

Snapshots of the “breaking” of the H–H bond in the oxidative addition of H₂ to a metal centre

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Abstract. Three new monocationic molecular hydrogen complexes of ruthenium of the type *trans*-[RuCl(η^2 -H₂)(PP)₂][BF₄] (PP = *bis*-1,2(diarylphosphino)ethane, aryl = *p*-fluorobenzyl, benzyl, *p*-methylbenzyl) have been prepared by protonating the precursor hydride complexes *trans*-[RuCl(H)(PP)₂] using HBF₄·Et₂O. These three dihydrogen complexes are quite stable and have been isolated in the solid state. The intact nature of the H–H bond in these derivatives has been established from the short spin-lattice relaxation times (*T*₁, *ms*) and the observation of substantial H, D couplings in the HD isotopomers. The H–H bond distances (*d*_{HH}, Å) increase from 0.97 to 1.01 Å as the electron donor ability of the diphosphine ligand increases from the *p*-fluorobenzyl to the benzyl to the *p*-methylbenzyl moiety. These dihydrogen complexes constitute the initial stages of elongation of the H–H bond enroute to its cleavage along the reaction coordinate for the oxidative addition of H₂ to a metal centre.

Keywords. Dihydrogen; hydride complexes; NMR spectroscopy; ruthenium.

1. Introduction

Binding of a molecular hydrogen to a metal centre leads to the elongation of the H–H bond and subsequently to its cleavage along the reaction coordinate for the oxidative addition of dihydrogen. Whereas a large number of dihydrogen complexes reported to date have H–H distances (*d*_{HH}, Å) between 0.8 and 1 Å, there are far fewer examples of complexes that possess *elongated* dihydrogen ligands (*d*_{HH} between 1 and 1.5 Å).^{1,2} The elongated dihydrogen complexes are considered the arrested intermediate states in the important process of oxidative addition of H₂ to metal centres. Current challenge in this area is to study the smooth gradation of the H–H distances along the continuum for the oxidative addition of H₂ to a metal centre and to determine at what point the H–H bond can be considered to be *broken*. Herein, we report the synthesis and characterization of three new dihydrogen complexes of ruthenium of the type *trans*-[RuCl(η^2 -H₂)(PP)₂][BF₄] bearing the *bis*-1,2(diarylphosphino)ethane ligands (aryl = *p*-fluorobenzyl, benzyl, *p*-methylbenzyl), wherein the electron donor ability of the chelating phosphine ligand can be increased incrementally by a choice of suitable substituent on the benzyl moiety. As expected, the H–H bond distance increases incrementally as the donor ability of the

chelating phosphine increases from the *p*-fluorobenzyl to the benzyl to the *p*-methylbenzyl derivatives. The H–H bond length in the case of complexes bearing the *bis*-1,2-(di-*p*-methylbenzylphosphino)ethane ligand gave an H–H distance of 1.01 Å which falls under the category of *elongated* dihydrogen complexes.

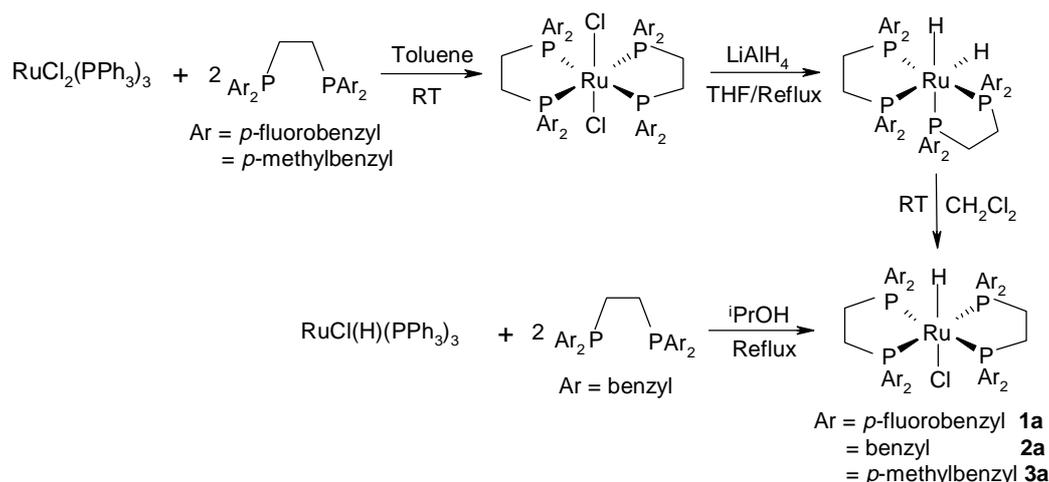
2. Results and discussion

The new ruthenium hydride complexes *trans*-[RuCl(H)(PP)₂] (PP = *bis*-1,2(diarylphosphino)ethane, aryl = *p*-fluorobenzyl **1a**, benzyl **2a**, *p*-methylbenzyl **3a**) were prepared via multi-step synthesis as reported by us recently.³ The sequence of steps is shown in scheme 1.

The hydride complexes were characterized using NMR and mass spectroscopy. The hydride ligand shows a quintet at δ –19.7, –19.6 and –19.9 respectively, for **1a**, **2a**, and **3a** in the ¹H NMR spectra due to coupling with the four *cis* phosphorus atoms of the diphosphine ligands with *J*(H, *P*_{cis}) in the range of 19.5 to 19.7 Hz. The ³¹P NMR spectra of these derivatives show only one signal for all the four P atoms suggesting that they are all equivalent and are in a plane.

The protonation of the hydride complexes *trans*-[RuCl(H)(PP)₂] under an atmosphere of H₂ at room

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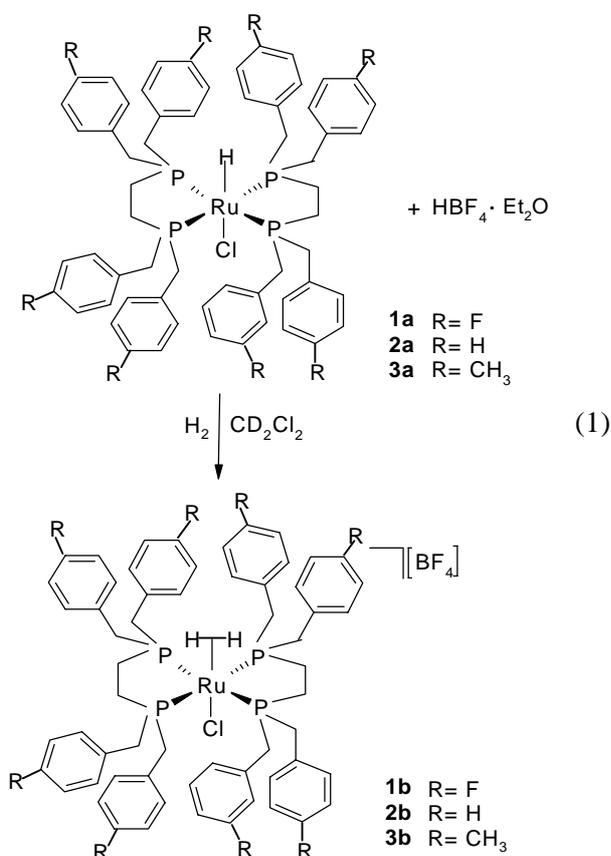
Scheme 1.

temperature with 1 equiv of $\text{HBF}_4 \cdot \text{Et}_2\text{O}$ in CD_2Cl_2 resulted in the corresponding dihydrogen complexes $\text{trans}-[\text{RuCl}(\eta^2\text{-H}_2)(\text{PP})_2][\text{BF}_4]$ (PP = *bis*-1,2(diarylphosphino)ethane, aryl = *p*-fluorobenzyl **1b**, benzyl **2b**, *p*-methylbenzyl **3b**) (1). The dihydrogen complexes were characterized using NMR spectroscopy. All of these complexes show the characteristic

broad singlet in the hydride region at δ -13.72, -13.78, and -13.85 for **1b**, **2b**, and **3b** respectively. Once again, the dihydrogen complexes exhibit a single resonance in the ^{31}P NMR spectra indicating the equivalence of the four P atoms and the *trans*-disposition of the dihydrogen and the chloride ligands in an octahedral geometry.

The intact nature of the H–H bond in **1b**, **2b**, and **3b** was established from the variable temperature ^1H spin-lattice relaxation time measurements (T_1 , ms; 400 MHz)⁴. The T_1 (min) were found to be 14.4 ms (263 K), 19.4 ms (253 K), and 20.9 ms (273 K) for **1b**, **2b**, and **3b**, respectively, from which the range of H–H distances (d_{HH} , Å) were calculated as reported earlier⁵. Thus, the d_{HH} for the fast and the slow rotation regimes of the bound H_2 were calculated to be 0.83–1.05 Å, 0.88–1.11 Å, and 0.89–1.12 Å respectively, for **1b**, **2b**, and **3b**.

In order to establish the intact nature of the H–H bond unambiguously in these derivatives, the HD isotopomers, $\text{trans}-[\text{RuCl}(\eta^2\text{-HD})(\text{PP})_2][\text{BF}_4]$ (PP = *bis*-1,2(diarylphosphino)ethane, aryl = *p*-fluorobenzyl **1b-d₁**, benzyl **2b-d₁**, *p*-methylbenzyl **3b-d₁**) were prepared by treating the dihydrogen complexes **1b**, **2b**, and **3b** with deuterium gas at room temperature in CD_2Cl_2 for about 15–20 min and the $J(\text{H},\text{D})$ couplings were measured using ^1H NMR spectroscopy. The ^1H NMR spectra of the H–D isotopomers were recorded at room temperature by nullifying the residual signal of the $\eta^2\text{-H}_2$ species by an inversion recovery pulse⁶. At 293 K, the ^1H NMR spectra in the hydride region show a very well-resolved 1:1:1 triplet due to H–D coupling at δ -13.79, -13.82 and -13.93 for **1b-d₁**, **2b-d₁**, and **3b-d₁** respectively.



Thus, the $J(\text{H}, \text{D})$ couplings were found to be 26.4, 25.4 and 24.4 Hz for **1b-d₁**, **2b-d₁**, and **3b-d₁** respectively. Each one of the 1 : 1 : 1 triplet signals in turn were further split into a quintet due to coupling of the HD with the four *cis*-phosphorus atoms with $J(\text{HD}, \text{P}_{\text{cis}})$ of 6.8 Hz for all the three complexes (figure 1). This coupling is a trifle less than the range (7.2–8.0 Hz) reported for complexes of the type $\text{trans}[\text{RuCl}(\eta^2\text{-HD})(\text{diphosphine})_2]^+$ (diphosphine = dppe $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$, dppm $\text{Ph}_2\text{PCH}_2\text{PPh}_2$).⁸

The H–H distances (d_{HH} , Å) were calculated from the $J(\text{H}, \text{D})$ couplings and found to be 0.97, 0.99 and 1.01 Å respectively for **1b-d₁**, **2b-d₁**, and **3b-d₁**.⁷ These distances seem to be more consistent with the slow

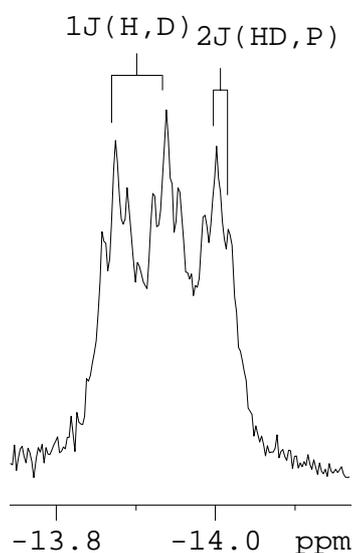


Figure 1. ^1H NMR spectrum of the hydride region of the HD isotopomer of $\text{trans}[\text{RuCl}(\eta^2\text{-H}_2)(\text{PP})_2][\text{BF}_4]$, **3b-d₁**.

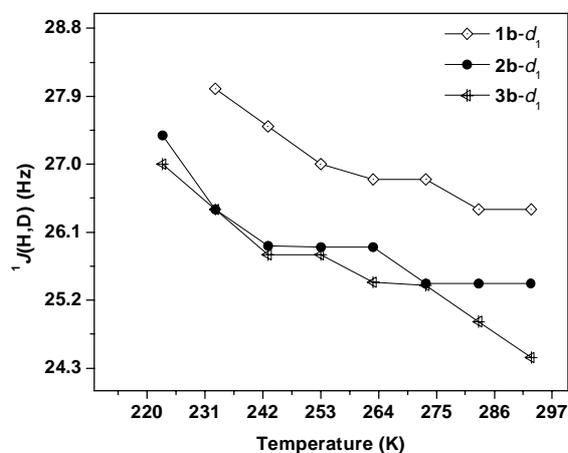


Figure 2. Plot of the variation of $J(\text{H}, \text{D})$ with temperature for **1b-d₁**, **2b-d₁** and **3b-d₁**.

rather than the fast rotation regime of the ruthenium-bound H_2 . The d_{HH} in complexes with a good π -donor like chloride, e.g., $\text{trans}[\text{RuCl}(\eta^2\text{-HD})(\text{PP})_2]^+$, were found to be 0.98 Å (PP = dppe) and 1.04 Å (PP = depe $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PET}_2$).⁹ The longer d_{HH} in the depe derivative compared to the dppe complex is a reflection of the greater donor ability of the depe moiety in comparison to the dppe ligand. In our present work, the H–H distance increases from 0.97 to 1.01 Å, again reflecting an increase in the electron donor ability of the co-ligand from fluorobenzyl to benzyl to *p*-methylbenzyl-substituted diphosphine. The greater the donation from the co-ligands, the greater is the back-donation from the filled ruthenium *d*-orbitals to the σ^* orbital of the H_2 , resulting in the elongation of the H–H bond.

We also carried out variable temperature $J(\text{H}, \text{D})$ measurements and found an interesting trend: $J(\text{H}, \text{D})$ increased with decrease in temperature and the variation was modest, increasing from 24.4 Hz at 293 K to 27.0 Hz at 223 K for **3b-d₁**. This behaviour has been observed for certain *elongated* dihydrogen complexes earlier.² A plot of the variation of the $J(\text{H}, \text{D})$ with temperature is shown in figure 2.

In conclusion, we have synthesized three new dihydrogen complexes of ruthenium bearing dibenzyl and *para*-substituted dibenzyl phosphinoethane co-ligands. These complexes are stable and isolable in the solid state. A systematic increase in the donor ability of the diphosphine ligand resulted in the progressive elongation of the H–H distance. It should be possible to prepare dihydrogen complexes with even more elongated H_2 moieties by incorporating even more strongly donating co-ligands. Efforts toward this direction are in progress in our laboratories.

Acknowledgments

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