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Cationic Dihydrogen Complexes of Rhodium and Cobalt: A Reinvestigation

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Since the initial discovery of Kubas and co-workers,[3] transition metal dihydrogen complexes have become the focus of intensive research activity.[4] While a large number of isolable complexes have been reported, definitive structural characterization data have been reported in only a few cases. The difficulty of structural characterization in the absence of neutron diffraction data has been described by Kubas.[5] Indirect spectroscopic methods have been developed, principally based on the measurements of ^1H relaxation rates (T_1 data)[6] or the measurement of J_{H-D} in partially deuterated samples. While the quantitative predictive power with respect to H-H distance of the T_1 method has been questioned,[7] 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.[8]

The majority of the currently reported *isolable* dihydrogen complexes have phosphine coligands. A less obvious indicator of the presence of a dihydrogen ligand can be inferred from a study of the reported ^1H NMR data. Specifically, the observed coupling $^2J_{H-P}$ in dihydrogen complexes is generally less than 10 Hz and is often not resolvable.[9] For metal *hydride* complexes of similar structure, significantly larger values of $^2J_{H-P}$ have generally been reported. These comparisons are necessarily somewhat imprecise, since exactly analogous structures generally cannot be compared.

In 1987, Bianchini and co-workers[10] reported a novel cationic dihydrogen complex of rhodium, formulated as $(PP_3)Rh(H_2)^+$ (**1**; $PP_3 = P(CH_2CH_2PPh_2)_3$). The cobalt analog $(PP_3)Co(H_2)^+$ (**2**) was reported in 1988.[11] In both cases, the dihydrogen formulation was primarily based on the observation of substantial H-D coupling in partially deuterated samples (J_{H-D} = 18 Hz for **1**; J_{H-D} = 28 Hz for **2**). Short T_1 values for the hydride ligands in complex **2** were also reported in support of the dihydrogen formulation. In contrast to the general trend of small couplings to phosphine coligands in dihydrogen complexes noted above, complexes **1** and **2** exhibit substantial values of J_{H-P} (67 Hz for **1**; 27-31 Hz for **2**). In the case of the complex **1**, 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 **1** are consistent with a dihydride structure in the solid state, but complex **2** 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.[12]

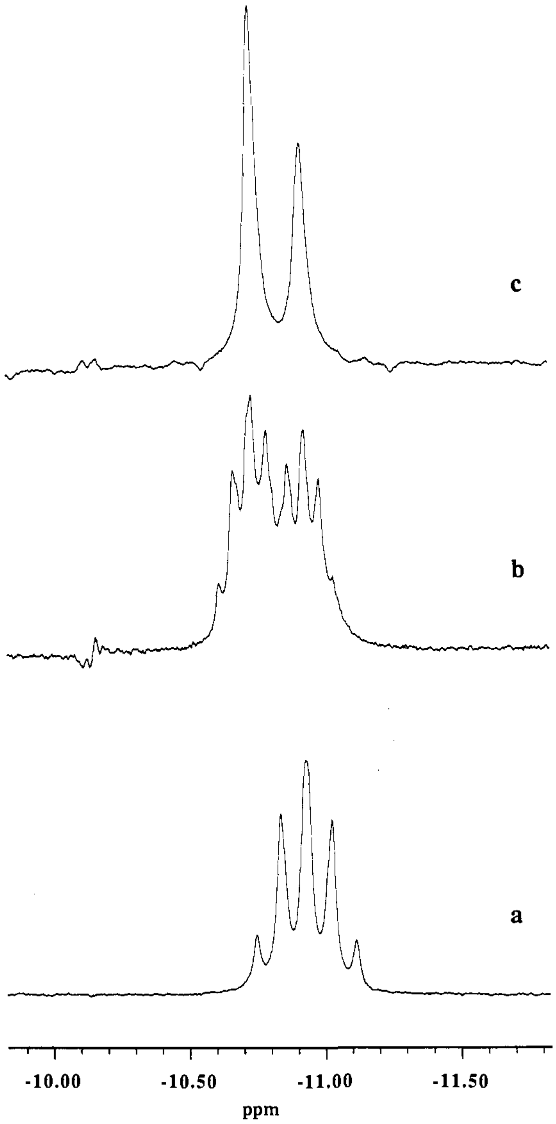

Figure 1. (a) Partial ^1H NMR spectrum (hydride region) of complex **2** (300 MHz, 298 K) in acetone-d_6. (b) After exposure to D_2 (1 atm) for 11 h (500 MHz). (c) $^1H\{^{31}P\}$ spectrum (500 MHz).

We now report the outcome of further investigations of the ^1H and $^1H\{^{31}P\}$ NMR spectra of complexes **1** and **2**. In both cases, partially deuterated samples have been examined. We find no evidence for the reported H-D coupling. In the case of complex **2**, a sample was prepared according to the published method (PF_6^- salt), and the ^1H NMR was recorded in acetone-d_6. The observed spectrum in the hydride region consists of a five line pattern centered at δ -10.93 ppm, in good agreement with the published data (see Figure 1). Exposure of this sample to

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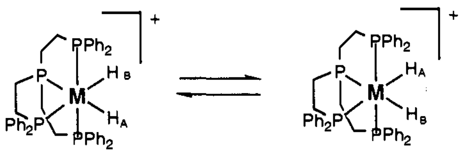
deuterium gas leads to the observation of a new signal at δ −10.73 ppm, which we attribute to **2**-d_1, generated by H_2/D_2 exchange. The appearance of signals due to H_2 and HD gas was also noted.[13] The resonance attributed to **2**-d_1 continues to grow over time. While there is no obvious indication of H–D coupling in the resonance due to **2**-d_1, the signal is complex due to coupling to ^{31}P. A ^{1}H{^{31}P} NMR spectrum was recorded in order to clarify the situation (see Figure 1). There is clearly no H–D coupling. The line width of the resonance due to **2**-d_1 is *ca.* 14 Hz and is slightly narrower than the hydride resonance due to **2**, due to relaxation effects discussed below.

Since no H–D coupling could be detected, it is necessary to reconsider the reported T_1 data for complex **2**. 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.[7] 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 **2**, 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 (minimum, 500 MHz) using the published solid state structure of **2** is *ca.* 97 ms. 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. The reported value for T_1 (minimum) of 19 ms for complex **2** was measured at 203 K on a 300 MHz instrument.[11] This value would correspond to a T_1 (minimum) of *ca.* 32 ms at 500 MHz. Our measurements of the hydride T_1 in **2** are consistent with the dihydride formulation. At 226 K (500 MHz), we find a T_1 (minimum) value of 95 ms for the hydride protons in **2**. At all temperatures, the single hydride in **2**-d_1 gives a T_1 value about 10% greater than that observed for **2**. These results confirm that hydride–hydride interactions are a small contribution to relaxation.

As noted above, the hydride resonance due to **2**-d_1 is observed at substantially lower field than the corresponding signal for **2**. 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.[14] The only 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 (IPR) and arises from nonstatistical occupation of inequivalent proton sites.[15] In the case of complex **2** and related molecules, a dihydride structure does provide for two inequivalent hydride sites, one trans to the unique P atom of the tetradentate ligand and the other cis to the unique P (eq 1). A rapid dynamic process permutes these two protons, leading to a single resonance at ambient temperature. A very similar explanation for a substantial downfield isotope effect was advanced by Bianchini and co-workers to explain the ^{1}H NMR spectrum of the neutral iron analog of **2**, $(PP_3)FeH_2$, which is a *dihydride*.[16] We have attempted to obtain evidence for two different hydride environments in complex **2** from low-temperature ^{1}H{^{31}P} NMR spectroscopy, but only a single resonance was observed at all accessible temperatures. In the course of these studies, we noted that the chemical shift difference between **2** and **2**-d_1 is dependent upon the temperature of observation, increasing from 200 ppb at 298 K to 300 ppb at 190 K. This is further confirmation that the isotope effect observed here is a manifestation of IPR.



(1)

In the case of the rhodium complex $(PP_3)Rh(H_2)^+$ (**1**), we have obtained very similar results. The ^{1}H{^{31}P} NMR spectrum of a mixture of **1** and **1**-d_1 exhibits two doublet resonances (the doublet pattern is due to coupling to ^{103}Rh; $^1J_{H-Rh}$ = 14 Hz) with no evidence of H–D coupling in the signal due to **1**-d_1. A downfield isotope shift of 0.25 ppm (250 ppb) is observed.

We conclude on the basis of the absence of H–D coupling in **1**-d_1 and **2**-d_1 that complexes **1** and **2** in solution exhibit an approximately octahedral *dihydride* structure. In the previous studies of Bianchini and co-workers, partially deuterated samples of these complexes were generated by the reaction of neutral monohydride precursors with D^+.[10,11] Under these conditions, it is reasonable to expect that samples of **1**-d_1 and **2**-d_1 would result. In fact, due to *intermolecular* proton (deuteron) exchange, a statistical mixture of d_0, d_1, and d_2 species (1:2:1) is rapidly formed. The latter is not observable by proton NMR spectroscopy, but a 1:2 mixture of d_0 and d_1 species will give two complex resonances *of equal intensity* separated by the small chemical shift differences arising from IPR that were noted above. While the spectra reported here were recorded at 500 MHz, the original reports of the NMR spectra of **1** and **2** indicate that the spectra were recorded at 80 and 300 MHz, respectively. At these lower fields, the overlap of resonances due to d_0 and d_1 species leads to a complex signal with multiplet structure that is easily misinterpreted.

Our interpretation of the solution NMR results is consistent with the dihydride structure reported for **1** in the solid state.[10] As noted above, the solid state structure of complex **2** is reported to depend upon the nature of the counteranion.[12] The PF_6^- salt (the complex studied here) is reported to adopt an approximately trigonal bipyramidal structure with a dihydrogen ligand. The possibility that complex **2** could have a quite different structure in solution and in the solid state remains intriguing.

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(13) It is of interest to note that simple exchange of H_2 for D_2 would lead only to loss of **2** and generation of **2**-d_2. The observation of **2**-d_1 implies that some pathway operates which allows for proton (deuteron) exchange. We propose that this reaction involves deprotonation of **2** via adventitious base present in the solution.

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