_2$ chemical shift comes upfield of the terminal hydride in the low-temperature spectra;[25] this is further evidence for the existence of two tautomers for this com-

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(43) Pregosin, P. S.; Kunz, R. W. *$^{31}$P and $^{13}$C NMR of Transition Metal Phosphine Complexes*; Springer-Verlag: New York, 1979. We find that, for the complexes *trans*-$MHX(diphosphine)_2$, the following relationships between $^{31}$P chemical shifts applies: $\delta$(PRu) ≈ 0.81$\delta$(PFe) − 6.1 and $\delta$(POs) ≈ 1.04$\delta$(PRu) − 34.8.

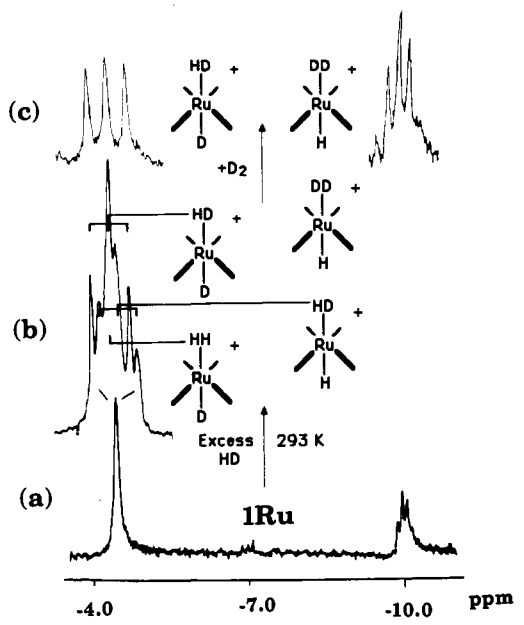



**Figure 2.** (a) $^1$H NMR spectrum at 200 MHz in the high-field region of $[Ru(H)(dppe)_2)(\eta^2\text{-}H_2)]BF_4$ (**1Ru**) in acetone-$d_6$ at 293 K, (b) overlapping $H_2$ and HD resonances produced when **1Ru** is exposed to HD for 5 min, and (c) **1Ru**-$d_2$ isotopomers produced by exposing **1Ru** to excess $D_2$ (300 MHz spectrum).

**Table II.** $^1$H NMR Data at 200 MHz in the Hydride Region for the Complexes in Acetone-$d_6$ ($CD_2Cl_2$ for **1Os**) and Couplings $^2J$(H, P) for the Complexes *trans*-[MH(diphosphine)$_2$(CO)]$^+$ (M = Fe,[a] Ru,[40,85] and Os)[29]

| complex | $T$, K | $\delta$(M-H) | $^2J$(H, P) | $\delta(H_2)$ | $^2J(H_2, P)$ | $^2J$(H, P)[b] |
|---|---|---|---|---|---|---|
| **1Fe** | 323 | −9.5 | nr[c] | −9.5 | nr[c] | |
| | 210 | −12.6 | −47 | −7.9 | −5 ± 5 | −47 |
| **1Ru** | 293 | −10.0 | −18 | −4.6 | 0 ± 2 | −19.5 |
| **1Os** | 210 | −9.0[d] | −17 | −6.8[e] | −5 ± 2 | −19.2 |
| **2Fe** | 290 | −11.9 | nr[c,f] | −11.9 | nr[c,f] | |
| | 220 | −14.6 | −47.0 | −10.5 | −1.8 | −47 |
| **2Ru** | 293 | −11.3 | −19.3 | −6.4 | 0 ± 2 | −20 |
| **2Os** | 220 | −9.7 | −17.5 | −10.0[g] | −5.5 | −20.4 |

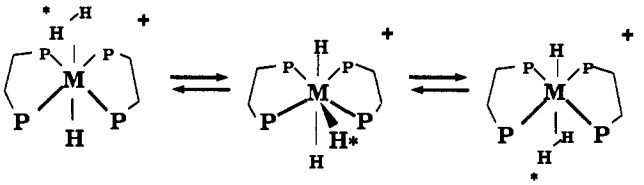
[a] This work, ref 40. [b] Values for the corresponding complex *trans*-[MH(diphosphine)$_2$(CO)]$^+$. [c] Not resolved, broad singlet. [d] Temperature dependent: $\delta$(M-H) = 0.0056$T$ − 10.20. [e] Temperature dependent: $\delta(H_2)$ = −0.0014$T$ − 6.49. [f] 17 Hz in ethanol-$d_6$.[11] [g] Temperature dependent: $\delta(H_2)$ = 0.0029$T$ − 10.61.

plex.[31] The spectra for **1Ru** (see Figure 2) and **2Ru** do not change as the temperature is lowered below 293 K apart from a broadening of the $H_2$ resonance. The spectra are consistent with the *trans*-$[M(H)(H_2)(PR_2CH_2CH_2PR_2)_2]^+$ formulation.

At 210 K and 200 MHz, the terminal hydride resonance of each complex **1** and **2** is a well-resolved, binomial quintet, with the magnitude of the $^2J$(H,P) constants typical of couplings between cis $^1$H and $^{31}$P nuclei in bonds at 90° angles for the respective metal in oxidation state II (see Table II; cf. the $^2J$(H,P) values for the analogous carbonyl complexes). Recent work verifies the negative sign of this coupling constant.[44,45]

The broad dihydrogen resonance at 210 K is found downfield of the quintet except for **2Os**. The Ru complexes, with the weakest interaction with the $H_2$ ligand, give the lowest field $H_2$ resonances here and in other complexes,[46] perhaps because they have the closest properties to free $H_2$, which resonates at 4.5 ppm. Another possible indicator of molecular $H_2$ character is the amount that the chemical shift of the dihydrogen differs from that of the hydride in the same molecule, $\delta$(dihydrogen) − $\delta$(terminal hydride). This quantity decreases in the expected order **1Ru > 2Ru > 1Fe > 2Fe > 1Os > 2Os** (refer to chemical shifts from low-temperature spectra in Table II). The reversal in positions of the $H_2$ and H resonances for **2Os** is explained by the fact that the trihydride tautomer predominates.[31]

**Scheme I.** Intramolecular Exchange of H Atoms between Hydride and Dihydrogen ($\Delta G^{\ddagger}$ = 12–17 kcal mol$^{-1}$)



The large line width of the dihydrogen resonance is explained by the rapid dipolar relaxation of these nuclei plus unresolved $^2J$(H,P) couplings (Table II gives estimates of these). Exchange of H atoms between $H_2$ and terminal hydride ligands is negligible below 220 K for these complexes (see below) and does not contribute to the broadening. A previous study of $T_1$ and $T_2$ of some of these complexes could not satisfactorily explain why the lines were so broad for **1Fe** and **2Os**. Explaining this effect as a slowing of the rotation of the $\eta^2$-$H_2$ ligand[14,20,24] is probably not correct since the rate of rotation is many orders of magnitude greater than the possible difference in resonance frequencies of the $^1$H nuclei.[13] The pronounced broadening of the $\eta^2$-$H_2$ resonance and the broadening of the hydride resonance as the temperature is lowered below 220 K is explained mainly by the expected decrease in $T_2$ of the nuclei.

**Temperature-Dependent $^1$H NMR Spectra Due to the Intramolecular Exchange of H Atoms between $\eta^2$-Dihydrogen and Terminal Hydride Ligands.** The fluxional process that explains the spectra of complexes **1Fe** (Figure 1), **2Fe**,[25] **1Os**, and **2Os** is an intramolecular exchange of hydrogen atoms between the $\eta^2$-dihydrogen and terminal hydride ligands (Scheme I).

The spectra can be simulated where two equivalent protons, $A_2$, in an $A_2X_4$ spin system with short $T_2$ values interchange with one proton, B, in a $BX_4$ spin system with a long $T_2$ value. $J_{AB}$ is assumed to be negligible. This is valid since none of the complexes can have a $J_{AB}$ ($^2J(H,H_2)$) coupling constant that exceeds 3 Hz due to the lack of resolvable additional coupling in the quintet of the terminal hydride. The simulation of the spectra of **1Os** and **2Os** has been described recently, and only the chemical shifts, coupling constants, and activation energies are included here (Tables II and IV). $J_{BX}$ values ($^2J$(H,P)) are obtained from the quintet at low temperature (see Table II). However, $J_{AX}$ values ($^2J(H_2,P)$) are obtained indirectly from band shape analysis since they are not resolved in the broad $H_2$ resonance at low temperatures. There is a large error in these values because most of the broadening of the $H_2$ resonance is due to the short $T_2$ (Table III) and not due to the unresolved quintet structure. Complex **2Fe** in acetone-$d_6$ gives a broad peak at −11.9 ppm at 293 K or above; however, in ethanol-$d_6$, it is reported to give a quintet in spectra at 293 K with a coupling $|J(H,P)|$ of 17 Hz, which results from the averaging (1:2) of the terminal hydride coupling $J_{BX}$ of −47 Hz with a $J_{AX}$ coupling of −1.8 Hz.[11] It is assumed in this calculation that $J_{AX}$ and $J_{BX}$ are temperature invariant. A less accurate $J_{AX}$ value of 5 Hz was previously reported for **2Fe** in acetone-$d_6$ by spectral simulation.[25] Complex **2Os** is a similar case. The $J_{AX}$ couplings must be negative to average correctly with the negative $J_{BX}$ couplings to produce the averaged $J$(H,P) coupling in the fast exchange spectrum.[44,45] Broad singlets instead of quintets are observed in the fast exchange spectra of **1Fe** and **1Os** up to 330 K so that $J_{AX}$ values of Table II for these complexes are rough estimates from the simulation of the line widths. It should be noted that no coupling $^2J$(H,P) is resolved in the sharp $^1$H NMR resonance (1:1:1 triplet) of the HD ligand of the deuterated complexes **1**, **2Fe**, and **2Ru** (see below) so that the $^2J(H_2,P)$ couplings of Table II can be considered as maximum possible values. Such couplings to the HD ligand have been resolved for

(44) Benn, R.; Joussen, E.; Lehmkuhl, H.; Lôpez Ortiz, F.; Rufinska, A. *J. Am. Chem. Soc.* **1989**, *111*, 8754–8756.
(45) Eisenschmid, T. C.; McDonald, J.; Eisenberg, R.; Lawler, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 7267–7269 and references therein.
(46) Antoniutti, S.; Albertin, G.; Amendola, P.; Bordignon, E. *J. Chem. Soc., Chem. Commun.* **1989**, 229–230.

**Table III.** $T_2$ Values and Rates of H Atom Exchange ($k$) from the Dihydrogen ($H_2$) Sites to the Terminal Hydride (H) Site Obtained by Line Shape Analysis and $T_1$ Values Measured by the Inversion Recovery Method[a]

| complex | $T$, K | $T_2(H_2)$, ms | $T_1(H_2)$, ms | $T_2$*(H), ms | $T_1$*(H),ms | $k$, $s^{-1}$ |
|---|---|---|---|---|---|---|
| **1Fe**[b] | 329 | 56 (56) | | 570 (570) | | 2300 |
| | 323 | 53 (53) | | 530 (528) | | 1700 |
| | 294 | 25 (25) | 40* (40*) | 350 (350) | 40* (40*) | 500 |
| | 256 | 13 (13) | | 188 (190) | | 15 |
| | 224 | 7.0 (7.0) | 10 (9) | 100 | 130 (131) | 7 |
| | 213 | 6 | 9 (8.5) | 80 (83) | 130 | 0 |
| **1Ru**[b] | 285 | 11* (25) | 29* (27*) | | 294* (357) | 2 |
| **2Fe**[b] | 322 | 134 (134) | | 298* (3070) | | 9000 |
| | 294 | 87 (87) | | 252* (1990) | | 1374 |
| | 276 | 63 (63) | | 220* (1445) | | 330 |
| | 257 | 25 (25) | | 190* (980) | | 58 |
| | 238 | 20 (20) | | 160* (630) | | 7.8 |
| | 219 | 15 (16) | | 130 (370) | | 0.7 |
| | 210 | 12 (13) | 12 | 120 (290) | 302 | 0.2 |
| | 200 | 10 (9) | | 100 (210) | | 0.03 |
| **2Fe**[c] | 270 | | 98* (84*) | | 107* (84*) | |
| | 230 | | 31* (31*) | | 145* (31*) | |
| | 213 | | 31 (19) | | 391 (428) | |
| | 211 | | 17 (17) | | 415 (410) | |
| | 190 | 7 (9) | 16 (17) | | 378 (393) | |
| | 180 | | 19 (20) | | 355 (462) | |
| **2Ru**[b] | 210 | | 11 | | 270 | 0 |
| **2Ru**[c] | 295 | | 70 (83) | | 241* (2132) | 10 |
| | 273 | | 56 (57) | | 895* (1457) | 1 |
| | 253 | | 40 (39) | | | |
| | 232 | | 26 (25) | | | |
| | 212 | | 18 (18) | | 502 (461) | |
| | 193 | | 16 (16) | | 403 (401) | |
| | 183 | | 20 (17) | | 424 (445) | |

[a] For $T_1$ data for **1Fe**, **1Ru**, **1Os**, and **2Os**, see also refs 13 and 29. Values in parentheses were calculated from temperature-dependent $T_1$ and $T_2$ equations as described in refs 13 and 48 by use of the parameters listed in Tables IV and V. The values with asterisks indicate that they are averaged due to the H atom exchange process. [b] 200 MHz, acetone-$d_6$. [c] 400 MHz, acetone-$d_6$.

$[Ru(Cp)(dmpe)(HD)]^+$[47] and $[OsD(depe)_2(HD)]^+$.[29]

The chemical shifts of the fast exchange spectra of complexes **1Fe** and **2Fe** are weighted averages (2:1) of $\delta(H_2)$ and $\delta$(H–M). This is not true of the osmium analogues unless temperature dependences of the chemical shifts of the $\eta^2$-$H_2$ and H ligands are accounted for (Table II).

Spectra calculated on the basis of this information match observed spectra very well (see Figure 1, refs 25, 29). The rate constant, $k$, for H atoms going from the dihydrogen sites to the terminal hydride site (the rate constant for the reverse process would be $2k$) and $T_2$ values from the simulations are listed in Table III. For complex **1Fe** in acetone-$d_6$, the $T_2$ values match those calculated with use of the temperature dependence of the correlation time from the $T_1$ measurements in the $T_2$ equation; the agreement was not as good for data obtained at 200 MHz with **1Fe** in $CD_2Cl_2$.[13] For **2Fe**, the $T_2$ values of the terminal hydride from the simulations are shorter than the ones calculated. Eyring plots of ln $(k/T)$ vs $1/T$ are linear, and from them the activation parameters listed in Table IV are derived.

At room temperature, the fluxional process of Scheme I is slow for complexes **1Ru** and **2Ru** but is detected by spin saturation transfer experiments and averaging of the $T_1$ values of the $H_2$ and hydride ligands (rate for **1Ru** at 285 K is given in Table III). An estimate of $\Delta G^{\ddagger}$ for this process for **1Ru** is given in Table IV. Above room temperature, intermolecular exchange of the ruthenium complexes with free $H_2$(g) dominates as indicated by continuous broadening of the peaks as the temperature is raised; thus, the observation of spectra characteristic of fast intramolecular exchange is not possible.

**Longitudinal Relaxation Times, $T_1$, of the $H_2$ and H Ligands.** The $T_1$ values of the dihydrogen nuclei, $T_1(H_2)$, and the hydride ligand, $T_1$(H), were determined over the temperature range of 190–300 K for the complexes in acetone-$d_6$ (Table III). When the rate of intermolecular H atom exchange exceeds about 10 $s^{-1}$ (Table III), then the rates of relaxation $(1/T_1)$ of the $H_2$ and hydride nuclei start to average. Above exchange rates of about 100 $s^{-1}$, the observed relaxation rates are averages of the $H_2$ and hydride rates weighted 2:1.

**Table IV.** Activation Parameters (kcal $mol^{-1}$) from the Eyring Equation for the Intramolecular Exchange of H Atoms between $\eta^2$-$H_2$ and Terminal H Sites and between cis and trans Isomers of Related Dihydride Complexes[a]

| complex | $\Delta H^{\ddagger}$ | $\Delta S^{\ddagger}$ | $\Delta G^{\ddagger}$ (300 K) |
|---|---|---|---|
| **1Fe** | 11.0 | −10.0 | 14.0 ± 0.3 |
| **1Ru** | | | 15.6 ± 0.5[b] |
| **1Os** | 9.9 | −11.5 | 13.3 ± 0.3 |
| **3Re** | | | 12.7 ± 0.5 |
| **2Fe** | 12.2 | −2.5 | 13.0 ± 0.2 |
| **2Ru** | | | >15 |
| **2Os** | 9.1 | −12.9 | 12.9 ± 0.2 |
| $FeH_2(dppe)_2$ | | | 14.3[54] |
| $RuH_2(dppe)_2$ | | | 19.3[54] |
| $OsH_2(dppe)_2$ | | | >20 |
| $FeH_2(dmpe)_2$[c] | | | 16.2[54] |

[a] The values for **1Os**, **2Os**, and **3Re** are from ref 29. [b] Estimated from the rate of $T_1$ averaging. [c] dmpe = $PMe_2CH_2CH_2PMe_2$.

The analysis of some of this data to obtain the H–H distance, $r_{H_2}$, of the complexes **1Fe** and **1Ru**[13] and **1Os** and **2Os**[29] has already been described. The calculations involve fitting the equations that describe the spin lattice relaxation by the dipolar mechanism[48] to the temperature dependent $T_1$ data by use of a computer program that varies $r_{H_2}$, $\tau_0$ (reflecting the size of the molecule), and $E_a$ (a measure of the viscosity of the solvent).[13] It is important to use a spectral density function that takes into account the spinning of the dihydrogen, which is a much higher frequency process than the tumbling of the molecule.[13] The best fit pa-

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

(48) The equation for dipolar relaxation is $1/T_1 = 0.3\gamma_H^4(h/2\pi)^2(J(\omega) + 4J(2\omega))/r_{HH}^6$. The spectral density function is given by $J(\omega) = A\tau/(1 + \omega^2\tau^2)$ where $A = 0.25$ for rapid rotation of the $H_2$ ligand or $A = 1.0$ for no rotation of the $H_2$. The temperature dependence of the correlation time is assumed to be $\tau = \tau_0 e^{E_a/RT}$. At the temperature of minimum $T_1$, $\tau = 0.62/(2\pi\nu)$ and these equations simplify to $r_{HH} = 4.611(T_1(\min)/\nu)^{1/6}$ for rapid rotation and $r_{HH} = 5.815(T_1(\min)/\nu)^{1/6}$ for no rotation ($\nu$ (MHz), $T_1$ (s)).

**Table V.** Minimum $T_1$ value ($T_1$(min)) for the Dihydrogen Ligand (at Temperature, $T$(min) and Spectrometer Frequency $\nu$) Obtained by Direct Observation and/or Fitting the Data of Table III to the Temperature-Dependent $T_1$ Equation by Using a Temperature-Dependent Correlation Time $\tau = \tau_0 e^{E_a/RT}$ [a,13]

| complex | $\nu$, MHz | $T$(min), K | $T_1$(min), ms | $\tau_0$, ps | $E_a$, kcal mol$^{-1}$ | $r_{H_2}$, Å min[b] | $r_{H_2}$, Å max[c] |
|---|---|---|---|---|---|---|---|
| **1Fe** | 200 | 207 | 8.5 ± 1 | 0.90 | 2.6 | 0.86 | 0.87 |
| | 400 | 230 | 17 ± 1 | 0.90 | 2.6 | 0.86 | 0.87 |
| **1Ru** | 200 | 205 | 10 ± 1 | 1.08 | 2.5 | 0.88 | 0.90 |
| | 400 | 230 | 20 ± 1 | 1.08 | 2.5 | 0.88 | 0.90 |
| **1Os** | 200 | 205 | 18 ± 1 | 0.90 | 2.6 | 0.98[e] | 1.02[d] |
| | 400 | 233 | 40 ± 1 | 0.90 | 2.6 | 0.99[e] | 1.02[d] |
| **2Fe** | 400 | 180 | 16 ± 1 | 0.17 | 2.9 | 0.85 | 0.86 |
| **2Ru** | 400 | 195 | 16 ± 1 | 0.18 | 2.8 | 0.85 | 0.86 |
| **2Os** | 400 | 203 | 80 ± 2 | 0.19 | 2.9 | (1.12)[e] | (1.17)[e] |

[a] The H–H distance of the dihydrogen ligand $r_{H_2}$ is calculated for the case of rapid rotation of the dihydrogen with respect to the tumbling of the molecule. $CD_2Cl_2$ solvent of **1Os**, acetone-$d_6$ for the others. [b] Obtained by fitting $T_1$ data to relaxation equations for rapid rotation of the $H_2$ ligand.[48] [c] Calculated by use of $T_1(H_2, \text{true})$ value as in eq 4. [d] The possibility of a high barrier to $H_2$ rotation has not been completely ruled out for **1Os**. If this were the case, then the H–H distance from a nonspinning $H_2$ unit would be about 1.3 Å. [e] This value is not correct because it results from the averaging of properties of two tautomers.[31]

rameters for all the complexes are found in Table V.

The distances $r_{H_2}$ obtained from the fit are listed as minimum distances in Table V. The distances will actually be slightly longer than these ($r_{H_2}$ maximum) because of dipolar interactions of the $H_2$ nuclei with other nuclei with spins in the molecule (see below). The distances were calculated assuming rapid spinning of the $H_2$ ligand ($A = 0.25$[48]). This is a good assumption for the complexes **2Fe**, **1Ru**, and **2Ru** based on their similarity to **1Fe**, which is known to have a rapidly spinning $H_2$, even in the solid state. If the correlation time of the $H_2$ were not shorter than the one for the tumbling of the molecule (i.e., no $H_2$ spinning), then the H–H distance could fall in a second range of distances (1.10–1.14 Å) ($A = 1.0$[48]); the observation of large $^1J$(H,D) values for these complexes (ca. 30–33 Hz) makes this an unlikely situation. Distances in the range 0.9–1.1 Å can be ruled out since they would arise from intermediate rotation rates that give plots of ln $T_1$ versus $1/T$ with curves characteristically different to those observed (see Figure 4 of ref 13). No fit to the data could be obtained by use of an intermediate H–H distance of around 1 Å and by letting $E_a$ and $\tau_0$ vary. The octahedral complex **1Os** should also have a spinning $H_2$, but this needs to be verified by inelastic neutron scattering. A longer H–H distance of 1.25 Å would be expected for **1Os** without $H_2$ spinning, but this is not consistent with the large $^1J$(H,D) value observed for the HD complex. The assumption of rapid spinning is not valid for complex **2Os**, which consists mainly of a trihydride with a nonspinning $H_2$ unit so that the H–H distance reported in Table V is an averaged one with little physical significance.[31]

The $\tau_0$ and $E_a$ parameters obtained by the fitting procedure describe fairly successfully the temperature dependence of the $T_1$ values of the terminal hydride (Table VI) as well as the $H_2$ nuclei (Table V). The $\tau_0$ values are smaller for the smaller depe complexes **2** than the dppe ones. Complexes with the same ligand have similar $\tau_0$ values; experimental uncertainties do not allow a definitive ranking of the sizes of the Fe, Ru, and Os complexes based on $\tau_0$.

Minimum $T_1(H_2)$ values were directly observed in either the 200- or 400-MHz series of measurements apart from **1Fe**, where the intramolecular H atom process masked the minimum at both frequencies. However, a minimum value is readily obtained from the fitted $T_1$ curve for this complex.[13] The smaller complexes **2** go through the minimum at a low temperature, $T$(min), of about 189 K at 200 MHz or 200 K at 400 MHz, whereas the larger complexes **1** have higher $T$(min) of 205 K at 200 MHz and 230 K at 400 MHz. The same dihydrogen bond distance $r_{H_2}$ (Table V, minimum value) is obtained from the fit to the data or from the $T_1$(min) value (when it is observed) according to the procedure of Hamilton and Crabtree.[19,48]

The true H–H distances are likely to be a little longer than $r_{H_2}$(min) of Table V because other protons on the dppe ligands contribute to the relaxation of the $H_2$ nuclei as do the phosphorus nuclei and possibly the metal (see below). The major contributor will be hydrogens on the ligands because phosphorus and the metals have much smaller magnetogyric ratios, $\gamma_X$, than hydrogen, $\gamma_H$, and heteronuclear dipolar relaxation depends on $\gamma_H^2/\gamma_X^2$. Also the P nuclei are farther away (≥ 2.6 Å) from the $H_2$ nuclei than are ligand hydrogens (2.0–2.2 Å). The contribution from these other sources of relaxation can be approximated by use of the observed minimum $T_1$ value of the terminal hydride, $T_1$(H, obs), since this hydride is in a similar environment to the $H_2$ ligand (eq 4).[49] As an example, complex **1Ru** has minimum values of

$$\frac{1}{T_1(H_2, \text{obs})} = \frac{1}{T_1(H_2, \text{true})} + \frac{1}{T_1(H, \text{obs})} \qquad (4)$$

$T_1(H_2, \text{obs}) = 0.020$ and $T_1(H, \text{obs}) = 0.27$ s at 400 MHz (Tables V and VI). The former value corresponds to an $r_{H_2}$ of 0.88 Å. The corrected minimum $T_1(H_2, \text{true})$ is 0.022 s, and the corrected maximum H–H distance is 0.90 Å, assuming rapid spinning. Note that the dihydrogen H–H distances for the Fe and Ru complexes are only slightly lengthened when the correction via eq 4 is applied (Table V), whereas there is a greater lengthening of the Os H–H distances.

From the minimum $T_1$ values for the terminal hydride resonances, one can estimate the distance ($r_{H\text{-}H}$) to protons on the ligands that cause it to relax. The distances given in ref 13 were calculated on the assumption that only one ligand proton comes close to the terminal hydride at a given time; this proton is likely to be a phenyl ortho proton for dppe or a methyl proton for depe.

**Table VI.** Observed Minimum $T_1$ Value ($T_1$(min)) for the Terminal Hydride Ligand Obtained by Direct Observation and Fitting to the Temperature-Dependent $T_1$ Equation (Same $T$(min), $\tau_0$, $E_a$ as Corresponding Complex Entry in Table V)[a]

| | | $^1$H NMR | | | $^{31}$P NMR | |
|---|---|---|---|---|---|---|
| | | | $r_{H\cdots H}$, Å | | | |
| complex | $\nu$, MHz | $T_1$(min), s | min[b] | max[c] | $T$(min), K | $T_1$(min), s |
| **1Fe** | 200 | 0.12 | 1.7 | 2.1 | | |
| | 400 | 0.24 | 1.7 | 2.1 | 192 | 0.24 |
| **1Ru** | 200 | 0.14 | 1.7 | 2.2 | | |
| | 400 | 0.27 | 1.7 | 2.2 | 196 | 0.37 |
| **1Os** | 400 | 0.28 | 1.7 | 2.2 | 200 | 0.52 |
| **2Fe** | 400 | 0.38 | 1.8 | 2.3 | | |
| **2Ru** | 400 | 0.4 | 1.8 | 2.3 | | |
| **2Os** | 200 | 0.17 | 1.8 | 2.2 | | |
| | 400 | 0.34 | 1.8 | 2.2 | | |

[a] The $T_1$ values for the phosphorus nuclei (determined at 162 MHz) are also included. [b] $r_{H\cdots H} = 5.815\,(T_1(\text{min})/\nu)^{1/6}$ with $r$ in angstroms, $T_1$ in seconds, and $\nu$, the spectrometer frequency, in megahertz.[48] [c] Multiply minimum distance by $4^{1/6}$ to account for four nearby protons.

(49) The dihydrogen protons, while they are spinning, could approach closer (by about 0.2 Å) than a terminal hydride to an ortho hydrogen on a dppe ligand or a hydrogen on a methyl of a depe ligand; however, the distance from the centroid of rotation of $H_2$ or from the terminal hydride to the ligand protons should be the same.

**Table VII.** $^1$H NMR Chemical Shifts of Some of the Isotopomers of the Complexes[a]

| | | $(H_2)$-M-H | (HD)-M-H | | | $(H_2)$-M-D | (HD)-M-D | | |
|---|---|---|---|---|---|---|---|---|---|
| | $T$ | $\delta(H_2)$ | $\delta$(HD) | $^1J$(H,D) | $^2J$(H,P) for HD | $\delta(H_2)$ | $\delta$(HD) | $^1J$(H,D) | $^2J$(H,P) for HD |
| **1Fe**[b] | 210 | −8.62 | −8.62 | 30 ± 2 | <5 | −8.55 | −8.56 | 31.5 ± 1.0[d] | <5 |
| **1Ru** | 293 | −4.57 | −4.57 | 32.0 ± 0.5 | <2 | −4.50 | −4.50 | 32.8 ± 0.5 | <2 |
| **1Os** | 230 | [c] | −6.62 | 25.5 ± 0.5 | <5 | −6.61 | | | |
| **2Fe** | 200 | −10.5 | | | | | −10.5 | 29.5 ± 0.5 | <5 |
| **2Ru** | 293 | −6.48 | −6.50 | 32.3 ± 0.5 | <2 | −6.42 | −6.47 | 31.8 ± 0.5 | <2 |
| **2Os**[d] | 200 | −10.03 | −10.10[e] | ≤10[f] | −5 | −9.93[g] | −10.02[h] | 10.5 ± 0.1 | −5.4 |

[a] 200 MHz, acetone-$d_6$ unless otherwise noted. The terminal hydride chemical shifts for the isotopomoers *trans*-$[M(H)(HD)L_2]^+$ and *trans*-$[M(H)(D_2)L_2]^+$ are within 0.02 ppm of the chemical shift $\delta$(H) for *trans*-$M(H)(H_2)$ (see Scheme II). [b] $CD_2Cl_2$. [c] −6.80 in $CD_2Cl_2$. [d] 400 MHz. [e] $\delta(HD) = 0.0031T - 10.65$. [f] From line shape analysis. [g] $\delta(H_2) = 0.0028T - 10.49$. [h] $\delta(HD) = 0.0034T - 10.70$.

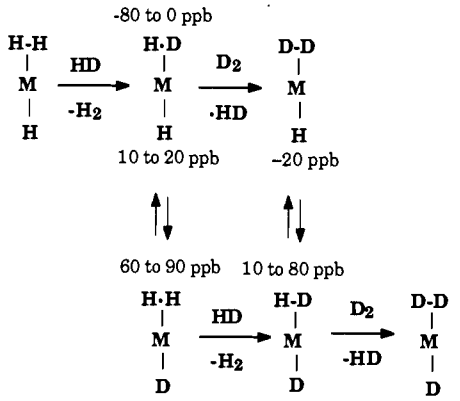
A maximum of about four ligand protons at equal distance to the hydride could cause its relaxation; then that distance can be longer than the previous case by a factor of $4^{1/6} = 1.26$; these $r_{H\cdots H}$ distances are indicated in Table VI as maximum values. For the sake of comparison, hydride to ortho hydrogen distances for **1Fe** of 1.9–2.2 Å were measured on a model built from the dimensions of the neutron diffraction structure. Similar distances were measured on a scale model of a similar osmium complex with 2.36-Å Os–P distances and a 1.7-Å Os–H distance. The range of distances of 1.7–2.3 Å calculated on the basis of the $T_1$ values is not unreasonable (Table VI). When the ligand protons are replaced by deuteria, the relaxation time for the terminal hydride of **1Fe** or **1Os** dramatically increases whereas the $T_1$ of the $H_2$ ligand is unaffected; this should be the case when the hydrogens ortho on the phenyls are the main contributors to the relaxation rate of the terminal hydride (deuterium, with its small $\gamma_D$ value, is a less efficient dipolar relaxation agent), whereas the hydrogens in the $H_2$ ligand are solely responsible for each other's relaxation rate.[13]

The long comparable $T_1$ value for the terminal hydride in each of the complexes supports the idea that relaxation of the nuclei is due to dipolar interactions and not due to paramagnetic impurities or other modes of relaxation. To examine this, we also determined the minimum $T_1$ value of the phosphorus nuclei in complexes **1** (Table VI). These values do parallel approximately the minimum $T_1$ values in Table VI of the hydride. The approach of correcting the $T_1(H_2, \text{obs})$ value with the terminal hydride's relaxation rate (eq 4) should account for these differences in relaxation due to the metal and other nuclei at varying distances from the dihydrogen nuclei in the molecule.

**$H_2/D_2$ Exchange.** A qualitative rate of hydrogen loss was obtained by shaking solutions of the complexes **2** in acetone-$d_6$ under $D_2$ at 1 atm and 295 K. The intensity of $^1$H NMR resonances in the hydride region drops to half the initial value as **2Ru** (<5 min) < **2Fe** (~2 h) < **2Os** (180 h). The rate of the reaction of $D_2$ with **2Fe** was independent of the $D_2$ pressure. Complexes **1** with the dppe ligand are noticeably more labile than their depe counterparts. Complex **1Ru** is so labile that it loses up to 1 mol of $H_2$ in the solid state at 25 °C under vacuum in 10 min to give orange-yellow $[RuH(dppe)_2]BF_4$. Hydrogen re-adds in seconds to this five-coordinate complex in the solid state or to $[RuH(acetone)(dppe)_2]BF_4$, $\nu$(CO) = 1673 cm$^{-1}$, in acetone solution to give **1Ru**.

**Preparation and Properties of the Deuterated Complexes.** A variety of isotopomers can be observed by $^1$H NMR as the Fe and Ru complexes in acetone-$d_6$ are progressively enriched in deuterium by exposure first to excess HD (prepared from NaH and $D_2O$) and then to $D_2$ gas (Figure 2). They are observed when intramolecular H atom exchange is slow (290 K for **1Ru**, **2Ru**; 210 K for **1Fe**, **2Fe**). The isotopomer first formed upon intermolecular exchange of $H_2$ with HD would be *trans*-$[M(H)(HD)L_2]^+$ (Scheme II). However, the isotopomer *trans*-$[M(H)(HD)L_2]^+$ also is formed quickly by intramolecular exchange of H atoms. The $d_1$ complexes can also be prepared by adding $HBF_4$ in $D_2O$ to the dihydride complex (as in eq 1). The complex **1Fe**-$d_2$ has been prepared by adding $HBF_4$ to $FeD_2(dppe)_2$ in ether. The Ru complexes are sometimes enriched in deuterium by slow exchange with acetone-$d_6$; an impurity may be involved in this reaction.

**Scheme II.** Successive Formation of Isotopomers of Complexes **1** and **2** as They Become Enriched in Deuterium[a]




[a] The isotope shifts (in parts per billion) refer to the chemical shift of the $^1$H in the isotopomer minus the shift of the corresponding resonance in the nondeuterated form of the complex (refer to Table VII).

**Table VIII.** Selected Electrochemical and Infrared Properties of the Complexes *trans*-$[M(H)(diphosphine)_2(L)]^+$

| | electrochemistry[a] | | infrared[b] | |
|---|---|---|---|---|
| complex | L = $H_2$, $E_a$,[c] V | L = $Cl^-$, $E_{1/2}$,[d] V | L = CO, $\nu$(CO), cm$^{-1}$ | L = $N_2$, $\nu(N_2)$, cm$^{-1}$ |
| $[Fe(H)(dppe)_2(L)]^+$ | 0.8[e] | −0.71 | 1950 | 2120 |
| $[Ru(H)(dppe)_2(L)]^+$ | >1[e] | −0.12 | 1987[f] | 2194 |
| $[Os(H)(dppe)_2(L)]^+$ | 1.15[g] | −0.14[g] | 2003[e] | |
| $[Fe(H)(depe)_2(L)]^+$ | 0.6 | −0.98[h] | 1929[i] | 2090[i] |
| $[Ru(H)(depe)_2(L)]^+$ | 1.1 | (−0.24)[j] | 1958[i] | 2163[i] |
| $[Os(H)(depe)_2(L)]^+$ | 1.0[e] | −0.46[g,k] | 1974[i] | 2136[i] |
| $Re(H)(dppe)_2(L)$ | −0.4[l] (**3Re**) | - | 1845[m] | 2006[m] |

[a] Versus $FeCp_2/FeCp_2^+$, THF solvent, 0.2 M *n*-$Bu_4NBF_4$, 200 mV s$^{-1}$ scan rate unless otherwise noted. [b] Nujol mull unless otherwise noted; this work unless otherwise noted. [c] Anodic peak potential of irreversible wave; complexes **2** are $BPh_4^-$ salts and give $E_a$ = 0.6 V for $BPh_4^-/BPh_4$ oxidation. [d] Values in parentheses are anodic peak potentials. [e] $CH_2Cl_2$ solvent. [f] Reference 85. [g] 0.2 M *n*-$Bu_4NPF_6$, 250 mV s$^{-1}$ scan rate. [h] $E_a$ at 0.50 V also; also cathodic peaks at $E_c$ = −1.06 and −0.26 V. [i] Reference 40. [j] $E_a$ at −0.06 and 0.22 V also; $E_c$ at −0.37, −0.17, and 0.10 V. [k] $E_{1/2}$ at 0.45 V also. [l] 0.19 V versus Ag/AgCl.[86] [m] Reference 87.

Couplings $^1J$(H,D) ≈ 30–32 Hz for the Fe complexes and 32–33 Hz for the Ru complexes can be resolved in the $^1$H NMR spectra at 210 K for Fe and 293 K for Ru (Table VII) and verify the presence of an H–H bond. There is no resolvable isotopic shift $\delta(HD) - \delta(H_2)$ when both the $H_2$ and HD are trans to H or when they are both trans to D in the complexes **1Fe**, **2Fe**, and **1Ru**; there are small shifts (−20 and −50 ppb, respectively, for **2Ru**) (Table VII). However, there is a shift of 30–70 ppb when trans hydride is replaced by trans deuteride in these complexes. This shift, which is in the expected downfield direction, is another manifestation of the high trans influence of deuteride compared to hydride.[50] This phenomenon was also observed for the isotopomers of

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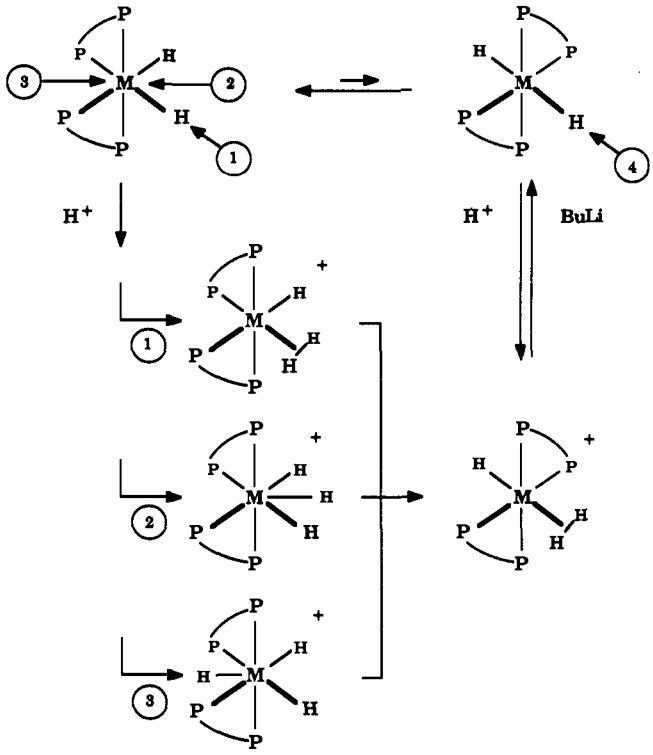
**Scheme III.** Stereochemical Aspects of the Formation of Dihydrogen Complexes by Protonation of Dihydride Complexes




*trans*-$[Os(H)(H_2)(meso\text{-tetraphos-1})]^+$.[12] The isotopomers of **2Os** display similar isotopic shifts, but it must be noted that these chemical shift differences are temperature dependent.

**Electrochemistry and Infrared Data.** Complexes **1** and **2** are difficult to oxidize and display an anodic wave at $E_a \approx 1$ V vs $FeCp_2/FeCp_2^+$ (Table VIII). The cathodic return wave is very broad and likely involves the reduction at the Pt electrode of protons produced in the oxidation reaction

$$[M(H_2)(H)L_2]^+ \xrightarrow{-e^-} [M(H_2)(H)L_2]^{2+} \xrightarrow{-H^+} [M(H)_2L_2]^+ \quad (5)$$

The oxidation of the metal by 1 (adding 1 to the positive charge on the complex) is expected to decrease the $pK_a$ of the coordinated dihydrogen ligand by about 20![51] In addition, the dihydrogen will become exceedingly labile in the oxidized complex, and thus loss of $H_2$ could also account for the irreversibility, at least for the Fe and Ru complexes. Removing one positive charge from **1** or **2** effectively gives a trihydride complex like **3Re**, which is easier to oxidize by about 1.4 V (Table VIII).

The infrared data for the corresponding carbonyl and dinitrogen complexes (Table VIII) reflect the electrochemical behavior of the $[MHL_2]^{n+}$ binding site in that the stretching frequencies for Re are much lower than those for complexes **1** and **2** as expected.[52]

The complexes *trans*-$M(Cl)(H)L_2$ display more reversible redox behavior. These data suggest that the binding sites $[MHL_2]^+$ with M = Fe are more reducing than the Ru and Os complexes and those with L = depe are more reducing than those with L = dppe.

## Discussion

**Formation of Dihydrogen Complexes by Protonation.** The fact that cis dihydride complexes lead to trans dihydrogen complexes in eq 1 provides some insight into the mechanism of formation of complexes **1** (Scheme III). The starting complexes of eq 1 have predominantly cis stereochemistry although $RuH_2(dppe)_2$ is ~5% trans according to $^{31}P$ NMR and $OsH_2(dppe)_2$ is 10% trans.[53] The Fe complex is isomerizing at a rate of 150 $s^{-1}$ and the Ru complex at a rate of <1 $s^{-1}$; the Os complex is essentially static.[54] The initial product of the very fast protonation of the cis complexes should be *cis*-$[M(H)(dppe)_2(H_2)]^+$ (route 1, Scheme III) since there is mounting evidence that protonation of basic hydride complexes takes place at the hydride ligand;[12,55-58] this might isomerize rapidly to its related trihydride form (route 2). Such cis intermediates must isomerize rapidly to the observed trans form; the cis form can only be stabilized by use of suitable tetraphos ligands as in $[Fe(H)(PP_3)(H_2)]^+$[14,59] and $[OsH_3(rac\text{-tetraphos-1})]^+$.[12] Attack at the metal between phosphorus atoms (route 3) would give the trans stereochemistry directly, but there is no evidence for the microscopic reverse of this process. For example, deprotonation of *trans*-$[Ru(H)(dppe)_2(\eta^2\text{-}H_2)]^+$ by BuLi at −80 °C gives thermally unstable *trans*-$Ru(H)_2(dppe)_2$ (Scheme III), which isomerizes to *cis*-$Ru(H)_2(dppe)_2$ at room temperature; the reverse of route 3 would lead to the incorrect cis stereochemistry.

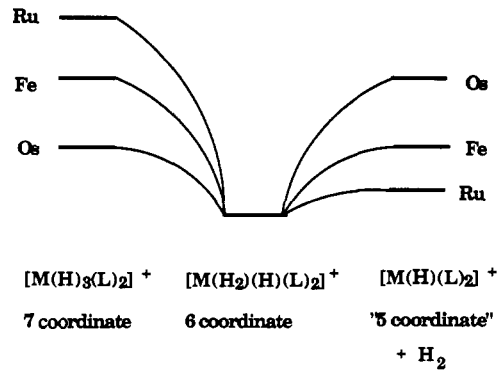



**Figure 3.** Qualitative energy level diagrams for (a) the seven-coordinate intermediates in the H atom exchange process of Scheme I and (b) the five-coordinate (or weakly solvated six-coordinate) complexes produced by the loss of $H_2$. The energy scales of the two sides of the diagram are not likely to be the same.

A strong acid for eq 1 is not required. The dihydride complexes $M(H)_2(dppe)_2$ are completely protonated by 1 equiv of $[Ru(C_5H_5)(H)_2(PPh_3)_2]BF_4$ ($pK_a \approx 8.3$) in THF[57] or by 1 equiv $HPCy_3^+BPh_4^-$ ($pK_a \approx 9.7$)[60] in THF.[51] The complexes $M(H)_2(depe)_2$ (M = Fe,[11] Ru, and Os) are so basic that they dissolve in EtOH ($pK_a \approx 15.9$) and are completely converted to the dihydrogen complexes **2** ($OEt^-$ counterion).[51] This unexpected reactivity with alcohol explains why the dihydride complexes could not be made by the standard method of reaction of $LiAlH_4$ with the dichloride complexes followed by deactivation and decomplexation of the aluminum salts by addition of alcohol.[61] Further investigation of the relative kinetic and thermodynamic acidities of complexes **1** and **2** is in progress.

**Metal Dihydrogen Interaction.** The qualitative rates of eq 3 and the $H_2/D_2$ exchange reactions give a sense of the relative strengths of the metal–dihydrogen interactions. Dihydrogen reacts rapidly with the five-coordinate complexes of all three metals generated by chloride removal as in eq 3. Five-coordinate complexes of this type are thought to have a square-pyramidal geometry[34,62,63] although it is possible that a sixth ligand (a solvent molecule or a phosphine C–H bond) may also be weakly coor-

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dinated.[2] The lability of dihydrogen as judged by the qualitative $H_2/D_2$ rates of exchange increases as Os < Fe < Ru. Thus, the equilibrium constant for $H_2$ binding and hence the strength of the $H_2$–metal bond likely increases as Ru < Fe < Os. Figure 3 qualitatively expresses the energetics of this equilibrium between five- and six-coordinate complexes. There is partial evidence that this ordering is valid in the solid state since **1Ru** is the only complex that reversibly loses and recoordinates $H_2$ gas in the solid state at 25 °C. The ordering of strength of the metal–$H_2$ interaction might be expected to parallel the magnitude of the coupling between the $H_2$ nuclei and $^{31}P$ nuclei in the complexes, $^2J(H_2,P)$; however, the uncertainties in this coupling only allow the conclusion that **2Os** has a stronger interaction with $H_2$ than the other complexes (Table II).

The ordering of $H_2$ lability is consistent with relative rates of substitution of the complexes; the complexes react irreversibly with $CH_3CN$ to give complexes *trans*-$[M(H)(CH_3CN)(L)_2]^+$ with qualitative rates increasing as Os ≪ Fe ≈ Ru. A similar trend in lability of dihydrogen was noted for complexes containing monodentate phosphine ligands, $[M(H)(H_2)\{PPh(OEt)_2\}_4]^+$.[5]

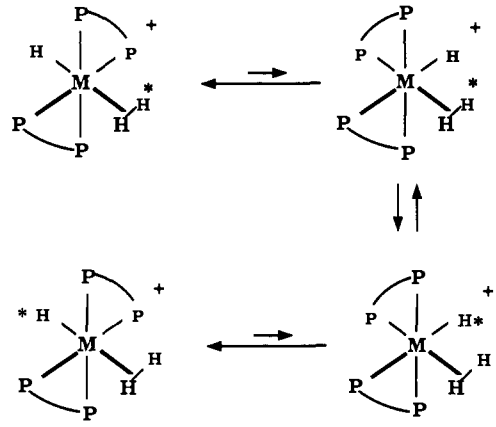
**H–H Bonding.** The $T_1$ and $^1J(H,D)$ measurements suggest an ordering of H–H bond length and strength. The H–H distances for the Fe and Ru complexes with rapidly spinning dihydrogen ligands are comparable at 0.87 ± 0.02 Å, considering the accuracy of the $T_1$ method, and are consistent with the value of 0.82 (2) for **1Fe** at 10 K as determined by neutron diffraction. This distance is apparently insensitive to the differences in the electronic properties of the metals (Ru versus Fe) and the ligands (dppe versus depe) as detected by electrochemistry. The Os complexes (**1Os** and the dihydrogen tautomer of **2Os**) have significantly longer H–H bonds (~1.0 Å). Thus, an overall ordering of increasing distances is Ru ≈ Fe < Os. There is a greater variation in $^1J(H,D)$ with regard to changes in metal and ligand in the complexes *trans*-$[M(D)(\eta^2\text{-HD})L_2]^+$. If this coupling gives an indication of H–H (H–D) bond order, then H–H bond strength should decrease in the order **1Ru** ≥ **2Ru** ≥ **1Fe** > **2Fe** > **1Os** ≈ **2Os**, although the actual coupling for the $\eta^2$-HD tautomer of **2Os** can only be estimated.[29]

If it is assumed that the H–H bond order decreases as the metal–$H_2$ interaction increases, then this H–H bond order ranking is consistent with the metal–$H_2$ interaction given above. This is understood in terms of bonding arguments where H–H bond order decreases and the M–H bond order increases as σ-withdrawal of electrons from the $\sigma(H_2)$ orbital by the metal increases and π-donation from $d_\pi$ orbitals into the $\sigma^*(H_2)$ orbital increases on going from Ru to Fe to Os and from less basic dppe complexes to more basic depe complexes. The π-back-bonding component to the bonding just mentioned is difficult to distinguish from an increase in σ-bonding to the separate H atoms since both processes involve orbitals of the same symmetry.

The simplest rationalization of the ordering down the triad is that π-back-bonding increases going from Ru(II) to Os(II) to Fe(II) and σ-bonding increases going from Fe to Ru to Os. Thus, Os would form the strongest M–$H_2$ bonds based on σ- and π-contributions, while Ru forms the weakest due to poor π-bonding. The increase in σ-bond strength down the triad is well-known,[64] and Os is expected to form the strongest σ-bonds because of improved overlap due to relativistic contraction of its orbitals.[65]

The ordering of capacity for π-back-bonding as Ru(II) < Os(II) < Fe(II) is more controversial. The results from cyclic voltammetry on the dihydrogen complexes do not provide a clear-cut ranking of electron richness because the redox behavior is irreversible. We propose that the $[FeH(depe)_2]^+$ unit is the best back-bonder since it forms the most reducing complexes (Table VIII) and has the CO and $N_2$ complexes with lowest stretching frequencies of the three metals. The corresponding Os complex should be more electron releasing than the Ru complex since it is slightly easier to oxidize (Table VIII) and back-bonds better to $N_2$. However, a comparison of the stretching frequencies of

**Scheme IV.** Intramolecular Exchange Process That is Unlikely



CO complexes of Ru and Os (Table VIII) suggests that Ru is a better back-bonder than Os. Subtle changes in overlap and energetics of the d orbitals must account for this difference. In classical coordination complexes, Os almost always gives complexes that are more reducing than isostructural Ru ones.[66] Taube and co-workers have shown that pentaammine Os(II) complexes are better π-bases than corresponding Ru(II) ones.[67] It is also possible that the single radial node of the 4d orbital of Ru falls in the M–H bonding region and thus decreases both σ- and π-overlap with ligand orbitals. In a series of isostructural, zero-valent alkyne complexes, $M(CO)_4(\eta^2\text{-}Me_3SiC_2SiMe_3)$, the π-back-bonding to alkyne increases as Fe(0) < Ru(0) < Os(0) but the Ru complex is the most labile.[68] Note, however, the difference in metal oxidation state, coordination geometry, and bonding, which involves 2p orbitals on C separated by 1.3 Å.

**Intramolecular H Atom Exchange and the Homolytic Cleavage of $H_2$.** There are several possible mechanisms for the exchange process of Scheme I. As we reported earlier, homolytic cleavage of the H–H bond to give a fluxional trihydride intermediate, which allows H atom exchange, is most consistent with the data.[25,29] Other possible mechanisms are considered below. The $\Delta G^\ddagger$ values decrease as Ru > Fe > Os and dppe > depe. This ordering differs from those observed for classical hydride complexes $MH_2(PR_3)_4$ where the barriers were relatively insensitive to ligand variation but decreased as Os > Ru > Fe.[69] The ordering also differs from that of $MH_2(diphosphine)_2$ (Table IV) where the dmpe complex has a higher barrier than the dppe one. This is the opposite order to **1** and **2** considering that depe and dmpe have similar properties as ligands.[54] The small $\Delta S^\ddagger$ values are in accord with an intramolecular process.[70]

Estimates of the rates of exchange between the two equivalent hydrides and the terminal hydride in the pentagonal bipyramidal trihydride $ReH_3(dppe)_2$ (**3Re**) (see Table IV, ref 29) were also examined. The $\Delta G^\ddagger$ value obtained for **3Re** fits well in the trend that, as the hydridic character of the dihydrogen ligand increases (**1Ru** ≈ **1Fe** < **1Os** < **3Re**), the barrier to rearrangement decreases. This trend supports the existence of a fluxional trihydride intermediate in Scheme I. The $\Delta G^\ddagger$ value for the interconversion of $W(CO)_3(H_2)(P(i\text{-}Pr)_3)_2$ to $W(H)_2(CO)_3(P(i\text{-}Pr)_3)_2$ is 16.0 kcal $mol^{-1}$.[71] The dihydride in this case is thought to have a capped octahedral geometry. The depe complexes have lower $\Delta G^\ddagger$ values than those of the dppe complexes. The more electron donating depe ligand would encourage the formation of the trihydride transition state more than the dppe ligand. Their smaller size

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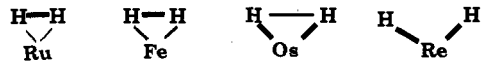
**Chart I.** Qualitative H–H Interactions and M–H Interactions as Expressed by Light Lines (Weak, Long Bonds) and Heavy Lines (Strong, Short Bonds)




would also stabilize this intermediate. The ordering of stability of seven-coordinate trihydride intermediates in the exchange process of Scheme I is illustrated in Figure 3; note that Ru is out of the periodic order.

An alternative mechanism involving a rapid equilibrium before the rate-determining step of trans ⇄ cis isomerization of the octahedral complexes to bring the exchanging groups cis to each other (Scheme IV) can be probably discarded because the coupling constant $^2J$(H,P) of the terminal hydride would be a weighted average of several cis $J$(H,P) couplings with a trans $J$(H,P) coupling constant to give values that would likely be temperature dependent and larger than the ones observed, at least for Ru and Os (Table II).[72] Furthermore, for all the complexes **1** and **2** at temperatures where H atom exchange is slow on the NMR time scale, only the trans isomer is observed. In addition, the observed ordering of $\Delta G^{\ddagger}$ values (Ru > Fe > Os) is not consistent with a six-coordinate intermediate since six-coordinate dihydride complexes give the ordering Os > Ru > Fe (see above). Certainly when $\eta^2$-$H_2$ and $H^-$ ligands are held cis to each other, as in $[Ir(C_{13}H_8N)(H)(H_2)(PPh_3)_2]^+$,[56] $[Re(H_2)(H)_2(CO)(PPh_3)_3]^+$,[73] or $[Fe(H)(H_2)(PP_3)]^+$,[14,59] rapid intramolecular exchange can proceed by a formal deprotonation of the dihydrogen by the hydride base or by formation of a trihydrogen ligand ($H_3$).

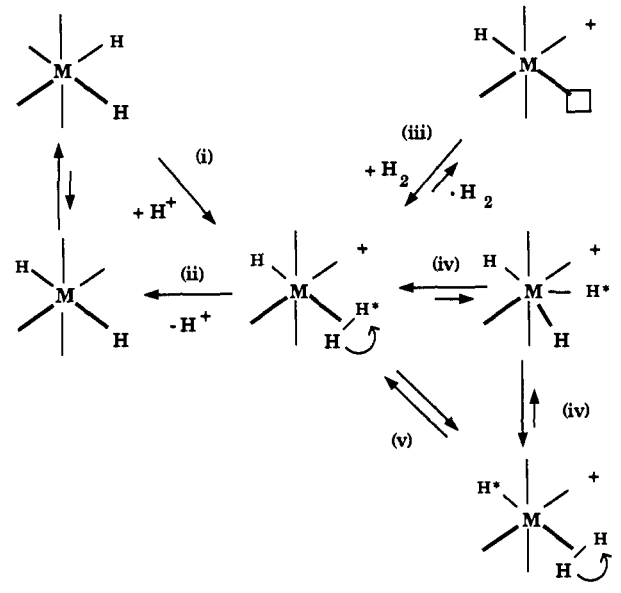
Intermolecular acid–base reactions where the terminal hydride of another complex or the solvent accepts a proton from the $H_2$ ligand cannot explain the spectra. The rate of H atom exchange is unperturbed by the addition of excess $HBF_4$. The $^2J$(H,P) couplings are not lost during H atom exchange, which is not consistent with intermolecular exchange. The isotopomers $[Os(HD)(H)L_2]^+$ and $[Os(HD)(D)L_2]^+$ of complexes **1Os** and **2Os** do not scramble $H^+/D^+$ by intermolecular exchange over a period of hours and hence do not give statistical mixtures of all possible deuterated species. Also the rate of proton transfer between complexes $[M(H)(dppe)_2(H_2)]^+$ and $M'H_2(dppe)_2$ is known to be much slower than H atom exchange.[51]

The rate-determining dissociation of one end of the diphosphine to give a six-coordinate trihydride intermediate, $[M(H)_3(P\text{–}P)(P\text{–}P^*)]^+$, where P* is not coordinated, can also be discounted. The M–P bond energies increase as Fe–P < Ru–P < Os–P, which is not the ordering of activation energies. For the Fe complexes, which are the most likely to have labile phosphorus donors,[74] the bond strengths should increase as Fe(dppe) < Fe(depe), and this is not the order of $\Delta G^{\ddagger}$ values.

## Conclusions

Chart I graphically represents the features of structure and bonding of the metal–dihydrogen unit in the complexes *trans*-$[M(HH)(H)(L)_2]^{n+}$ ($n$ = 0 for Re; $n$ = 1 for Fe, Ru, and Os) as deduced in this work. The Fe and Ru complexes have similar H–H distances in their rapidly spinning dihydrogen ligands. However, the Ru complexes have weaker interactions with the dihydrogen ligand than Fe (or Os). This difference is explained by the better back-bonding capability of the Fe center. The H–H distances in the Os complexes are significantly longer, and in the case of **2Os** there are dihydrogen–hydride and trihydride tautomers present.[31] The Os complexes have the strongest metal–$H_2$ bond of the triad because of the greater $\sigma$-bond energy than that of corresponding Fe complexes and greater $\sigma$- and $\pi$-energies than those of corresponding Ru complexes. The complex **3Re** is a trihydride because Re–H bonds are strong and the neutral ReH-$(dppe)_2$ unit is strongly electron releasing as indicated by the electrochemistry and infrared data.

**Scheme V.** Chemical and Dynamic Processes of the Dihydrogen Complexes




The dihydrogen ligand undergoes a rich variety of chemical and dynamic processes as summarized in Scheme V: acid–base chemistry (routes i and ii), intermolecular loss/recoordination of $H_2$ (route iii), homolytic cleavage of $H_2$ leading to a trihydride tautomer (route iv) that leads to intramolecular H atom exchange (route v), and finally spinning of $H_2$.

There is a continuous decrease in $^1J$(H,D) (Table VII), in the lability of the dihydrogen, in the barrier to site exchange (Table IV), and in the chemical shifts difference, $\delta$(dihydrogen) – $\delta$(terminal hydride) (Table II), as one goes from **1Ru**, **2Ru** ≥ **1Fe**, **2Fe** > **1Os** > **2Os** > **3Re**. The $T_1$(min) values decrease in almost exactly the opposite order. Electrochemical and infrared data both indicate that the ease of oxidation of the binding sites for $N_2$ and $Cl^-$ decreases as $ReH(dppe)_2 \gg [FeH(depe)_2]^+ > [FeH(dppe)_2]^+ > [MH(depe)_2]^+ > [MH(dppe)_2]^+$ (M = Ru, Os).

Thus, the Ru dihydrogen complexes have properties that are out of place in the periodic order. The $[RuHL_2]^+$ unit is a poorer $\pi$-back-bonder than the corresponding Fe complex because of its less energetic 4d electrons. Ru is a poorer $\sigma$-bonder and $\pi$-back-bonder than Os probably because the Os valence orbitals, due to relativistic contraction effects, have better overlap with ligand orbitals.

We propose that, for this series of iron group complexes, the energy difference between dihydrogen on an octahedral, $d^6$ center and dihydride on a seven-coordinate $d^4$ center is high for the Fe and Ru complexes but drops to a low value at Os where the metal center is sufficiently electron releasing (or $\sigma$-bonding becomes sufficiently strong) to give an elongated dihydrogen H–H distance of about 1.0 Å. Neutron diffraction will play a key role in determining the structure of such hydrides in this transition region.

## Experimental Section

Unless otherwise noted, all manipulations were done in an Ar or $H_2$ atmosphere by use of Schlenk techniques. Solids were handled in a Vacuum Atmosphere drybox under $N_2$. All solvents were dried over appropriate reagents[75] and distilled under $N_2$ before use. $D_2$ was obtained from Matheson Gas Products. Phosphines ligands were purchased from Strem Chemical Co. or Digital Specialty Chemicals Ltd. Literature methods were used to make $FeH_2(dppe)_2 \cdot 2C_7H_8$,[76] $FeH(C_6H_4PPhCH_2CH_2PPh_2)(dppe)$,[77] $[FeH(dppe)_2]BPh_4$,[78] $FeCl_2(depe)_2$,[79]

(72) However, the cis intermediate might be present in such a small concentration that its contribution to the averaged coupling would be undetectable.

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$FeHCl(depe)_2$,[80] and $Ru(cod)(cot)$.[81] An improved synthesis of $RuH_2(dppe)_2$[81] in two steps from $RuCl_2(DMSO)_4$[82] is given below. The osmium complexes were prepared as described previously.[29,61] Infrared spectra were recorded with use of a Nicolet 5DX FTIR spectrometer as Nujol mulls on NaCl plates or in the stated solvent in 0.1 mm KBr solution cells. NMR spectra were obtained on a Varian XL-400 operating at 400.00 MHz for $^1H$ and 161.98 MHz for $^{31}P$ or on a Varian XL-200 operating at 200.00 MHz for $^1H$ and 80.98 MHz for $^{31}P$. Some variable-temperature $^{31}P$ NMR and selective hydride decoupling experiments were carried out by use of the Bruker WP400 spectrometer at the South Western Ontario Regional NMR facility. Chemical shifts refer to room temperature conditions unless specified otherwise. All $^{31}P$ NMR were proton decoupled. $^{31}P$ chemical shifts were measured relative to ~1% $P(OMe)_3$ in $C_6D_6$ sealed in coaxial capillaries but are reported in parts per million from 85% $H_3PO_4$ ($\delta(P(OMe)_3) = 140.4$ ppm). $^1H$ chemical shifts (ppm) were measured relative to partially deuterated solvent peaks but are reported relative to tetramethylsilane. $T_1$ measurements were made by using the inversion recovery method.[13] Care was taken in the preparation of the complexes to avoid paramagnetic species like $[FeH(depe)_2]^+$, which would contribute to the overall rate of relaxation. Dynamic NMR spectra were simulated with use of a modified version of the program DNMR4,[83] and second-order spectra were simulated with use of the LAOCN 5 program.[84]

Microanalyses were performed by the Canadian Microanalytical Service, Ltd., Westminster, 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-Haber probe-type capillary; THF or $CH_2Cl_2$ solutions were 0.002 M in the complexes and 0.2 M in $n$-$Bu_4NBF_4$. Reported potentials are referenced to ferrocene, which was added to these solutions.

**Preparation or *trans*-[FeH(dppe)$_2$($\eta^2$-H$_2$)]BF$_4$ (1Fe).** Dinitrogen as well as dioxygen must be excluded at all stages by use of a $H_2$ or Ar atmosphere. Method 1: $FeH_2(dppe)_2 \cdot 2C_7H_8$ (0.5 g, 0.58 mmol) was partially dissolved in 50 mL of diethyl ether to produce a yellow suspension. Under 1 atm of argon or hydrogen, 0.5 mL of $HBF_4 \cdot Et_2O$ (excess) was added dropwise over a period of 1 min with stirring. Immediately a pale yellow, powdery solid precipitated out, causing the solution to turn almost colorless. The solid was filtered off and washed several times with diethyl ether (80% yield). The product can be recrystallized by slow diffusion of diethyl ether into a THF solution of **1Fe** and washed with cold THF, MeOH, and diethyl ether. The product contains THF and ether in the lattice as verified by X-ray diffraction. Anal. Calcd for $C_{52}H_{51}BF_4FeP_4 \cdot (C_4H_8O)_2(C_4H_{10}O)$: C, 66.22; H, 6.7. Found: C, 66.27; H, 6.0. IR (Nujol): 1919 (Fe–H), 1050 cm$^{-1}$ ($BF_4^-$). UV/vis: $\lambda_{max}$ 380 nm ($\epsilon$ 255). $^1H$ NMR: see Figure 1. Method 2: When $HBF_4 \cdot Et_2O$ (35 $\mu$L, 0.25 mmol) was added to a solution of $FeH(C_6H_4PPhCH_2CH_2PPh_2)$(dppe) (200 mg, 0.23 mmol) in toluene at −5 °C under $H_2$, a purple precipitate ($[FeH(dppe)_2]BF_4$, see ref 78) formed immediately but then turned to a light yellow solid (**1Fe**) within 1 min.

**Preparation of *trans*-[Fe(H)(dppe)$_2$($\eta^2$-H$_2$)]BPh$_4$ (1FeBPh$_4$) from FeClH(dppe).** $FeClH(dppe)_2$ (0.064 g, 0.072 mmol) was dissolved in 15 mL of a THF/EtOH mixture (50% by volume) to form a deep purple solution. To this solution was added a solution of $NaBPh_4$ (0.026 g, 0.076 mmol) in 5 mL of EtOH under $H_2$. Within 10 min, the deep purple color of the solution had lightened to pink, and after it was stirred for 12 h the solution was cloudy yellow. The yellow solid (0.053 g, 0.045 mmol), isolated by filtration, was washed with benzene, water, and diethyl ether to give **1FeBPh$_4$** in 62% yield, which is spectroscopically pure ($^1H$, $^{31}P$, cyclic voltammetry).

**Preparation of *cis*-RuCl$_2$(dppe)$_2$.** $RuCl_2(DMSO)_4$ (0.500 g, 1.00 mmol) was dissolved in 7 mL of $CH_2Cl_2$. Dppe (0.830 g, 2.10 mmol) in 5 mL of $CH_2Cl_2$ was added, and this clear yellow solution was stirred for 1 h. After this time, the solvent was removed and the resulting yellow solid was washed with hexanes. The solid was then vacuum dried and recrystallized from THF/hexane. The product contained a mixture of cis/trans isomers in an approximate ratio of 3:1, and further recrystallization was therefore necessary to eliminate the unreactive trans isomer ($\delta$ 43.6 in $^{31}P$ NMR spectrum). This was achieved by making a concentrated solution in $CH_2Cl_2$ and carefully placing a layer of hexanes above this. Upon cooling, the pure cis isomer crystallized out in 60% yield. $^{31}P$ NMR (81 MHz, $CD_2Cl_2$): 49.9 (t), 36.9 (t, cis isomer, $^2J_{PP}$ = 19.7 Hz).

***cis*- and *trans*-RuCl$_2$(depe)$_2$** was prepared in a similar manner in 71% yield. $^{31}P$ NMR (81 MHz, $C_6D_6$, cis/trans ~8): 47.7 (s, trans isomer), 59.0 (t), 47.4 (t, cis isomer, $^2J_{PP}$ = 22.4 Hz).

**Preparation of *cis*-RuH$_2$(dppe)$_2$.** *cis*-$RuCl_2(dppe)_2$ (0.500 g, 0.51 mmol) was dissolved in a mixture of THF (8 mL) and EtOH (2 mL). Under 1 atm of $H_2$ or Ar, 0.140 g of NaOEt (2.00 mmol) was added with stirring. This yellow solution was stirred for 15 h. After this time, the solution slightly discolored to pale yellow. The solvent was removed, and the solid was redissolved in benzene. The NaCl formed was filtered off through Celite, and the volume of the filtrate was reduced to 2 mL. Addition of hexane caused precipitation of the cream-colored $RuH_2(dppe)_2$ in 60% yield (0.277 g). $^1H$ NMR (200 MHz, $C_6D_6$, cis/trans ~20): −8.17 (q, $J_{HH} \approx 17$ Hz, *trans*-$RuH_2$), −8.33 (AA′ part of AA′MM′$X_2$ pattern, $J_{AA'} = -1$ or −4, $J_{MM'} = -4$ or −1, $J_{AM} = J_{A'M'} = 68$, $J_{AM'} = J_{A'M} = -15.2$, $J_{AX} = J_{A'X} = -23.5$ Hz, *cis*-$H_2Ru$). $^{31}P$ NMR (81 MHz, $C_6D_6$, cis/trans ~20): 83.4 (s, *trans*-$H_2Ru$), 79.0 ($X_2$ part of MM′$X_2$ pattern, $^2J_{MX} \approx 15.5$ Hz), 65.0 (MM′ part of MM′$X_2$ pattern).

**Preparation of *trans*-[RuH(dppe)$_2$($\eta^2$-H$_2$)]BF$_4$ (1Ru) from RuH$_2$(dppe)$_2$.** Method 1 for the preparation of **1Fe** was followed except that $RuH_2(dppe)_2$ was used. All solutions were kept under 1 atm of dihydrogen, and the solid product was dried in a stream of dihydrogen. IR (Nujol): 1961 (Ru–H), 1050 cm$^{-1}$ ($BF_4^-$). $^1H$ NMR: see Figure 2.

**Preparation of *trans*-[RuH(dppe)$_2$($\eta^2$-H$_2$)]BPh$_4$ (1RuBPh$_4$) from RuCl$_2$(dppe)$_2$.** A mixture of *cis*- and *trans*-$RuCl_2(dppe)_2$ (0.500 g, 0.51 mmol) was dissolved in 10 mL of THF. Under 1 atm of $H_2$, $NaBPh_4$ (0.700 g, 2.0 mmol) was added with stirring; immediately the cloudy yellow mixture changed to orange and after approximately 0.5 min discolored back to yellow. This mixture was stirred for 3.5 h after which time it was filtered through Celite and the filtrate removed under reduced pressure. Under 1 atm of $H_2$, the residue was dissolved in a minimum of acetone. Addition of MeOH resulted in the precipitation of a cream solid (0.288 g, 46%), which was washed with MeOH and dried under a stream of dihydrogen. Anal. Calcd for $C_{76}H_{69}BP_4Ru$ (sample that lost $H_2$): C, 74.94; H, 5.71. Found: C, 74.59; H, 5.77.

**Observation of *trans*-RuH$_2$(dppe)$_2$ by Reaction of 1RuBPh$_4$ with BuLi.** A solution of **1Ru** (0.026 g, 0.021 mmol) in 2 mL of acetone-$d_6$ was cooled to 200 K under 1 atm of $H_2$. BuLi in hexane (0.014 mL of 1.6 M) was then added by syringe, and the solution was stirred at 200 K under $H_2$ for 2 h. The $^1H$ NMR spectrum in the hydride region showed only a broad quintet for the product at −8.62 ppm ($^2J(H,P)$ = 18 Hz). When this solution warmed to room temperature, the only hydride resonance present was the multiplet due to *cis*-$RuH_2(dppe)_2$ at −8.75 ppm. The resonances for a small amount of the trans isomer could be hidden under this multiplet.

**Preparation of *trans*-[Fe(H)(depe)$_2$($\eta^2$-H$_2$)]BPh$_4$ (2Fe) from FeClH(depe)$_2$.** $FeClH(depe)_2$ (0.28 g, 0.56 mmol) was dissolved in 25 mL of acetone. Under 1 atm of $H_2$, $NaBPh_4$ (0.24 g, 0.7 mmol) was added and the mixture was stirred for 30 min. The resulting NaCl was filtered off through Celite, and the volume of the filtrate was reduced to 5 mL. MeOH (5 mL) was added, and the solution was cooled overnight to give yellow-orange crystals of **2Fe** (0.12 g, 0.168 mmol) in 30% yield, which were washed with cold MeOH and diethyl ether. Anal. Calcd for $C_{44}H_{71}BFeP_4 \cdot CH_3OH$: C, 65.70; H, 9.19. Found: C, 65.80; H, 8.86.

**Preparation of *trans*-[Fe(H)(depe)$_2$($\eta^2$-H$_2$)]BPh$_4$ (2Fe) Directly from FeCl$_2$(depe)$_2$.** Sodium ethoxide/EtOH solution (0.25 mL, 0.217 M) was added via syringe to a solution of $NaBPh_4$ (0.0187 g, 0.055 mmol) in 15 mL of EtOH. The solution was cooled to 14 °C, $FeCl_2(depe)_2$ (0.0291 g, 0.054 mmol) was added, and the mixture was placed under $H_2$. The color changed from light green to yellow initially; over the course of 5 min, the solution became clear and the white product precipitated out. Hydrogen uptake was measured to be 1.7 mol of $H_2$/Fe over the course of this reaction. The solid was collected by filtration and washed with EtOH, water, and finally diethyl ether. It was pure according to spectroscopic and electrochemical methods.

**Preparation of *cis*- and *trans*-RuH$_2$(depe)$_2$.** Ru(cod)(cot) (0.300 g, 0.95 mmol) was dissolved in THF (8 mL). Under 1 atm of hydrogen, depe (0.395 g, 1.9 mmol) was added dropwise. This bright yellow solution was stirred for 24 h after which time it had discolored to a pale yellow. The solvent was removed under reduced pressure. Under 1 atm

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of Ar, cold acetone was added to the residue, affording a white solid (0.080 g, 16%). $^1$H NMR (200 MHz, $C_6D_6$, cis/trans ~2: −10.24 (q, $^2J$(H,P) = 22.4 Hz, *trans*-$H_2$Ru), −10.64 (AA′ part of AA′MM′$X_2$ pattern, $J_{AA'}$ = −24 or 0, $J_{MM'}$ = 0 or −24, $J_{AM} = J_{A'M'}$ = 60, $J_{AM'} = J_{A'M}$ = −12, $J_{AX} = J_{A'X}$ = −24 Hz, *cis*-$H_2$Ru). $^{31}$P NMR (81 MHz, THF, cis/trans ~2): 84.3 (s, *trans*-$H_2$Ru), 76.0 ($X_2$ part of MM′$X_2$ pattern, $J_{MX} = J_{M'X}$ = −22.4 Hz, *cis*-$H_2$Ru), 62.7 (MM′ part of MM′$X_2$ pattern, *cis*-$H_2$Ru).

**Preparation of *trans*-[Ru(H)(depe)$_2$($\eta^2$-H$_2$)]BPh$_4$ (2Ru).** RuHCl(depe)$_2$ (0.185 g, 0.33 mmol) was dissolved in acetone (5 mL). Under 1 atm of hydrogen, $NaBPh_4$ (0.173 g, 0.50 mmol) was added with stirring. This yellow solution was stirred overnight after which time it was filtered through Celite under an argon atmosphere. The volume of the filtrate was reduced to 2 mL. Addition of methanol caused the precipitation of a white solid, which was washed with MeOH and dried in vacuo (0.190 g, 68%). Anal. Calcd for $C_{44}H_{71}BP_4Ru$: C, 63.22; H, 8.56. Found: C, 63.06; H, 8.45.

**Preparation of *trans*-[Ru(H)(depe)$_2$($\eta^2$-H$_2$)]BPh$_4$ (2Ru) Directly from RuCl$_2$(depe)$_2$.** $RuCl_2(depe)_2$ (0.030 g, 0.051 mmol) was dissolved in 3 mL of THF and 1 mL of ethanol. Under 1 atm of $H_2$, $NaBPh_4$ (0.018 g, 0.051 mmol) and NaOEt (0.007 g, 0.103 mmol) were added with stirring. This mixture was stirred for 1 h and then filtered through Celite under an atmosphere of argon. The solvent was removed under reduced pressure, and under an atmosphere of hydrogen the yellow-white residue was redissolved in a minimum of acetone. Addition of methanol caused the precipitation of the white product (0.020 g, 46%); unreacted *trans*-$RuCl_2(depe)_2$ remained dissolved in the methanol.

**Preparation of *trans*-[Ru($\eta^2$-H$_2$)(H)(depe)$_2$]BF$_4$ (2RuBF$_4$).** $RuH_2(depe)_2$ (0.050 g, 0.10 mmol) was dissolved in diethyl ether (20 mL). Under 1 atm of hydrogen, 0.1 mL of $HBF_4$·$Et_2O$ (excess) was added dropwise with stirring. A white solid immediately precipitated. This white solid was allowed to settle, and the ether supernatant was syringed out. The solid (0.042 g, 72%) was then washed with diethyl ether (2 × 5 mL) and cold MeOH (5 mL) to remove any excess acid and dried in vacuo.

**Preparation of FeD$_2$(dppe)$_2$.** $FeCl_2$ (9 mg, 0.07 mmol) was added to the dppe (64 mg, 0.16 mmol) in THF (25 mL) and stirred for 5 min, producing a tan-colored solution. $NaBD_4$ (9 mg, 0.24 mmol) in EtOD (4 mL) was added to the stirring solution. The solution was stirred for 12 h at 20 °C in darkness. After the boron-containing salts and excess $FeCl_2$ were filtered off, the volume of the yellow filtrate was reduced to approximately 3 mL and then 3 mL of diethyl ether and 7 mL of hexane were added to give the product (36 mg, 60%).

**Preparation of 1Fe-*d*$_2$.** $FeD_2(dppe)_2$ (35 mg, 0.042 mmol) was dissolved in diethyl ether. Under 1 atm of argon, $HBF_4$·$Et_2O$ (0.20 mL, excess) was added over a period of 1 min with stirring. The resulting pale yellow precipitate (20 mg) was filtered and washed with diethyl ether. The $^1$H NMR sample in acetone-$d_6$ was placed under 1 atm of $D_2$ for 45 min. In the hydride region of the $^1$H NMR spectrum at 213 K, there was a 1:1:1 triplet at −8.8 ppm and a quintet at −13.2 ppm. In similar experiments in $CD_2Cl_2$, the 1:1:1 triplet for **1Fe-*d*$_1$** was also partially resolved.

**Observation of Isotopomers of 1Ru and 2Ru.** Acetone-$d_6$ solutions of **1Ru** or **2Ru** were placed under 1 atm of HD (made by adding NaH to $D_2O$) for 5 min. The $^1$H NMR spectra were recorded after every 15 min. H/D exchange with the acetone-$d_6$ resulted in progressive enrichment of the complexes in D so that first the $d_1$ and then the $d_2$ species were observed. The mixtures were also examined by D NMR.

**Preparation of 1Fe-*d*$_1$.** $FeH_2(dppe)_2$ (0.066 g, 0.07 mmol) was added to 10 mL of $Et_2O$ containing 0.1 mL of $D_2O$. Approximately 0.05 mL of $HBF_4$·$Et_2O$ was then added to produce $DBF_4$ in situ. The white precipitate was filtered and washed with three 5-mL volumes of $Et_2O$.

**Preparation of Isotopomers 2-*d*$_1$.** These complexes were synthesized from HD, $NaBPh_4$, and *trans*-MClH(depe)$_2$ as described above. The HD was generated by adding NaH to $D_2O$.

**Preparation of Isotopomers 2-*d*$_2$.** These complexes were synthesized from $D_2$, $NaBPh_4$, and *trans*-MClH(depe)$_2$ as described above. **Os-*d*$_2$** was obtained in 50% yield.

**Deuterium-Exchange Experiments.** An NMR tube containing a solution of a complex (**2**) (27 mg, 0.03 mmol) and 10 μL of $C_6D_6$ was put under $D_2$ (1 atm) by bubbling $D_2$ through the solution for two min at 20 °C. The tube was shaken to overcome gas diffusion problems. After 1 h, Ar was bubbled through the solution to displace the $D_2$. D NMR showed incorporation of D by the appearance of a deuteride peak(s), which corresponded with the hydride patterns of complexes **2**. There was no incorporation of D into the phosphine ligands. Integration of the deuteride peak(s) against the $C_6D_6$ peak allowed the calculation of a "half-life" or the time required for half the hydride and molecular hydrogen protons to be replaced by D atoms. Integration of the hydride resonances in the $^1$H NMR as a function of time of exposure to $D_2$ against that of added silicone grease, which served as a standard, also gave a measure of the half-life.

To determine whether the rate of $H_2/D_2$ exchange was dependent on the pressure of $D_2$, the $^1$H NMR spectra of three samples of **2Fe** in acetone-$d_6$ containing initial partial pressures of deuterium mixed with argon of 0, 0.5, and 1.0 atm were recorded. Again, the disappearance of the hydride resonance was monitored by integrating it with respect to silicon grease. There was no noticeable pressure dependence.

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