Dynamic processes of H-atom site exchange in *trans* dihydrogen hydride complex of ruthenium

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A new dihydrogen hydride complex of ruthenium of the type *trans*-[(dppm)Ru(H)(η^2-H$_2$)(PPh$_3$)$_2$][BF$_4$] (1) (dppm = Ph$_2$PCH$_2$PPh$_2$) has been prepared by protonating the precursor dihydride complex *cis*-[(dppm)Ru(H)$_2$(PPh$_3$)$_2$] using HBF$_4$.Et$_2$O. The formulation of (1) as a dihydrogen complex has been based upon the variable temperature T_1 measurements (T_1(min) = 12.4 ms at 273 K, ClCD$_2$CD$_2$Cl, 400 MHz) and the observation of a substantial H-D coupling constant (J(H,D) = 32 Hz, 243 K, ClCD$_2$CD$_2$Cl) for the corresponding HD isotopomer *trans*-[(dppm)Ru(H)(η^2-HD)(PPh$_3$)$_2$][BF$_4$]. The T_1 and the H-D coupling constant measurements have been carried out in the temperature range 243 – 283 K. The dihydrogen and the hydride ligands of (1) show dynamic behavior and undergo rapid H-atom site exchange at 343 K. At 273 K (1) shows a static structure. The dynamics of (1) involving a trihydride intermediate has been studied by variable temperature NMR spectroscopy. The barrier to site exchange of the H-atom between the dihydrogen with the hydride ($\Delta G^{\ddagger}$) has been determined to be 14.4 kcal/mol at 303 K. Compound (1) has been found to be stable up to 343 K in solution and no loss of the H$_2$ ligand has been observed at that temperature; in addition, the compound is stable in solution at room temperature for a period of two days.

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Introduction

Ever since the report of the first transition metal η^2-H$_2$ complexes[1], the question of polyhydride complexes exhibiting fluxional processes involving a dihydrogen ligand has been extensively studied[2]. In addition, the dynamic processes in complexes containing a dihydrogen and a hydride ligand have also attracted enormous attention due primarily to their serving as prototypical examples of the polyhydride class of compounds. Depending upon the orientations of the dihydrogen and the hydride ligands with respect to one another in an octahedral complex, two possibilities arise, dihydrogen and the hydride ligands in: (a) *cis* conformations and (b) *trans* conformations. There have been quite a few reports on the studies of the dynamic processes for situation (a)[3] as well as case (b)[4]. The *trans* dihydrogen hydride complexes usually exhibit high barriers for the dihydrogen-hydride site exchange, whereas the *cis* compounds, relatively smaller barriers[4]. Maseras *et al.*[5] carried out theoretical studies to determine the relative stabilities of the six- and seven-coordinate isomers of [MH$_3$L$_4$]$^+$ (M = Fe, Ru, Os; L = monodentate phosphine ligands) species. Berke and co-workers[6] followed up Maseras' theoretical work with certain experiments on the structural diversity and dynamics of [MH$_3$L$_4$]$^+$ type complexes. Prior to these reports, Morris and co-workers[7] investigated besides other studies, dynamics of complexes of the type [(dppe)$_2$MH(η^2-H$_2$)]$^+$ and determined the $\Delta G^{\ddagger}$ for such derivatives. Morris proposed that the H-atom exchange in these derivatives involves significant movement of the ditertiaryphosphine P atoms that would contribute to the high barriers to the site exchange (Scheme 1).

We have been interested in preparing *cis* dihydrogen hydride complexes in order to study the dynamic processes of H-atom site exchange in such derivatives. Gusev *et al.*[6a,b] compiled the dynamics data for the known [MH$_3$L$_4$]$^+$ complexes (M = Fe, Ru, Os) with respect to the type of L ligand, viz., monodentate, bidentate, tridentate + monodentate, or tetradentate. In addition to these, others have reported systems such as [MH$_3$P$_2$(LX)]$^+$ (P = monodentate phosphorus ligands, LX = bidentate, monoanionic ligand)[6c] and [MH$_3$P$_2$(LL)]$^+$ (P = monodentate phosphorus ligands, LL = bipyridyl)[3a]. Notably missing from these listings is a case where L$_4$ is a
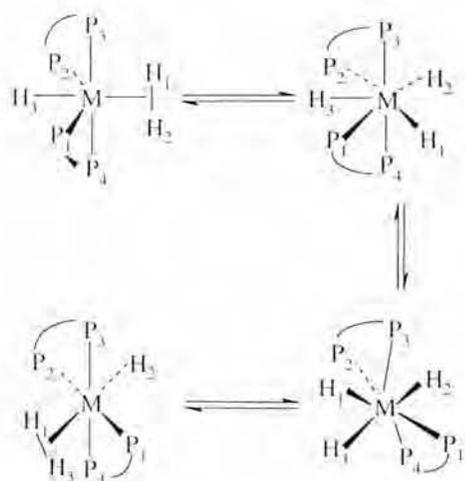
Scheme 1

combination of a bidentate and two mondentate ligands, all consisting of phosphorus donors. In order to examine the effect of having two monodentate ligands and a bidentate ligand (all consisting of phosphorus donors) on the structure and dynamics, we have attempted to prepare one such derivative, cis-[(dppm)Ru(H)(η^2-H$_2$)(PPh$_3$)$_2$][BF$_4$] by protonating the precursor dihydride complex, cis-[(dppm)RuH$_2$(PPh$_3$)$_2$][8] using HBF$_4$.Et$_2$O. However, upon protonation, only the trans-[(dppm)Ru(H)(η^2-H$_2$)(PPh$_3$)$_2$][BF$_4$] complex was realized. There are several examples of complexes exhibiting the trans stereochemistry for the hydride and dihydrogen ligands in the family of compounds of the type [MH$_3$L$_4$]$^+$ (M = Ru; L = monodentate ligand or two bidentate ligands) that are relevant to the current work[9]. In this paper, we report our investigations on the dynamic behaviour of the dihydrogen and the hydride ligands in trans-[(dppm)Ru(H)(η^2-H$_2$)(PPh$_3$)$_2$][BF$_4$].

Materials and Methods

General Procedure

All reactions were carried out under purified and dried N$_2$ atmosphere except the ones involving the dihydrogen complex at room temperature using standard Schlenk[10] and inert atmosphere techniques unless otherwise stated. Reactions involving the dihydrogen complexes were performed under H$_2$ atmosphere and the solvents used for the preparation of the dihydrogen complexes were thoroughly saturated with H$_2$ just before use.

The NMR spectra were obtained using an Avance Bruker 400 MHz spectrometer. The shift of the residual protons of the deuterated solvent was used as an internal reference. Variable-temperature proton T_1 measurements were carried out at 400 MHz using the inversion recovery method[11]. The ^{31}P{^{1}H} NMR spectra were recorded relative to 85% H$_3$PO$_4$ (aqueous solution) as an external standard. Bis(diphenylphosphino)methane[12] and cis-[(dppm)RuH$_2$(PPh$_3$)$_2$][8] were prepared by literature methods.

Preparation of trans-[(dppm)Ru(H)(η^2-H$_2$)(PPh$_3$)$_2$][BF$_4$] (1)

To a suspension of cis-[(dppm)RuH$_2$(PPh$_3$)$_2$] (15 mg, 0.014 mmol) in Et$_2$O (1 mL) was added 54% HBF$_4$.Et$_2$O (3 µL, 0.022 mmol). Immediate reaction was evident and the product precipitated out. The product was washed with Et$_2$O few times to remove the excess acid and dried under a stream of H$_2$ gas. For NMR characterization, the dihydrogen complex was dissolved in CD$_2$Cl$_2$, which was previously freeze-pump-thaw degassed and saturated with H$_2$ and transferred to a 5 mm NMR tube flushed with H$_2$ gas. ^{1}H NMR (CD$_2$Cl$_2$, 303 K): δ –6.41 (br s. 1H, Ru–H); –1.71 (br s, 2H, η^2-H$_2$); 4.16 (m, 2H, PCH$_2$P); 6.60–8.80 (m, 50H, PPh$_2$, PPh$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, 303 K): δ 4.2 (d, 2P, Ph$_2$PCH$_2$PPh$_2$, J(P,P$_{trans}$) = 186 Hz); 48.2 (d, 2P, PPh$_3$). The dihydrogen hydride complex (1) was prepared similarly in ClCD$_2$CD$_2$Cl solvent for variable temperature NMR experiments. ^{1}H NMR (ClCD$_2$CD$_2$Cl, 303 K): δ –6.37 (br s, 1H, Ru–H); –1.59 (br s, 2H, η^2-H$_2$); 4.27 (m, 2H, PCH$_2$P); 6.60–8.40 (m, 50H, PPh$_2$, PPh$_3$). ^{31}P{^{1}H} NMR (ClCD$_2$CD$_2$Cl, 303 K): δ 3.4 (d, 2P, Ph$_2$PCH$_2$PPh$_2$, J(P,P$_{trans}$) = 188 Hz); 47.3 (d, 2P, PPh$_3$).

Observation of the H-D Isotopomer of trans-[(dppm)Ru(H)(η^2-H$_2$)(PPh$_3$)$_2$][BF$_4$]

The H-D isotopomer was obtained by purging HD gas (generated from D$_2$O and NaH) at a steady rate through a ClCD$_2$CD$_2$Cl solution of the dihydrogen complex for ca. 5 min. The HD isotopomer formed was observed by ^{1}H NMR spectroscopy.

Results and Discussion

Preparation and characterization of the dihydrogen-hydride complex trans-[(dppm)Ru(H)(η^2-H$_2$)(PPh$_3$)$_2$][BF$_4$] (1)

The dihydrogen hydride complex (1) was prepared by protonating the precursor dihydride complex cis-[(dppm)RuH$_2$(PPh$_3$)$_2$] using HBF$_4$.Et$_2$O
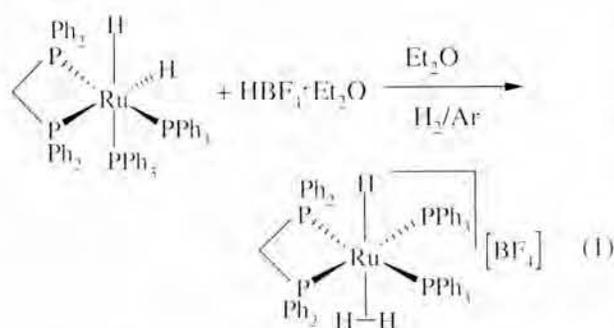
(Eq. 1). The product was obtained as a cream-colored solid. The complex (1) was found to be stable in halogenated solvents at room temperature for *ca.* 2 days before it decomposes into a species that we have not been able to identify[13]; it is however, stable for much longer periods typically 1 week or more at low temperatures (*ca.* –5 to –10 °C).

The ^1H NMR spectrum of (1) at room temperature in CD_2Cl_2 shows two featureless broad signals in the hydride region at δ –1.71 and –6.41 that integrate to 2 to 1 number of protons respectively indicating that the downfield signal could be assigned to the η^2-H_2 and the upfield one to the hydride moiety. The broadness of both the hydride and the dihydrogen signals in the room temperature spectrum suggests that a dynamic process was apparent. The $^{31}P\{^1H\}$ NMR spectrum gave only two doublets at δ 4.2 and 48.2 with a $J(P,P_{trans})$ of 186 Hz indicating that the four P atoms were in plane with the two PPh_3 *trans* to the two dppm phosphorus atoms.

^1H NMR T_1 measurements

The variable-temperature spin-lattice relaxation times (T_1) for the η^2-H_2 and the hydride hydrogen signals were determined in the temperature range 243-283 K in $ClCD_2CD_2Cl$ solvent. The data are summarized in Table 1. As is evident, the T_1 data for the dihydrogen ligand shows a parabolic behaviour with the $T_1(min)$ (400 MHz) of 12.4 ms at 263/273 K whereas the T_1 values for the hydride moiety continually decrease from 243 to 283 K, thus the hydride loses its identity at the high temperature limit[11], indicating a fluxional process involving the hydride and the dihydrogen ligands. The H–H distance has been calculated from the T_1 minimum[7b] and found to be 1.03 and 0.82 Å for the slow and fast rotation regimes. At temperatures greater than 263 K, the T_1 values are weighted averages for the rapidly interconverting tautomers involving the H-atom site

exchange (see later). However, from the line widths of the H_2 and the hydride signals in the ^1H NMR spectra as a function of temperature, it is apparent that the interconversion actually sets in at temperatures greater than 273 K.

Variable temperature ^1H NMR spectra of (1) in the hydride region

The temperature-dependent ^1H NMR spectra of (1) in $ClCD_2CD_2Cl$ in the hydride region is shown in Fig. 1. The temperature dependence of the hydride and the dihydrogen signals is due to an intramolecular H-atom site exchange process (see discussion later). At 273 K and below 400 MHz, the hydride resonance is a well-resolved binomial quintet arising from the H-P_{cis} couplings on the order of 17 Hz. The hydride resonance broadens at temperatures greater than 273 K and goes into the base line at *ca.* 313 K. The broad
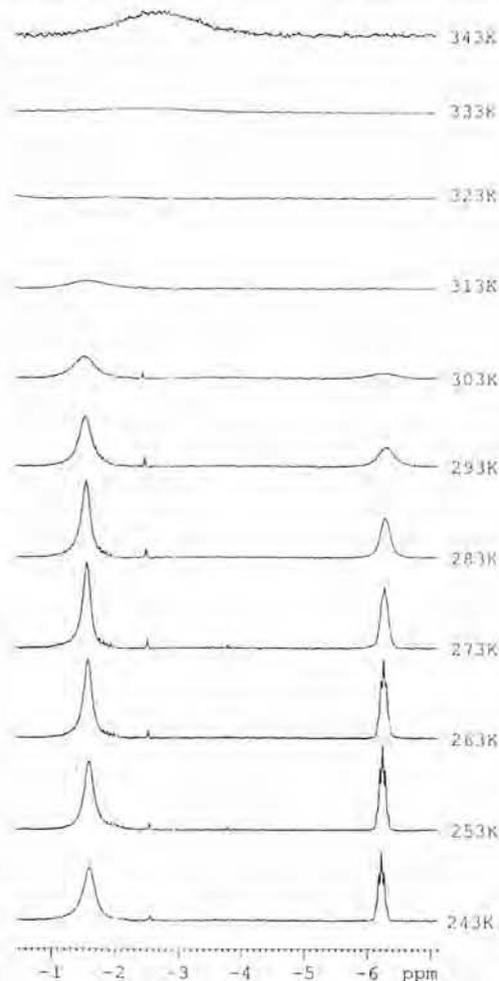

Fig. 1 — Variable temperature 400 MHz ^1H NMR spectra of the hydride region of *trans*-[(dppm)Ru(H)(η^2-H_2)(PPh_3)$_2$][BF_4] in $ClCD_2CD_2Cl$

signal downfield to that of the hydride due to the dihydrogen moiety remains broad in the temperature range studied (243-313 K). The large line width of this resonance is due to the rapid dipolar relaxation of these nuclei leading to short T_1[14] and T_2 values[15]; the unresolved H_2, P couplings are embedded in this signal. The broadening of the H_2 signal below 273 K is caused by the expected decrease in T_2 of the nuclei. The hydride and the dihydrogen signals undergo broadening above 273 K and at 323 K, coalesce into the base line. A broad resonance reappears at δ –2.90 at 343 K indicating the fast exchange limit of the H-atom between the dihydrogen and the hydride ligands.

From the NMR spectral peaks, the T_2 values were obtained and the rates of H-atom exchange (k) from the dihydrogen (H_2) to the hydride (H) site. The rate constant data is summarized in Table 1. An Eyring plot of ln (k/T) vs 1/T was found to be linear from which the activation parameters for the dynamic process were calculated to be $\Delta H^{\ddagger}$ = 19.6 kcal/mol, $\Delta S^{\ddagger}$ = 17.2 cal/mol, and $\Delta G^{\ddagger}$ (303 K) = 14.4 kcal/mol. The small $\Delta S^{\ddagger}$ value indicates that the process is intramolecular. The $\Delta G^{\ddagger}$ obtained for complex (**1**) falls within the range observed for the H-atom site exchange processes for certain dihydrogen-hydride complexes of the type *trans*-[(diphosphine)$_2$RuH (η^2-H_2)]$^+$ as reported by Morris *et al.*[7b] The $\Delta G^{\ddagger}$ values for similar processes in *cis* dihydrogen-hydride

complexes are much smaller[3,4,16].

Variable temperature ^{31}P{^{1}H} NMR spectra of (1)

In order to probe the rearrangements of the phosphorus ligands around the metal center, we carried out the VT ^{31}P{^{1}H} NMR study of (**1**) in the temperature range 283-348 K in ClCD$_2$CD$_2$Cl. Fig. 2 shows the VT ^{31}P{^{1}H} NMR spectra illustrating the dynamics of the P atoms. The spin system is expected to be AA'XX' at low temperatures, however, we observed only two doublets in the ^{31}P{^{1}H} NMR spectra. At temperatures of 303 K and higher, the coupling constants average out. Thus, there is movement of the phosphorus nuclei from one site to the other. Even at 348 K, the dynamic process involving rapid interchange of the axial and equatorial P atoms (see discussion of the mechanism later) is not fast enough to render the two resonances into two singlets.

Preparation, properties, and variable temperature ^{1}H NMR study of the H-D isotopomer

The   H-D   isotopomer   *trans*-[(dppm)Ru(H)

Table 1 — T_1 (400 MHz, ClCD$_2$CD$_2$Cl) values for the hydride and the dihydrogen ligands and rates of H-atom exchange (k) from the dihydrogen site to the hydride site in *trans*-[(dppm) Ru(H)(η^2-H_2)(PPh$_3$)$_2$][BF$_4$]

T, K	T_1 (ms), η^2-H_2	T_1 (ms), H	k, s^{-1}
243	17.3	288.6	
253	13.9	137.5	
263	12.4	67.7	
273	12.4	37.5	
283	15.2	24.5	22
293			110
303			305
313			577
333			4185
343			10291
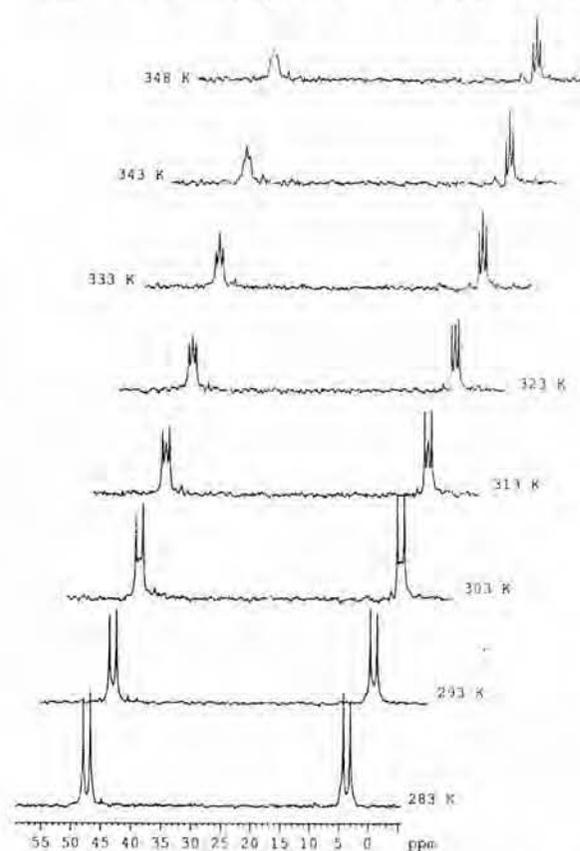
Fig. 2 — Variable temperature 400 MHz ^{31}P{^{1}H} NMR spectra of *trans*-[(dppm)Ru(H)(η^2-H_2)(PPh$_3$)$_2$][BF$_4$] in ClCD$_2$CD$_2$Cl

$(\eta^2\text{-HD})(PPh_3)_2]^+$ was prepared by exposing the $\eta^2\text{-H}_2$ complex to HD gas. Various isotopomers differing in the extent of deuterium incorporation are possible. They are formed when the intramolecular H-atom exchange is slow. The first isotopomer formed upon exchange of H_2 with HD is *trans*-[(dppm)Ru(H)$(\eta^2\text{-HD})(PPh_3)_2]^+$ which can transform into *trans*-[(dppm)Ru(D)$(\eta^2\text{-H}_2)(PPh_3)_2]^+$; further reaction with more HD gas could result in HD_2 species.

The $\eta^2\text{-HD}$ ligand of *trans*-[(dppm)Ru(H)$(\eta^2\text{-HD})(PPh_3)_2]^+$ was observed in the ^1H NMR spectrum (Fig. 3) at 243 K by nullifying the residual $\eta^2\text{-H}_2$ signal by an inversion recovery pulse sequence[7b,17]. A signal with almost 1:1:1 intensity ratio was obtained for the HD isotopomer with a $J(H,D)$ of 32 Hz. The H–H distance (d_{HH}) calculated from the inverse relationship between d_{HH} and $J(H,D)$ of the HD isotopomer[18,19] is 0.88 Å. This value is consistent with the H-H distance of 0.82 Å obtained from T_1 measurements assuming rapid rotation of the H_2 ligand. In addition, each one of the three signals shows an approximate quintet pattern due to the coupling with the four *cis* phosphorus atoms with a $J(H_2,P_{cis}) = 5\text{-}7$ Hz. At temperatures higher than 273 K, the onset of site exchange process causes line broadening and the H-D couplings are averaged out. We were able to resolve the H-D coupling at 263 and 253 K and found to be 28 and 31 Hz respectively. At temperatures higher than this, the resolution was poor circumventing the measurement of $J(H,D)$. At the
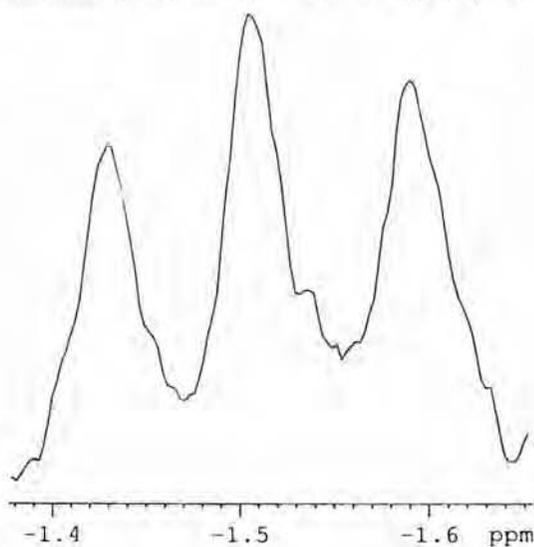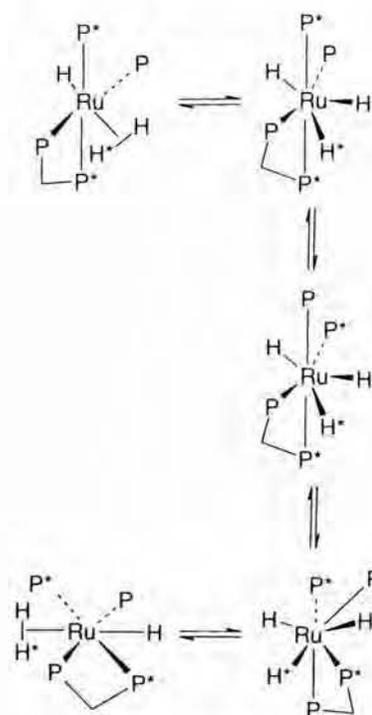
fast-exchange limit the $J(H,D)$ would be expected to be small due to rapid intramolecular exchange of H/D atoms in the HD_2 isotopomer. Morris suggested that three nuclei (H, D, D) need not retain bonds between themselves in order to give an averaged $J(H,D)$ value[7a]. Small isotopic upfield shifts of 3-8 ppb were noted in the HD isotopomers. This upfield shift is typical for dihydrogen complexes[20].

Mechanism of the intramolecular H-atom exchange

Based on the VT ^1H NMR spectroscopic studies, we propose that the H-atom site exchange involves the homolytic cleavage of the H-H bond to give a fluxional trihydride intermediate, which allows for the exchange of the H-atom. The barriers for the H-atom site exchange for *trans* disposition of the hydride and the dihydrogen ligands are usually higher compared to the systems that have the hydride and the H_2 ligands in *cis* conformations[3]. Thus, the proposed mechanism shown in Scheme 2 is consistent with a high value of $\Delta G^\ddagger$ of 14.4 kcal/mol. Significant rearrangements have to take place involving a fluxional seven coordinate pentagonal bipyramidal structure; the VT ^{31}P NMR spectral data is consistent with a site exchange of the axial and the equatorial P atoms as shown in the scheme. Another possible mechanism involving the isomerization of the *trans*

Fig. 3 — ^1H NMR spectrum (hydride region) of *trans*-[(dppm) Ru(H)$(\eta^2\text{-HD})(PPh_3)_2$][BF$_4$] (400 MHz, 243 K) in ClCD$_2$CD$_2$Cl with the residual signal due to $\eta^2\text{-H}_2$ ligand nullified

Scheme 2

dihydrogen hydride complex to the *cis* isomer followed by the exchange of the H-atom could be ruled out because no observable $H-P_{trans}$ couplings were seen in the ^1H NMR spectra at any temperature[21].

Interaction of H_2 with the metal center

It is interesting to note here that the chemical shift of the H_2 signal in (**1**) is quite downfield (δ –1.71 in CD_2Cl_2; δ –1.59 in $ClCD_2CD_2Cl$). In addition to our complex, there are few other dihydrogen complexes reported in the literature that show far downfield chemical shifts of the η^2-H_2 ligand[22,9cal]. The appearance of the H_2 at a significantly downfield region might suggest that the interaction of H_2 with the metal is very weak and perhaps has properties close to those of free H_2. On the contrary, we found that despite heating the complex (**1**) to *ca.* 343 K, no H_2 loss was observed. More work is needed to understand this behaviour. Upon cooling the sample back to room temperature, the independent resonances for the hydride and the dihydrogen moieties reappeared.

Conclusion

A new dihydrogen hydride complex *trans*-$[(dppm)Ru(H)(\eta^2$-$H_2)(PPh_3)_2][BF_4]$ has been prepared and characterized. This complex was found to be dynamic: H-atom undergoes exchange between the H_2 and the hydride ligands. The mechanism involves a trihydride species with a $\Delta G^{\ddagger}$ of 14.4 kcal/mol at 303 K for the dynamic process.

Acknowledgement

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