

Cationic Dihydrogen/Dihydride Complexes of Osmium: Structure and Dynamics

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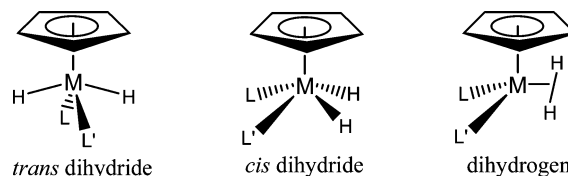
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Reaction of Cp*Os(CO)₂Cl with [Et₃Si][BAR^F₄] under hydrogen gas affords the cationic hydrogen complex [Cp*Os(CO)₂(H₂)] [BAR^F₄] (**1**) (Cp* = C₅Me₅; Ar^F = C₆F₅). When this reaction is carried out with HD gas, complex **1-d**₁ results, with *J*_{HD} = 24.5 Hz. When solutions of complex **1** are monitored by ¹H NMR spectroscopy over several days, the gradual formation of a *trans* dihydride species is observed. Similarly, reaction of CpOs(dppm)Br with Na[BAR^F₄] (Ar^F* = 3,5-(CF₃)₂C₆H₃) under hydrogen affords the cationic dihydride complex [CpOs(dppm)H₂][BAR^F₄] (**2**). At 295 K, complex **2** exists as a 10:1 mixture of *cis* and *trans* isomers. The ¹H NMR spectrum of the *cis* form in the hydride region exhibits a triplet with *J*_{HP} = 6.5 Hz, due to rapid exchange of the hydrogen atoms. At low temperature, static spectra of the HH'PP' spin system can be obtained, revealing quantum mechanical exchange coupling between the two hydride ligands. The observed *J*_{HH'} is temperature dependent, varying from 133 Hz at 141 K to 176 Hz at 198 K. This is the first report of detectable exchange coupling between pairs of chemically equivalent hydrogen atoms.

Following the seminal work of Kubas and co-workers in 1984,¹ the coordination chemistry of dihydrogen developed very rapidly into an active field of study.² Bound dihydrogen exhibits great variability in structure and reactivity, along with interesting dynamic behavior. The key structural parameter is the distance between the two hydrogen atoms, designated as *d*_{HH}. Complexes with *d*_{HH} < 1.0 Å are usually considered to be complexes of dihydrogen, while complexes with *d*_{HH} > 1.5 Å are regarded as conventional dihydride complexes. Molecules with intermediate *d*_{HH} values have been variously termed elongated dihydrogen complexes or compressed dihydride complexes. There are now several examples of such complexes exhibiting novel structures and dynamic behavior, including temperature-dependent structures.³ Particularly interesting is the cationic Ru complex [Cp*Ru(dppm)(H₂)]⁺, in which the unusual isotope-dependent structure⁴ is attributed to a very soft, anharmonic potential energy surface for the Ru–H and H–H interactions.⁵ This Ru complex is one representative of an extensive set of cationic complexes of the form [Cp/Cp*RuLL'(H₂)]⁺, which exhibit a wide range of *d*_{HH} values. The observed *d*_{HH} seems to depend

upon the steric and electronic contributions of L and L'.⁶ Many of the Ru complexes also exhibit equilibria between dihydrogen and *trans* dihydride structures (below). In spite of extensive studies, it remains very difficult to predict which of several possible structures of similar energy will be adopted by these molecules.



Preparation of Os analogues of these Ru complexes has been less explored. In general, the dihydride structures are more accessible for Os. There is limited evidence for bound dihydrogen in this type of osmium complex. Reaction of Cp*Os(CO)₂H with triflic acid was reported to afford a cationic species initially thought to be a dihydride.⁷ Subsequently, studies of relaxation times were interpreted in terms of an equilibrium between dihydrogen and dihydride forms.⁸

Similarly, Jia and co-workers have reported the preparation and properties of [CpOs(dppm)H₂]⁺ (dppm = bis-diphenylphosphinomethane).⁹ In this complex, both *cis* and *trans* dihydride isomers were observed, with the *cis* form predominating. The suggestion of a *cis* dihydride structure is novel, in that such a structure has never been observed for Ru. This structural

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proposal was based on the relatively long value of the minimum spin lattice relaxation time $T_{1(\text{min})}$ and the low observed value of J_{HD} in the HD derivative ($^1J_{\text{HD}} = 3$ Hz). Averaging of $^2J_{\text{HP}}$ couplings at the lowest reported temperature suggests that there is a rapid dynamic process that interchanges the two hydrogen atoms.

We now report new synthetic approaches to the preparation of $[\text{Cp}^*\text{Os}(\text{CO})_2(\text{H}_2)]^+$ and $[\text{CpOs}(\text{dppm})\text{H}_2]^+$. Further investigation of the structure of $[\text{Cp}^*\text{Os}(\text{CO})_2(\text{H}_2)]^+$ gives new insight into the equilibrium between the dihydrogen and dihydride forms of this complex. Using very low-temperature ^1H NMR, the dynamic behavior of $[\text{CpOs}(\text{dppm})\text{H}_2]^+$ has been investigated, revealing quantum mechanical exchange coupling (QMEC) between the hydrides in the *cis* isomer. This is the first reported example of QMEC between two chemically equivalent but magnetically inequivalent hydrogen atoms.

Experimental Section

All complexes were prepared using standard Schlenk techniques under argon. NMR spectra were obtained at 500 MHz on a Bruker Avance DRX series spectrometer. Spin lattice relaxation times (T_1) as a function of temperature were measured using a standard inversion recovery pulse sequence. $\text{CDFCl}_2/\text{CDF}_2\text{Cl}$ mixtures were prepared by the method of Siegel and Anet.¹⁰ NMR spectra were simulated using gNMR 4.1 (Ivorysoft). $\text{Cp}^*\text{Os}(\text{CO})_2\text{H}$ was prepared as previously reported.¹¹

$\text{Cp}^*\text{Os}(\text{CO})_2\text{Cl}$. $\text{Cp}^*\text{Os}(\text{CO})_2\text{H}$ was dissolved in CCl_4 at room temperature. $\text{Cp}^*\text{Os}(\text{CO})_2\text{Cl}$ formed cleanly in >95% yield. $\text{Cp}^*\text{Os}(\text{CO})_2\text{Cl}$ is a light yellow air-stable solid. IR (CH_2Cl_2): 2016 (s), 1956 (s) cm^{-1} . ^1H NMR (CD_2Cl_2): δ 2.01 (s, C_5Me_5).

$[\text{Cp}^*\text{Os}(\text{CO})_2(\text{H}_2)]/[\text{Cp}^*\text{Os}(\text{CO})_2\text{H}_2][\text{BAR}^{\text{F}}_4]$ (1). A J. Young NMR tube was charged with $[\text{Et}_3\text{Si}][\text{BAR}^{\text{F}}_4]$ prepared from $[\text{Ph}_3\text{C}][\text{BAR}^{\text{F}}_4]$ (20 mg, 25 μmol) and excess Et_3SiH .¹² To this was added $\text{Cp}^*\text{Os}(\text{CO})_2\text{Cl}$ (5 mg, 12 μmol). CD_2Cl_2 was added by vacuum transfer. The head space was filled with H_2 and kept frozen with liquid N_2 until just before the first NMR spectrum was acquired. ^1H NMR (CD_2Cl_2): δ 2.42 (s, Cp^* , $\text{Os}(\text{H}_2)$), 2.35 (s, Cp^* , *trans*- OsH_2), -7.61 (s, $\text{Os}(\text{H}_2)$), -10.05 (s, *trans*- OsH_2). T_1 (ms, *trans*- OsH_2): 2900 (156 K), 2700 (161 K), 2900 (166 K), 3100 (171 K), 3500 (177 K), 3900 (182 K); (ms, $\text{Os}(\text{H}_2)$): 29 (156 K), 26 (161 K), 25 (166 K), 25 (171 K), 27 (177 K), 29 (182 K), 35 (192 K), 56 (218 K).

$[\text{CpOs}(\text{dppm})\text{H}_2][\text{BAR}^{\text{F}}_4]$ (2). A J. Young NMR tube was charged with $\text{CpOs}(\text{dppm})\text{Br}$ (4.4 mg, 6.1 μmol)^{9,13} and $\text{Na}[\text{BAR}^{\text{F}}_4]$ (6.3 mg, 7.0 μmol).¹⁴ CD_2Cl_2 was added via vacuum transfer, and the head space was backfilled with H_2 gas. Complete formation of $[\text{CpOs}(\text{dppm})\text{H}_2][\text{BAR}^{\text{F}}_4]$ took several days. CD_2Cl_2 was replaced with a mixture of CDCl_2F and CDCIF_2 for low-temperature experiments. ^1H NMR spectrum (CD_2Cl_2 , hydride region, 295 K): δ -10.50 (t, $J_{\text{HP}} = 32$ Hz, H_2), -11.33 (t, $J_{\text{HP}} = 6.5$ Hz, H_2). T_1 (ms, *trans*- OsH_2): 2540 (166 K), 1400 (171 K), 1280 (177 K), 1120 (187 K), 1080 (198 K), 1150 (208 K), 1110 (218 K), 1220 (223 K), (ms, *cis*- OsH_2), 480 (171 K), 415 (177 K), 319 (187 K), 271 (198 K), 248 (208 K), 240 (218 K), 243 (223 K).

Results

Synthesis and Characterization of $[\text{Cp}^*\text{Os}(\text{CO})_2(\text{H}_2)]^+$ (1) and $[\text{CpOs}(\text{dppm})\text{H}_2]^+$ (2). $\text{Cp}^*\text{Os}(\text{CO})_2\text{Cl}$ was prepared by

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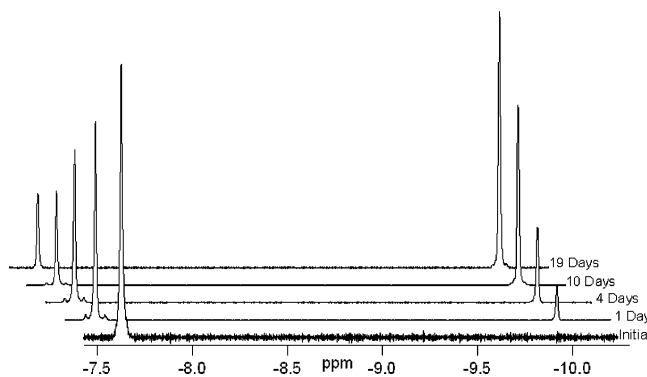


Figure 1. Hydride region of the ^1H NMR spectrum of complex **1** as a function of time.

reaction of $\text{Cp}^*\text{Os}(\text{CO})_2\text{H}$ with CCl_4 . This is more convenient than the previously reported preparation from $\text{Cp}^*\text{Os}(\eta^4\text{-COD})\text{-Cl}$.¹⁵ Reaction of $\text{Cp}^*\text{Os}(\text{CO})_2\text{Cl}$ with $[\text{Et}_3\text{Si}][\text{BAR}^{\text{F}}_4]$ in methylene chloride under 1 atm of hydrogen gas affords the hydrogen complex $[\text{Cp}^*\text{Os}(\text{CO})_2(\text{H}_2)][\text{BAR}^{\text{F}}_4]$ (**1**) ($\text{Ar}^{\text{F}} = \text{C}_6\text{F}_5$). In the hydride region of the ^1H NMR spectrum, complex **1** exhibits a single resonance at -7.61 ppm. The T_1 of this resonance was measured as a function of temperature using an inversion recovery sequence. The maximum rate of relaxation ($T_{1(\text{min})}$) is 24 ms at 180 K (500 MHz). When the preparative reaction was carried out under HD gas, a mixture of **1** and **1-d**₁ was obtained. The resonance due to **1-d**₁ exhibits $J_{\text{HD}} = 24.5$ Hz.

Reaction of $\text{CpOs}(\text{dppm})\text{Br}$ in methylene chloride with $\text{Na}[\text{BAR}^{\text{F}}_4]$ under H_2 gas (1 atm) over the course of 3 days affords $[\text{CpOs}(\text{dppm})\text{H}_2][\text{BAR}^{\text{F}}_4]$ (**2**) ($\text{Ar}^{\text{F}} = 3,5\text{-(CF}_3)_2\text{C}_6\text{H}_3$). Complex **2** was characterized by ^1H and ^{31}P NMR spectroscopy and by measurement of the $T_{1(\text{min})}$, which is consistent with the previous observations of Jia and co-workers.⁹

Isomerization of Complex 1. At 295 K, samples of **1** in methylene chloride slowly isomerize to give a new hydride resonance at -10.05 ppm. The minimum relaxation time T_1 of this signal is 2700 ms, and it is assigned to the *trans* dihydride complex. Over the course of several days, equilibrium is reached with a dihydride:dihydrogen ratio of 3.5:1 (Figure 1). The rate of approach to equilibrium exhibited considerable variability across samples (see Discussion).

Low-Temperature ^1H NMR Spectroscopy of Complex 2. In CD_2Cl_2 , the ^1H NMR spectrum of complex **2** in the hydride region consists of two triplet resonances in the ratio of 10:1 at -11.3 ppm ($J_{\text{PH}} = 6.5$ Hz) and -10.6 ppm ($J_{\text{PH}} = 32$ Hz). The major resonance is assigned to the *cis* dihydride complex based on the prior observations of Jia and co-workers.⁸

The ^1H NMR spectrum of complex **2** in the hydride region has now been examined at lower temperature using $\text{CDFCl}_2/\text{CDF}_2\text{Cl}$ mixtures. The resonance due to **2-cis** obtained at 187 K is shown in Figure 2. The fitting of the observed spectra to the calculated spectra is described in the Discussion section.

The observed value of J_{HH} is dependent on the observation temperature, varying from 133 Hz at 141 K to 176 Hz at 198 K. Simulations of spectra were carried out using $J_{\text{PP}} = 70$ Hz, $J_{\text{PH}} = \pm 12$, $\kappa = 25$ Hz, and fitting for J_{HH} . The HH coupling cannot be determined above 198 K due to the onset of rapid hydride ligand permutation, which leads to line broadening.

Discussion

Preparation and Isomerization of Complex 1. Complex **1** was previously prepared by protonation of $\text{Cp}^*\text{Os}(\text{CO})_2\text{H}$ with

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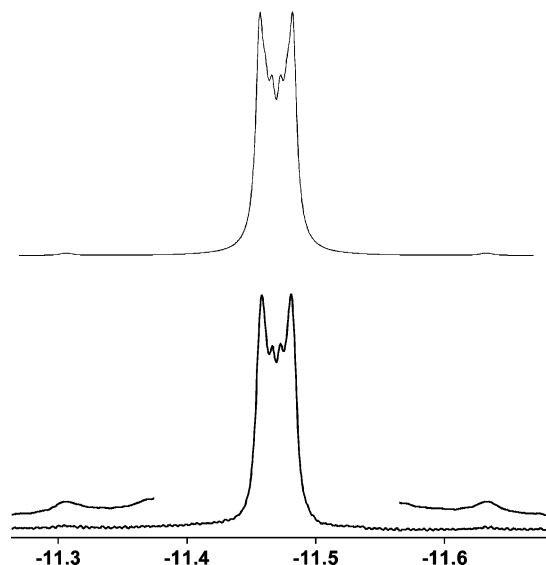
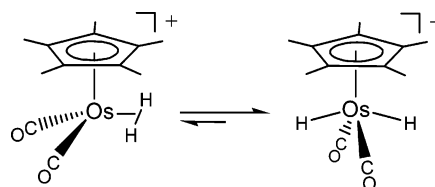


Figure 2. Partial ^1H NMR spectrum of complex **2-cis** at 187 K in $\text{CDFCl}_2/\text{CDF}_2\text{Cl}$. Bottom: Experimental spectrum, inset with 3 Hz line broadening. Top: Calculated spectrum with $J_{\text{PP}} = 70$ Hz, $J_{\text{PH}} = \pm 12$, $\kappa = 25$ Hz, $J_{\text{HH}} = 148$ Hz, and hydride permutation at 5 s^{-1} .

triflic acid.⁷ On the basis of T_1 data, a hydridic resonance at -7.6 ppm was attributed to the dihydrogen form of **1**. This assignment was complicated by a proton exchange process between the highly acidic complex **1** and triflate. We have now prepared complex **1** directly from hydrogen gas, which allows for an unambiguous determination of the structure. The resonance at -7.6 ppm exhibits a $T_{1(\text{min})}$ value of 24 ms at 180 K (500 MHz). Using the method of Halpern and co-workers,¹⁶ this value corresponds to $d_{\text{HH}} = 1.1$ Å, suggestive of a moderately elongated dihydrogen complex. This is confirmed by the preparation of **1-d₁** (from HD gas), which exhibits $J_{\text{HD}} = 24.5$ Hz. On the basis of the correlation between HD coupling and d_{HH} , this coupling is consistent with $d_{\text{HH}} = 1.02$ Å.¹⁷ The two methods of determination of d_{HH} are reasonably consistent, and the presence of a dihydrogen ligand in complex **1** is confirmed. This value of d_{HH} can be compared to the previously reported ruthenium analogue, $[\text{Cp}^*\text{Ru}(\text{CO})_2(\text{H}_2)]^+$, which exhibits $J_{\text{HD}} = 32$ Hz, consistent with a somewhat shorter d_{HH} of 0.89 Å.¹⁸ While this ruthenium complex is quite labile to loss of H_2 , complex **1** is stable at room temperature in the absence of oxygen and water.

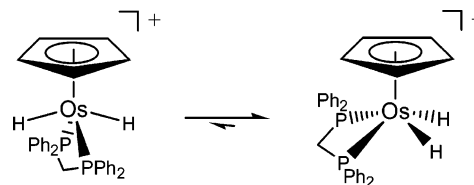
While the dihydrogen form of complex **1** is formed initially when hydrogen gas binds to the metal center, monitoring by ^1H NMR spectroscopy at room temperature reveals a slow isomerization to an equilibrium mixture of dihydrogen complex and a new species, which exhibits a resonance at -10.0 ppm (Figure 1). The $T_{1(\text{min})}$ for this resonance is observed to be 2700 ms at 161 K (500 MHz), consistent with assignment as a *trans* dihydride complex.¹⁹ At equilibrium, the *trans* dihydride form of complex **1** is slightly favored, with a dihydride: dihydrogen ratio of 3.5:1 at 295 K. This situation is directly

analogous to the previously reported study of $[\text{CpRu}(\text{dmpe})(\text{H}_2)]^+$, where protonation of the corresponding neutral hydride at low temperature gives exclusively the dihydrogen complex as a kinetic product, which then undergoes isomerization to an equilibrium mixture in which the dihydrogen form remains predominant.²⁰



While several cationic ruthenium dihydrogen complexes of the general form $[\text{Cp}/\text{Cp}^*\text{RuL}_2(\text{H}_2)]^+$ are known, the observation of a significant concentration of dihydrogen complex at equilibrium rather than a dihydride is unusual for osmium.² We attribute this to the relatively electron-deficient metal center resulting from the presence of two carbonyl ligands. Attempts to quantify the rate of approach to equilibrium were frustrated by a lack of reproducibility from sample to sample. The previous studies of complex **1** by Bullock and co-workers noted facile interconversion of the dihydrogen and dihydride forms, sufficiently rapid to cause T_1 averaging.⁸ This isomerization likely proceeds via rapid proton exchange possibly mediated by the presence of triflate. When complex **1** is prepared directly from hydrogen using an unreactive anion, isomerization is slowed by approximately 6 orders of magnitude. Our observations of somewhat irreproducible rates of isomerization are consistent with the presence of small, variable amounts of basic impurities such as water, which can provide a pathway to facilitate isomerization via reversible proton transfer from **1**. The observed isomerization reaction may be consistent with a minor protonation pathway that leads directly from $\text{Cp}^*\text{Os}(\text{CO})_2\text{H}$ to the *trans* dihydride complex. Alternatively, the isomerization could be a strictly intramolecular process, as reported²⁰ for $[\text{CpRu}(\text{dmpe})(\text{H}_2)]^+$. The latter possibility seems less likely, since it is not clear why such an intramolecular process would be accelerated by the presence of triflate.

Structure and Dynamic Behavior of Complex 2. In contrast to **1**, phosphine donors in complexes such as $[\text{CpOs}(\text{dppm})(\text{H}_2)]^+$ (**2**) lead to a dihydride structure. Complex **2** was previously studied by Jia and co-workers, who observed the occurrence of *cis* and *trans* forms of this complex, with the former predominant. Apparently due to geometric constraints, the dppm ligand disfavors the formation of the *trans* dihydride structure, so complex **2** adopts a very unusual *cis* dihydride structure. In contrast, the direct ruthenium analogue $[\text{CpRu}(\text{dppm})(\text{H}_2)]^+$ is a dihydrogen complex, with no observed dihydride form.²¹



Consistent with the observations reported by Jia and co-workers, we find that the $T_{1(\text{min})}$ value for the hydride resonance due to the *cis* form of complex **2** is 240 ms at 218 K (500 MHz). Application of the method of Halpern and co-workers¹⁶ gives

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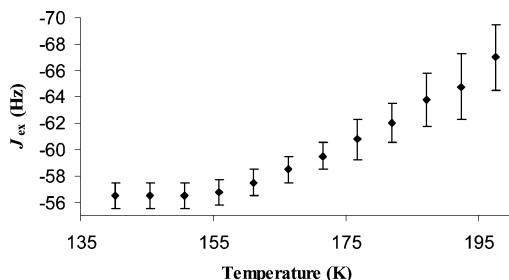


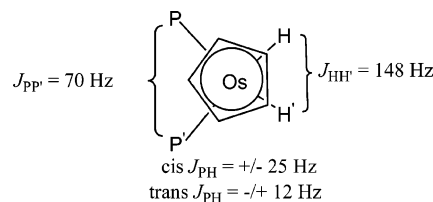
Figure 3. Exchange coupling (J_{ex}) in complex **2** as a function of temperature. Errors in J values increase with temperature due to line broadening caused by the onset of thermal exchange.

an HH distance of 1.6 Å. This is similar to the distance derived¹⁷ from T_1 data for the related *dicationic* Ir complex $[\text{Cp}^*\text{Ir}(\text{dmpm})\text{H}_2]^{2+}$. This Ir dihydride has $J_{\text{HD}} = 7.5\text{--}9$ Hz, consistent with the relaxation time data. In the case of complex **2**, the observed J_{HD} of 3.0 Hz corresponds to an HH distance of ca. 1.8 Å, inconsistent with the HH distance derived from the relaxation time data. While the correlation between HD coupling and HH distance seems to be quite reliable for shorter HH distances, this inconsistency demonstrates that this correlation may become unreliable at very long HH distances. For these structures, the coupling is dominated by two bond terms that depend upon the identity of the metal and the bond angles. For molecules of this type, the HH distance is best defined by relaxation time measurements.

Jia and co-workers studied the ^1H NMR spectrum of **2** in methylene chloride at various temperatures down to 190 K and reported that the triplet resonance due to **2-cis** became a poorly resolved broad resonance at low temperature.²² As noted by Jia and co-workers, the single triplet hydride resonance of the *cis* structure is suggestive of a dynamic process that rapidly interchanges the two hydride environments. In the absence of such a process, the hydride resonance for **2-cis** should be quite complex, since the two hydrides are magnetically inequivalent, with the spin system corresponding to $\text{HH}'\text{PP}'$. Alternatively, the same triplet spectrum can be obtained if there is a very large coupling J_{HH} between the two hydride nuclei. Such large couplings are attributed to the operation of quantum mechanical exchange coupling (QMEC). QMEC has been observed in a number of transition metal polyhydride complexes. The previous studies have been summarized in an excellent review article.²³

We have found that by recording the ^1H NMR spectrum at very low temperature in Freon solvents, it is possible to obtain well-resolved static spectra. A typical low-temperature spectrum is shown in Figure 2. Input of the HP, HH, and PP couplings in this species allows for the calculation of the appearance of the low-temperature spectrum. The HH coupling can be estimated from the reported value of $J_{\text{HD}} = 3.0$ Hz for **2-d₁**. Since $\gamma_{\text{H}}/\gamma_{\text{D}} = 6.514$, the expected value of J_{HH} is approximately 19.5 Hz. Based on previously reported dppm complexes, J_{PP} will be approximately 70 Hz. The two values for the *cis* and *trans* HP couplings are more difficult to estimate. It is known that *cis* and *trans* HP couplings in four-legged piano stool complexes of this type are opposite in sign.²⁴ In the case of complex **2**, the observed averaged HP coupling is 6.5 Hz, suggesting that the difference between the *cis* and *trans*

couplings must be 13 Hz. The observed low-temperature ^1H NMR spectrum for complex **2-cis** in the hydride region can be simulated using HP couplings of 25 and 12 Hz (with opposite sign), along with $J_{\text{PP}} = 70$ Hz. The anticipated $J_{\text{HH}'}$ value of 19.5 Hz does not give a satisfactory simulation. A J_{HH} value of 148 Hz is required to fit the spectrum (Figure 2). The outer wings in the spectrum shown in Figure 2 are broader than expected. This line broadening can be fit by adding hydride permutation at 5 s^{-1} to the simulation.



The fact that the observed value of $J_{\text{HH}'}$ greatly exceeds the expected value suggests that QMEC is operative here. Further evidence for this is provided by the observation that $J_{\text{HH}'}$ is highly temperature dependent, ranging from 133 Hz at 140 K to 176 Hz at 198 K. For two hydride ligands bonded to a metal center, if each H atom is strongly localized in its respective potential energy well, then the vibrational motions of each can be treated independently. In some cases, with relatively short HH distances d_{HH} and soft potential energy surfaces, the orbital wave functions may overlap. The vibrational motions of the two atoms can no longer be treated independently. This overlap gives rise to symmetric and antisymmetric combinations of the two single particle wave functions, which differ in energy by $2J_{ex}$, where J_{ex} is the exchange coupling. This interaction is manifest in the ^1H NMR spectra in combination with the magnetic component of the coupling according to $J_{\text{obs}} = J_{\text{mag}} - 2J_{ex}$, where J_{mag} is the contribution to the overall observed coupling J_{obs} due to the Fermi contact term. This term can be evaluated by noting as mentioned above that $J_{\text{HD}} = 3.0$ Hz, so the magnetic contribution to the observed HH coupling must be 19.5 Hz. In previous studies of related four-legged piano stool complexes $[\text{CpIr}(\text{PR}_3)_3\text{H}_3]^+$, it was found that the sign of J_{mag} is positive.²⁴ Assuming this to be true in complex **2**, the actual values of J_{ex} as a function of temperature range from -57 Hz at 140 K to -67 Hz at 198 K (Figure 3).

The increase in the magnitude of J_{ex} with increasing temperature is consistent with previous examples of exchange coupling. In the case of the related Ir complexes of the form $[\text{CpIr}(\text{PR}_3)_3\text{H}_3]^+$, coupling data were available over a wide range of temperatures, making it possible to fit the data quantitatively to a two-dimensional harmonic oscillator model.²⁴ In the case of complex **2**, limited data for J_{ex} as a function of temperature are available, preventing the quantitative application of this model.

Conclusions

Convenient preparations of complexes **1** and **2** directly from hydrogen gas have been developed. In the case of complex **1**, the initially formed product is confirmed as a dihydrogen complex by measurement of HD coupling. Very slow isomerization to an equilibrium mixture of dihydride and dihydrogen

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forms is observed. Samples of **1** prepared from hydrogen gas exhibit rates of dihydrogen to dihydride isomerization that are several orders of magnitude slower than previous observations using samples with triflate counterion.

With the more basic ligand environment provided by the dppm ligand, a greater degree of HH bond activation is observed, and the structure of **2** is a *cis* dihydride. The dynamics of the hydride ligands in complex **2** have been studied by very low-temperature NMR spectroscopy, which reveals that QMEC is operative. This is the first report of QMEC in a chemically equivalent pair of hydrogen atoms.

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