Dihydride Complexes of the Cobalt and Iron Group Metals: An Investigation of Structure and Dynamic Behavior

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Abstract: The previously reported cationic dihydride complexes $(PP_3)MH_2^+$ (M = Co, Rh and Ir; $PP_3 = P(CH_2CH_2PPh_2)_3$) have been prepared using improved synthetic methods. Variable-temperature ^1H and ^{31}P NMR spectra of these complexes reveal complex dynamic behavior. The hydride region ^1H NMR spectra have been accurately simulated at all temperatures using a simple site permutation model after taking into consideration the opposite signs of the *cis* and *trans* H−P coupling constants. Partial deuteration of the hydride ligands in the rhodium and cobalt complexes is achieved by exposure to D_2. In the partially deuterated samples, no evidence is found for a bound dihydrogen ligand, but the involvement of a dihydrogen species in the dynamic process which interchanges the two hydride positions remains a mechanistic possibility, as indicated by a kinetic isotope effect $k_H/k_D = 1.3(1)$. The partially deuterated samples exhibit large and temperature-dependent isotope effects on the ^1H NMR chemical shifts observed for the hydride resonances, which are attributed to isotopic perturbation of resonance. This arises from non-statistical occupation of the two different hydride sites and also leads to perturbation of the averaged H−P coupling constants. Similar observations have been made for the neutral iron complex $(PP_3)FeH_2$.

The structure and reactivity of transition metal hydride complexes is an area of great interest due to the central importance of such species in catalytic processes. In this context, the oxidative addition reaction of H_2 with various transition metal complexes to give dihydride complexes has been extensively investigated. An additional area of research has developed since the initial discovery of transition metal dihydrogen complexes by Kubas and co-workers.[1] While a large number of isolable dihydrogen complexes have been reported,[2] definitive structural characterization data are available in only a few cases. The difficulty of structural characterization in the absence of neutron diffraction data has been described by Kubas.[3] Indirect magnetic resonance methods have been developed based on the measurement of ^1H relaxation rates (T_1 data)[4] or the measurement of J_{H-D} in partially deuterated samples. While the quantitative relationship between H−H distance and the T_1 of the bound H_2 ligand is more complex than first thought,[5] qualitatively there is a clear correlation of short H−H distances with rapid dipole−dipole relaxation (short T_1 values). The measurement of J_{H-D} values of 10−35 Hz is usually considered to be a definitive indication of the presence of an intact dihydrogen ligand.[6]

Bianchini and co-workers have reported novel cationic dihydrogen complexes of the form $(PP_3)M(H_2)^+$ ($PP_3 = P(CH_2CH_2PPh_2)_3$; M = Co (**1**), Rh (**2**)).[7,8] In both cases, substantial H−D coupling in partially deuterated samples ($J_{H-D} = 18$ Hz for **2**; $J_{H-D} = 28$ Hz for **1**) was observed. In the case of complex **2**, an equilibrium between two isomeric forms was postulated based on variable temperature NMR data. A trigonal bipyramidal dihydrogen complex is believed to predominate at higher temperatures, while an octahedral dihydride is favored at low temperatures. X-ray diffraction data for **2** are consistent with a dihydride structure in the solid state, but complex **1** has been reported to have either a dihydrogen or a dihydride structure in the solid state, depending on the nature of the counteranion employed. It is reported that the PF_6^- salt crystallizes as the dihydrogen complex, while the BPh_4^- salt adopts the dihydride structure.[9]

There is considerable precedent in the literature for rapid equilibration of dihydrogen and dihydride complexes, such as the tungsten complexes of Kubas and co-workers,[10] cationic $[CpRu(diphos)]^+$ complexes,[11] and complexes of $[Cp^*Os(CO)_2]^+$.[12] In all cases previously reported, considerable structural reorganization accompanies the dihydrogen/dihydride isomerization reaction. In contrast to these examples, the dihydride/dihydrogen equilibration postulated for the rhodium complex seems to involve relatively little rearrangement of the phosphine coligands.

We now report the outcome of further investigations of the synthesis and properties of complexes **1** and **2**, including a detailed analysis of ^1H and $^1H\{^{31}P\}$ NMR spectra of partially deuterated derivatives, which indicates that these complexes are correctly formulated as highly dynamic dihydride species. With

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[6] Osmium complexes recently reported by Taube and co-workers have very low values of J_{HD}: (a) Hasegawa, T.; Li, Z.-W.; Parkin, S.; Hope, H.; McMullan, R. K.; Koetzle, T. F.; Taube, H. *J. Am. Chem. Soc.* **1994**, *116*, 4352−4356. (b) Li, Z.-W.; Taube, H. *J. Am. Chem. Soc.* **1994,** *116*, 9506−9513.

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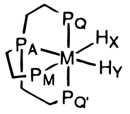
suitable values of the H−P coupling constants, the ^1H NMR spectra can be simulated accurately at all temperatures using a permuation model which interchanges the two hydride nuclei H_X and H_Y as well as permuting the phosphorus nuclei P_M, P_Q, and $P_{Q'}$.



A similar procedure has also been successful in the case of the neutral iron analog $(PP_3)FeH_2$. A preliminary account of some of our observations has appeared.[13]

Results

Synthesis. The compounds studied were prepared following published procedures with modifications which are described in the Experimental Section. An exception was the synthesis of PP_3RhH which was generated from $(PPh_3)_4RhH$[14] *via* ligand exchange with PP_3 in hot toluene. This method proved more convenient and gave higher yields than the previously reported synthesis starting from PP_3RhCl.

NMR Observations: (a) $[PP_3CoH_2]PF_6$ (1). The ^1H NMR spectrum of $[PP_3CoH_2]PF_6$ in acetone-d_6 exhibits a pseudo doublet of quartets in the hydride region centered at δ −10.93 ppm, in good agreement with published data[8] (Figure 1a). Exposure of the sample to D_2 leads to the observation of a new signal at δ −10.73 ppm (Figure 1b) attributable to **1**-d_1. Signals due to H_2 and HD gas are observed at 4.54 (singlet) and 4.51 ppm (1:1:1 triplet, $J_{HD} = 42$ Hz) respectively. Over time, the signal at −10.73 ppm continues to grow, while the signal at −10.93 decreases and eventually disappears. The $^1H\{^{31}P\}$ NMR spectrum shows two singlet resonances (Figure 1c); no H−D coupling is observed in **1**-d_1. The separation of the two resonances is temperature dependent. At 190 K the chemical shifts are −10.56 (**1**-d_1) and −10.86 ppm (**1**).

When a sample of **1**-d_2 is placed under H_2 gas, a resonance corresponding to **1** appears in the hydride region after 5 min; the signal continues to grow over time. A signal for **1**-d_1 appears only after 2.5 h and remains weak compared to the signal for **1**.

The T_1 (min) for the hydride protons in **1** (500 MHz) was 95 ms at 226 K (see Figure 2). T_1 values for the hydride in **1**-d_1 were typically about 10% greater than those observed for **1**.

(b) $[PP_3RhH_2]BF_4$ (2). Consistent with the observations of Bianchini and co-workers,[7] we find that the ^1H NMR spectrum of **2** (hydride region) at ambient temperature exhibits only a single resonance (d of quintets at −7.52 ppm). Upon lowering the temperature the signal broadens and disappears into the baseline below 190 K. At 173 K two separate signals appear in the hydride region due to non-equivalence of the two hydride ligands. We were able to supercool a sample of **2** in THF-d_8 down to 160 K, and observed two well-resolved doublets with a line width of 65 Hz at −4.93 ($J_{HP} = -139$ Hz) and −10.01 ppm ($J_{HP} = -135$ Hz). Using selective ^{31}P decoupling it was determined that the downfield resonance is due to the proton trans to the bridgehead phosphorus atom (P_A) and the upfield resonance is due to the proton trans to the terminal phosphorus atom (P_M).

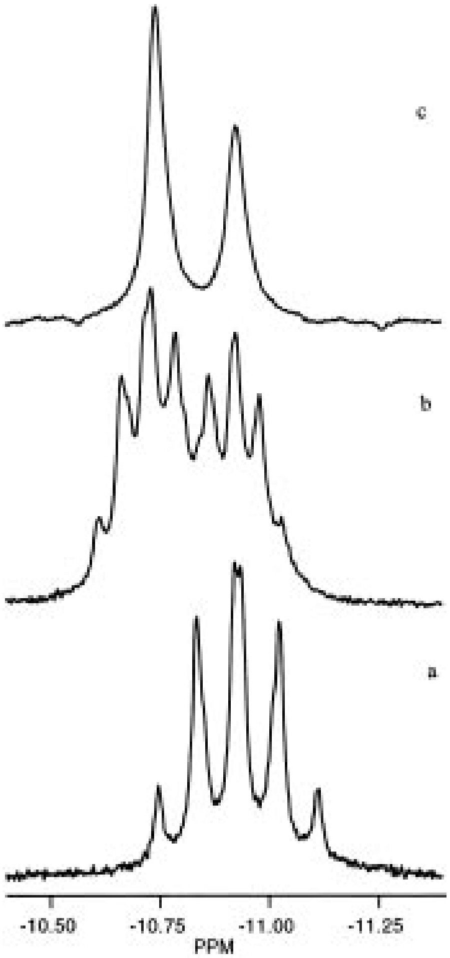


Figure 1. (a) Partial ^1H NMR spectrum (hydride region) of complex **1** (300 MHz, 298 K) in acetone-d_6 and (b) after exposure to D_2 (1 atm) for 11 h (500 MHz). (c) $^1H\{^{31}P\}$ spectrum (500 MHz).

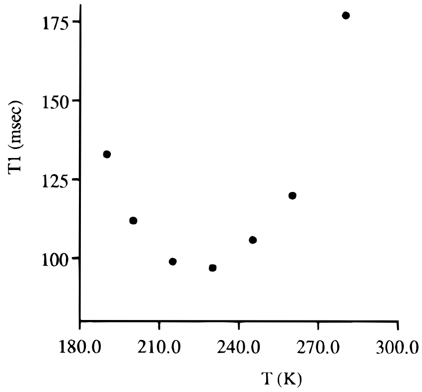


Figure 2. T_1 (ms) vs T(K) for $PP_3Co(H)_2^+$ in acetone-d_6 at 500 MHz.

When a sample of **2** is placed under a D_2 atmosphere a signal due to $[PP_3RhHD]^+$ (**2**-d_1) is observed to grow in at −7.33 ppm, partially overlapping the signal due to **2** at −7.52 ppm (Figure 3a). The ^1H $\{^{31}P\}$ spectrum (Figure 3b) of this mixture exhibits two doublet resonances, with the doublet pattern due to a 14.7 Hz coupling to ^{103}Rh. There is no evidence for H−D coupling in the resonance due to the HD species. The separation between the signals for **2** and **2**-d_1 is temperature dependent. At 340 K, $\Delta\delta = 161$ ppb, increasing to 209 ppb at 277 K.

(c) $[PP_3IrH_2]Cl$. The room temperature ^1H NMR spectrum of $[PP_3IrH_2]Cl$ (**3**) exhibits two broad doublets in the hydride region at −7.62 and −12.55 ppm, consistent with the observations of Bianchini *et al.*[15] Upon lowering the temperature the

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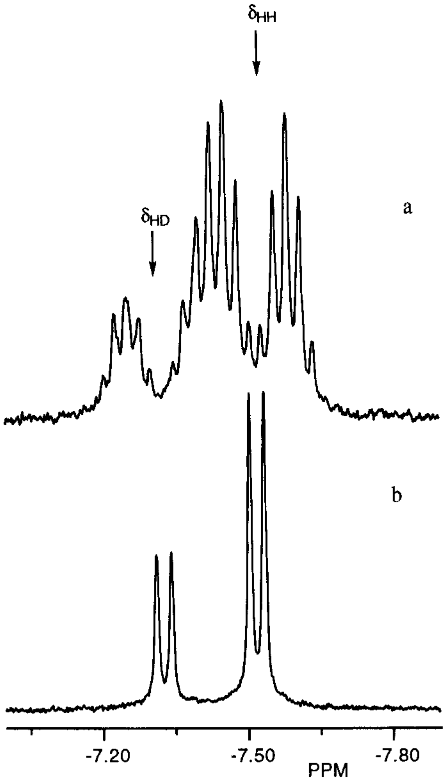

Figure 3. (a) Partial ^1H NMR spectrum (hydride region) of complex **2** (500 MHz, 298 K) in THF-d_8 after exposure to D_2 (1 atm) for 7 h. (b) $^1H\{^{31}P\}$ spectrum (500 MHz).

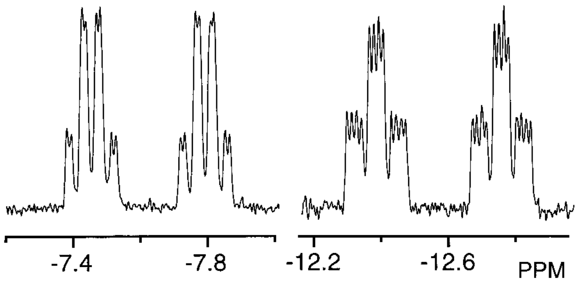

Figure 4. Partial ^1H NMR spectrum (hydride region) of complex **3** (200 MHz, 260 K) in THF-d_8.

peaks sharpen and at 260 K resolve into two well-resolved multiplets (Figure 4). The downfield resonance is due to the hydride trans to the bridgehead phosphorus P_A ($J_{H_YP_A} = -100$ Hz, $J_{H_YP_M} = J_{H_YP_Q} = +13.0$ Hz), the upfield resonance is due to the hydride trans to the terminal phosphorus P_M ($J_{H_XP_A} = +8.3$ Hz, $J_{H_XP_M} = -110$ Hz, $J_{H_XP_Q} = +19.7$ Hz). The $J_{H_XH_Y}$ coupling constant accounts for the residual coupling of 3.6 Hz. These values of the coupling constants were obtained by comparing simulated spectra with the observed resonance positions and intensities.

Coalescence of the two hydride signals was not observed at any accessible temperature (up to 360 K in DMSO-d_6) and no incorporation of deuterium was observed after prolonged exposure of **3** to D_2 gas at 360 K.

(d) PP_3FeH_2 (4). A variable-temperature ^1H NMR study of this dihydride as well as a room temperature ^1H NMR spectrum of a mixture of **4** and PP_3FeHD (**4**-d_1) in toluene-d_8 have been published.[16] In order to separate the signals for **4** and **4**-d_1 and to resolve all high-temperature coupling constants, a spectrum was taken at 500 MHz (Figure 5). The resonance for **4** appears at −10.85 ppm ($J_{HP_M} = 41.5$ Hz; $J_{HP_A} = 3.7$ Hz); the resonance for **4**-d_1 appears at −10.58 ppm ($J_{HP_M} = 42.1$ Hz; $J_{HP_A} = 5.5$ Hz).

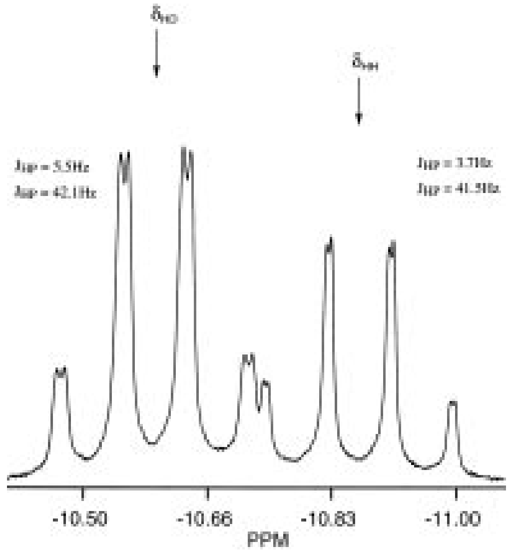

Figure 5. Partial ^1H NMR spectrum (hydride region) of complex **4** and **4**-d_1 (500 MHz, 298 K) in THF-d_8.

Below 170 K (in THF-d_8) the signal decoalesces into two broad ($\nu_{1/2} = 160$ Hz) resonances at −7.2 (H_Y) and −14.2 ppm (H_X). Individual couplings could not be resolved even at 140 K in $CDFCl_2$.

Discussion

Structure of the Cobalt and Rhodium Complexes. The high-temperature $^1H\ \{^{31}P\}$NMR spectra in the hydride region of partially deuterated samples of complexes **1** and **2** show no evidence for H−D coupling (Figures 1 and 3). In the case of the cobalt complex, the line width of the hydride resonance due to **1**-d_1 is *ca.* 14 Hz. The rhodium complex **2**-d_1 gives a line width of *ca.* 6 Hz. While it is possible that a small H−D coupling remains unresolved in these spectra, such a coupling would be outside the range usually associated with dihydrogen complexes.

Additional support for the previous formulation of **1** as a dihydrogen complex was provided by relaxation time data. Since no H−D coupling could be detected, it is necessary to reconsider the reported T_1 data for complex **1**. Halpern and co-workers have recently examined in detail the use of T_1 measurements to determine the structure of transition metal hydride and dihydrogen complexes.[5] It is clear from this work that all sources of relaxation, including relaxation due to metal nuclei which have high magnetogyric ratios (γ), must be taken into account. Since cobalt has a very high γ, protons directly bonded to cobalt are quite rapidly relaxed. In the case of complex **1**, assuming a dihydride structure with a Co−H distance of 1.55 Å and a H−Co−H angle of 80°, the calculated T_1 (min, 500 MHz) using the published solid state structure of **1** is *ca.* 97 ms.[9] Using this structural model, the proton relaxation is primarily due to the cobalt nuclear spin, with smaller contributions from the adjacent hydride, the ligand ^{31}P nuclei, and the ortho hydrogen atoms of the phenyl rings. Alternatively, a dihydrogen ligand bound to cobalt with an H−H distance of 0.90 Å is predicted to have a T_1(min) of ca. 7 ms, with the relaxation now dominated by H−H contributions.

The reported value for T_1(min) of 19 ms for complex **1** was measured at 203 K on a 300-MHz instrument. This value would

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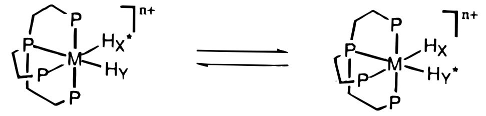
[16] Bianchini, C.; Laschi, F.; Peruzzini, M.; Ottaviani, F. M.; Vacca, A.; Zanello, P. *Inorg. Chem.* **1990**, *29*, 3394−3402

correspond to a T_1(min) of *ca.* 32 ms at 500 MHz.[5] At 226 K (500 MHz), we find a T_1(min) value of 95 ms for the hydride protons in **1** (see Figure 2). At all temperatures, the single hydride in **1**-d_1 gives a T_1 value about 10% greater than that observed for **1**. These results confirm that hydride−hydride interactions are a small contribution to relaxation.

Our measurements of the hydride T_1 in complex **1** are consistent with the dihydride formulation and are inconsistent with the formulation of complex **1** as a dihydrogen complex. These data combined with the lack of resolvable H−D coupling in **1**-d_1 and **2**-d_1 indicates conclusively that these species are correctly formulated as dihydride complexes. A similar conclusion has been recently communicated by Bianchini and co-workers.[17] The previously reported J_{H-D} values for **1** (18 Hz) and **2** (28 Hz) are now believed to result from misinterpretation of overlapping spectra arising from unusually large isotope effects on the chemical shift of the hydride resonance in **1**-d_1 and **2**-d_1. We now attribute these large chemical shift differences to isotopic perturbation of resonance (*vide infra*).

It is important to note that our observations of monodeuterated species require a mechanism for atom exchange. For example, we find that complex **1**-d_2 reacts quickly with H_2 gas to initially give a mixture of **1** and **1**-d_2, and then more slowly forms **1**-d_1. While we have not studied the mechanism of the latter reaction, we postulate that an intermolecular proton (deuteron) exchange process is facilitated by adventitious base (such as water).

Variable-Temperature NMR Observations. The octahedral dihydride structure of these complexes provides for two inequivalent hydride sites: one trans to the unique P atom of the tetradentate ligand, the other cis to the unique P atom. We therefore expect two resonances in the hydride region of the ^{1}H NMR spectrum. With the exception of the iridium complex, all complexes studied exhibit a single resonance for the hydride protons at ambient temperature, indicating a rapid dynamic process which interchanges the two hydride positions (eq 1). Low-temperature spectra showing the separate hydride resonances have been previously reported for M = Rh,[7] Ru,[18] and Os.[19]



(1)

In the case of the cobalt complex **1**, we observed only a single resonance in the hydride region of the ^{1}H NMR spectrum at ambient temperature, as noted above. Other than slight line broadening, the spectrum is unaffected by cooling the sample to 170 K. For the rhodium analog **2**, separate signals can be frozen out below 175 K in THF-d_8; at 160 K we observed two well-resolved doublets with a line width of 65 Hz at −4.93 (J_{HP} = −139 Hz) and −10.01 ppm (J_{HP} = −135 Hz). Using selective ^{31}P decoupling it was determined that the upfield resonance (H_X) is due to the proton trans to a terminal phosphorus atom (P_M), and the downfield resonance (H_Y) is due to the proton trans to the bridgehead phosphorus atom, P_A. The smaller coupling constants of each hydride to the phosphorus atoms cis to it could not be resolved. The sign of these two bond H−P couplings is presumed to be negative, based on the observations of Field and co-workers on closely related Rh complexes.[20] Our observations are consistent with those reported[7] by Bianchini *et al.*, but we have collected data at slightly lower temperatures and observe correspondingly reduced line widths.

At room temperature, we find that the ^{1}H NMR spectrum (hydride region) of the iridium dihydride complex (**3**) consists of two broad doublets centered at −7.62 and −12.55 ppm as reported by Bianchini.[15] At 260 K all couplings can be resolved to give two complex multiplets (Figure 4). The splitting pattern of the downfield resonance (due to the hydride trans to P_A) arises from a large trans coupling to the bridgehead phosphorus ($J_{H_YP_A}$ = −100 Hz) and equivalent couplings to the three terminal phosphorus atoms ($J_{H_YP_M} = J_{H_YP_Q}$ = +13.0 Hz). The upfield resonance (due to the hydride trans to P_M) shows a large doublet splitting due to coupling to the trans terminal phosphorus ($J_{H_XP_M}$ = −110 Hz), a smaller triplet splitting due to coupling to the two cis terminal phosphorus atoms P_Q ($J_{H_XP_Q}$ = +19.7 Hz), and a small doublet coupling to the cis bridgehead phosphorus ($J_{H_XP_A}$ = +8.3 Hz). The $J_{H_XH_Y}$ coupling constant accounts for the residual coupling of 3.6 Hz. A similar splitting pattern was reported in the low temperature spectrum of the osmium analog.[19]

Previous investigations of the ^{1}H NMR spectra of iron complex **4** were reported in deuterated toluene.[16] We find that by recording spectra in THF-d_8 we were able to freeze out the separate hydride signals at 170 K. They appear as two broad ($\nu_{1/2}$ = 160 Hz) resonances at −7.2 (H_Y) and −14.2 ppm (H_X). No H−P couplings could be resolved.

While the temperatures of coalescence vary depending upon the central metal, in all cases except M = Ir, the hydride resonances broaden and coalesce and at high temperature give a single resonance. The chemical shift of this resonance is found at the average of the chemical shifts for each proton (eq 2):

$$\delta_{HH} = {}^1/_2(\delta_{H_X} + \delta_{H_Y}) \tag{2}$$

The doublet of quartets splitting pattern at high temperature arises from coupling of the hydrides to one bridgehead and three terminal phosphorus atoms (in complex **2** a doublet of quintets is observed due to $J_{H-Rh} \approx J_{H-P_M}$). The value of the averaged coupling constant is described by eqs 3 and 4:

$$J_{doublet} = {}^1/_2(J_{H_XP_A} + J_{H_YP_A}) \tag{3}$$

$$J_{quartet} = {}^1/_6(J_{H_XP_M} + J_{H_XP_Q} + J_{H_XP_Q'} + J_{H_YP_M} + J_{H_YP_Q} + J_{H_YP_Q'}) \tag{4}$$

These equations were used to calculate those HP coupling constants that could not be resolved at low temperature (*vide infra*).

Isotopic Perturbation of Resonance. In all of the dihydride complexes where high-temperature averaged spectra have been reported, the signal due to the d_1 species is observed at substantially lower field than the corresponding signal for the d_0 species. This isotope effect is remarkable in both magnitude and direction, in that most known dihydrogen and polyhydride complexes exhibit *upfield* isotope shifts of modest magnitude upon partial deuteration.[21] Exceptions to this general trend are found in complexes where a rapidly established equilibrium between two different proton sites is perturbed by deuteration. This phenomenon is denoted isotopic perturbation of resonance

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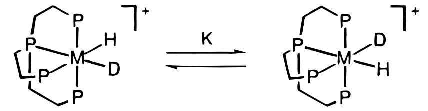
(21) Luo, X. L.; Crabtree, R. H. *J. Am. Chem. Soc.* **1990**, *112*, 4813−4821

Table 1. Isotope Shifts and Calculated Equilibrium Constants (300 K)

M	$\delta H_X - \delta H_Y$, ppm	$\Delta\delta$(300 K), ppb	K (300 K)
Co	~5(est)	200	1.17
Rh	5.08	193	1.16
Ir	4.93		
Fe	7.0	270	1.17

(IPR) and arises from non-statistical occupation of inequivalent proton sites.[22]



(5)

In the monodeuterated compound the deuterium atom has a site preference, which causes a perturbation of the equilibrium in eq 5. It can be shown that the magnitude of the isotope shift ($\delta_{\mathrm{HD}} - \delta_{\mathrm{HH}}$ or $\Delta\delta$) is dependent on both K and the difference in chemical shifts of the two hydrite sites according to eq 6:

$$\Delta\delta = \left[\frac{1-K}{2(K+1)}\right](\delta_X - \delta_Y) \qquad (6)$$

The chemical shift difference between H_X and H_Y has been determined for the Rh, Ir, Fe, Ru, and Os dihydride complexes and ranges from *ca.* 5 to 7 ppm. The separate hydride resonances could not be frozen out for $PP_3CoH_2^+$, but a chemical shift difference of *ca.* 5 ppm was assumed in order to calculate K_{eq}. Using selective ^{31}P decoupling it was determined that the downfield resonance in these complexes is due to the proton trans to the bridgehead phosphorus. Since the observed isotope shift upon deuteration is downfield, we conclude that deuterium concentrates in the site trans to the terminal phosphorus (labeled as H_X). No equilibrium constant was calculated for the Ir analog, since the fast exchange spectrum was not observed. The calculated values for K are tabulated in Table 1.

Isotopic Perturbation of Coupling. The non-statistical site preference which leads to deuterium concentration in the H_X site (trans to the terminal phosphorus) also leads to measurable perturbation of the averaged high-temperature H−P coupling constants. These effects are subtle, and careful measurement in well-resolved spectra is required. An example of this effect is the observation that J_{HP} increases from 3.7 Hz in **4** to 5.5 Hz in **4**-d_1 (see Figure 5).

A perturbation of the J_{HP} was also observed upon deuteration in rhodium complex **2**. At 300 K, the small H−P coupling in **2** is 13.5 Hz, which combined with the 14.7 Hz coupling to Rh gives rise to a pseudoquintet. In **2**-d_1 the small H−P coupling is reduced to 11.2 Hz; a doublet of quartets is observed (see Figure 3a). At 320 K the small H−P coupling in **2**-d_1 is 11.4 Hz. This can be quantified by use of eqs 7 and 8:

$$J_{\mathrm{doublet}} = \frac{J_{\mathrm{H_XP_A}} + K(J_{\mathrm{H_YP_A}})}{1+\mathrm{K}} \qquad (7)$$

$$J_{\mathrm{quartet}} = \frac{J_{\mathrm{H_XP_M}} + J_{\mathrm{H_XP_Q}} + J_{\mathrm{H_XP_{Q'}}} + K(J_{\mathrm{H_YP_M}} + J_{\mathrm{H_YP_Q}} + J_{\mathrm{H_YP_{Q'}}})}{3K+3} \qquad (8)$$

If $K = 1$, all couplings contribute equally to the averaged coupling observed at high temperature and eqs 6 and 7 reduce to eqs 3 and 4, respectively. For complex **2**, partial deuteration leads to $K = 1.16$, as determined from the IPR effects noted above. The corresponding isotopic perturbation of coupling causes a small change in the H−P coupling observed at high temperatures.

Table 2. Coupling Constants for the Dihydride Complexes[a]

M	$J_{\mathrm{H_XH_Y}}$	$J_{\mathrm{H_YP_A}}$	$J_{\mathrm{H_YP_M}}$	$J_{\mathrm{H_YP_Q}}$	$J_{\mathrm{H_XP_A}}$	$J_{\mathrm{H_XP_M}}$	$J_{\mathrm{H_XP_Q}}$
Fe	−5	−26.6			+19.3		
Ru	−3	**−71**	**+13**	**+20**	+11	**−70**	**+26**
Os[b]	**−5.2**	**−48.7**	**+14.6**	**+14.6**	**+5.6**	**−55.9**	**+28.2**
Rh	−5	**−139**	+16.7	+16.7	+6.0	**−136**	+2.2
Ir	**−3.6**	**−100**	**+13**	**+13**	**+8.3**	**−110**	**+19.7**

[a] Bold type indicates values obtained from experimental data; other values obtained from computer simulations. [b] Data from ref 19.

While the low-temperature spectra of complex **2** do not show any fine structure even at 160 K, the actual H−P couplings can be calculated from the above equations and the values of the $H-P_{\mathrm{trans}}$ couplings obtained from the low-temperature data. The only assumption made was that coupling of H_Y to all terminal phosphorus atoms was the same, as was found experimentally for the analogous Ir and Os species. The calculated couplings are shown in Table 2. The small values of the coupling constants are consistent with the line widths of the doublet resonances observed for complex **2** at 160 K ($\nu_{1/2}$ = 65 Hz).

The trans H−P coupling constants are presumed to have negative signs, based on results reported by Field and co-workers on closely related rhodium complexes.[20] Our results require that the relative signs of the cis and trans H−P couplings are opposite. The sign of the H−H coupling is believed to be negative, based on the results of a polarization transfer experiment reported for a rhodium dihydride complex.[23]

Mechanism of Hydride Permutation. All of the dihydride complexes of the form $[PP_3MH_2]^{n+}$ exhibit dynamic behavior, which leads to averaging on the NMR time scale of the two hydride environments and also renders equivalent the three terminal phosphorus atoms. We have studied in detail the rhodium complex **2.** For compound **2**, the coupling constants derived above were used to simulate spectra for various rates of exchange at 15 temperatures ranging from 170 to 300 K. The permutation matrix employed in the calculations permutes P_M with the two P_Q nuclei while also exchanging the positions of the hydride ligands. An Eyring plot of these data gives $\Delta H^‡ = 6.8 \pm 0.3$ kcal/mol and $\Delta S^‡ = -8 \pm 1$ eu, leading to $\Delta G^‡_{(300\mathrm{K})} = 9.2 \pm 0.5$ kcal/mol. The small negative entropy of activation and retention of H−P coupling at all temperatures is consistent with a degenerate *intramolecular* process.

We have made a similar study of PP_3RuH_2 including the low-temperature limiting spectrum, which we have obtained in THF-d_8 at 200 K. The rate constants obtained from simulated spectra in the range 200−300 K were used in an Eyring plot which gives $\Delta H^‡ = 10 \pm 0.5$ kcal/mol, $\Delta S^‡ = -2 \pm 2$ eu, and $\Delta G^‡_{(300\mathrm{K})} = 9.4 \pm 0.7$ kcal/mol. In the case of the iron complex PP_3FeH_2 (**4**), we have obtained very limited low-temperature data and are not able to extract all of the static couplings. From the available data, an approximate value of $\Delta G^‡_{(300\mathrm{K})} = 7.2$ kcal/mol for the hydride rearrangement process was obtained.

These activation energy values can be compared to $\Delta G^‡_{(300\mathrm{K})} = 12$ kcal/mol reported for the osmium analog PP_3OsH_2.[19] It can be concluded based on these data that the trend in activation energy is Os > Ru > Fe. Within the cobalt group a similar trend is observed (based on coalescence temperatures) with Ir

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(22) IPR has been invoked to explain the ^1H NMR spectra of partially deuterated iridium hydride complexes: Heinekey, D. M.; Oldham, W. J., Jr. *J. Am. Chem. Soc.* **1994**, *116*, 3137−3138.

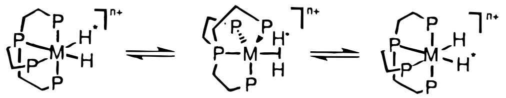
(23) Bowers, C. R.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1987**, *109*, 5541−5542.

> Rh > Co. While the nature of the central metal atom seems to be the primary factor determining the facility of these rearrangements, changes in the tetradentate ligand also have an effect. Field and co-workers report an activation energy of 15.3 kcal/mol for hydride site exchange in PP_3FeH_2 ($PP_3 = P(CH_2CH_2CH_2PMe_2)_3$).[24]

Hydride site exchange in complexes of the general type $H_2M(PR_3)_4$ has been the subject of extensive mechanistic study.[25] While the topology of the dynamic process is well understood, detailed understanding of the mechanism is limited. Based on permutational considerations, Muetterties and co-workers proposed mechanisms described as a tetrahedral jump or trigonal twist for various metal and ligand combinations.[25] Only recently has the possibility been considered that a dihydrogen species could be on the reaction coordinate. Studies by Berke and co-workers[26] of hydride site exchange in complexes of the form $Re(CO)(NO)H_2(PR_3)_2$ using a combination of experimental and computational methods suggest the intermediacy of a dihydrogen complex in this rearrangement.

In principle, mechanistic insight can be gained by measurement of the kinetic isotope effect upon replacement of hydride ligands with deuterium. To this end, we have studied carefully the $^1H\{^{31}P\}$ NMR spectra of mixtures of **2** and **2**-d_1. By inspection, the spectra in the temperature range 260−300 K show that the rearrangement is slightly faster for **2**. Simulation of the observed line shapes leads to $k_H/k_D = 1.3(1)$. Within experimental error, this isotope effect is temperature independent. This is the first report of a kinetic isotope effect in an intramolecular hydride rearrangement of this type. It should be noted that our measurement differs from other data on processes such as reductive elimination reactions, where a dideuteride is usually compared to a dihydride complex. In our case, we chose to examine a monodeuteride so that ^1H NMR spectra of both the dihydride and hydridodeuteride could be recorded in the same sample, eliminating systematic errors such as temperature variations. Had we been able to accurately measure the rate of rearrangement for the dideuteride in comparison to the dihydride complex, the KIE would have been larger.

The observation of a KIE for the rearrangement process suggests that the M−H interactions change significantly between the ground state and the transition state. Our observations can be put in context by noting that isotope effects for reductive elimination of hydrogen are generally modest, and in some cases inverse effects have been reported ($k_H/k_D < 1$).[27] A highly relevant comparison can be made to the observations reported by Hoff and co-workers, who found $k_H/k_D = 1.08 \pm 0.04$ for the conversion of a tungsten *dihydride* complex to the corresponding *dihydrogen* species.[28] Based on our observed KIE, we postulate that the rearrangement reaction in **2** may proceed *via* a transition state with some degree of H−H bonding. The tetradentate ligand system used here is known to stabilize five coordinate trigonal bipyramidal complexes,[29] so we suggest the mechanism outlined below:



This mechanism would require relatively little movement of the heavy atoms. Rapid rotation of the dihydrogen ligand would facilitate the exchange process. Some M−H bond breaking is required, so the observed trends in the activation energy for rearrangement are consistent with the reported observation that M−H bonds are stronger for the second- and third-row metals than for first-row metals.[30]

Conclusion

In contrast to previous reports, we find that the cationic complexes $[(PP_3)CoH_2]^+$ and $[(PP_3)RhH_2]^+$ are correctly formulated as dihydrides. The large isotope shifts in the ^1H NMR spectra observed upon deuteration have been quantitatively analyzed in terms of isotopic perturbation effects. A mechanism for the hydride rearrangement involving a transition state with substantial H−H interactions is proposed based on the observed kinetic isotope effect.

Experimental Section

All syntheses and chemical manipulations were conducted under Ar or N_2 using standard Schlenk and vacuum line techniques. Toluene, tetrahydrofuran, diethyl ether, pentane, and heptane were distilled from NaK/benzophenone; ethanol was distilled from magnesium (all under dry nitrogen). Distilled water, dimethylformamide, and acetone were purged with argon before use. Deuterated solvents were purchased from Cambridge Isotope Laboratories, degassed, and stored in Pyrex bulbs fitted with Kontes vacuum valves. Tetrahydrofuran-d_8 and benzene-d_6 were dried over NaK/benzophenone, and acetone-d_6 was dried over activated molecular sieves.

^1H NMR spectra were obtained on Bruker AC-200, AF-300, and WM-500 spectrometers. Chemical shifts were referenced against residual protio solvent and are reported in ppm relative to TMS. $^{31}P\{^1H\}$ NMR spectra were recorded on the Bruker AC-200 instrument at 81 MHz with chemical shifts relative to an external 85% H_3PO_4 standard. $^1H\{^{31}P\}$ spectra were recorded on the Bruker WM-500 instrument referenced to TMS. Variable-temperature $^1H\{^{31}P\}$ NMR experiments used a Bruker B-VT 1000 temperature controller with copper/constantan thermocouple. All temperatures were calibrated using the ^1H chemical shifts of methanol.[31] Simulations of NMR spectra were obtained on a Macintosh Quadra 900 using the Dynamac program.

$CoCl_2$ was obtained from Aldrich Chemicals, dried under vacuum at 180 °C for 24 h and stored under Ar. Et_3OPF_6, $NaBH_4$, PPh_3 (Aldrich), and $P(CH_2CH_2PPh_2)_3$ (Strem Chemicals) were used without further purification. $RhCl_3{\cdot}3H_2O$ was prepared from rhodium residues following the procedure of Anderson and co-workers.[32] $HB(Ar')_4{\cdot}(Et_2O)_2$,[33] $(PPh_3)_4RhH$,[14] PP_3CoH,[34] PP_3IrCl,[15] and PP_3FeH_2[16] were prepared following literature procedures.

In the six-coordinate complexes P_A indicates the bridgehead phosphorus, P_Q and $P_{Q'}$ the two axial PPh_2 groups, and P_M the equatorial PPh_2 group. The ^1H NMR spectra of all compounds studied are consistent with previously published data.

$[PP_3CoH_2]PF_6$ (1). PP_3CoH (30 mg, 0.041 mmol) was dissolved in 5 mL of diethyl ether to give a bright yellow solution. Dropwise addition of $HPF_6{\cdot}Et_2O$ (freshly prepared by stoichiometric reaction of ethanol with Et_3OPF_6) immediately affords a reddish brown precipitate.

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Addition of HPF_6 was continued until the supernatant was completely colorless. The supernatant was removed via cannula and the precipitate washed with 3 × 5 mL of diethyl ether, then dried in vacuo. Yield 95%.

$[PP_3CoHD]PF_6$ (1-d_1). An NMR tube was charged with 8 mg of $[PP_3CoH_2]PF_6$ and 0.5 mL of acetone-d_6. The frozen sample was put under D_2 (0.5 atm) and the NMR tube was then flame sealed. NMR spectra were acquired at $t = 0$, 7, 11, and 16 h. Prolonged exposure to D_2 combined with periodic replacement of the gas with fresh D_2 leads to complete deuteration of the hydride positions.

PP_3RhH. A solution of 250 mg (0.37 mmol) of PP_3 in 10 mL of warm toluene was added to a solution of 420 mg (0.36 mmol) of $(PPh_3)_4RhH$ in 40 mL of warm toluene. The resulting yellow solution was stirred at 90 °C for 5 h, then for 14 h at room temperature. Upon reduction in volume and cooling to −18 °C a yellow microcrystalline solid precipitated. The supernatant was removed by cannula, and the solid product washed with diethyl ether and pentane, then dried in vacuo. Yield 200 mg (72%).

$[PP_3RhH_2]BF_4$ (2). To a solution of 36 mg (0.046 mmol) of PP_3RhH in 5 mL of THF at 0 °C under H_2 atmosphere was added an excess (0.1 mL) of $HBF_4{\cdot}Et_2O$. Addition of 20 mL of ethanol, followed by cooling to −18 °C for 48 h affords complex **2** as colorless microcrystals. The supernatant was cannulated off and the product washed three times with cold diethyl ether and dried in vacuo. Yield: 30 mg (76%). Complex **2**-d_1 was prepared by exposure of **2** to D_2, as outlined above for the cobalt complex.

Synthesis of $[PP_3IrH_2]Cl$. To a bright yellow solution of 50 mg (0.056 mmol) of PP_3IrCl in 40 mL of ethanol and 10 mL of dimethylformamide was added 80 mg of solid $NaBH_4$. The solution was stirred overnight, turning pale yellow. The excess of $NaBH_4$ and any BH_4^- adduct formed were hydrolyzed by addition of 3 drops of concentrated HCl. NMR samples were obtained by evaporating 5 mL of the solution to dryness and redissolving the residue in THF-d_8. ^1H NMR (THF-d_8, 265K): δ 8.0 (br s, 12H, Ph); δ 7.50−6.70 (m, 18H, Ph); δ 3.55−2.75 (m, 12H, aliphatic); δ −7.62 (ddq, 1H, $J_{HP_A} = -100$ Hz, $J_{HP_M} = J_{HP_Q} = +13.0$ Hz, $J_{H_XH_Y} = +3.6$ Hz, Ir−H_Y); δ −12.55 (dddt, 1H, $J_{HP_A} = 8.3$ Hz, $J_{HP_M} = -110$ Hz, $J_{HP_Q} = +19.7$ Hz, $J_{H_XH_Y} = +3.6$, Ir−H_X).

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