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# Dynamics of H-atom exchange in stable *cis*-dihydrogen/hydride complexes of ruthenium(II) bearing phosphine and N–N bidentate ligands†

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Synthesis and characterization of *cis,trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(N–N)][OTf] (N–N = 2,2′-bipyridyl (bpy) **1a**, 2,2′-bipyrimidine (bpm) **2a**; OTf = trifluoromethane sulfonate ($CF_3SO_3$)) complexes are reported. The *cis*-$H_2$/hydride ligands are involved in H-atom site exchange between the two moieties. This dynamics was investigated by variable temperature NMR spectral studies based on which the mechanism of the exchange process was deduced. The $\Delta G^{\neq}$ for the exchange of H-atoms between the $\eta^2$-$H_2$ and hydride ligands was determined to be around 8 and 13 kJ mol$^{-1}$, respectively, for **1a** and **2a**. The H–H distances ($d_{HH}$, Å) in complexes **1a** and **2a** have been calculated from the $T_1$(minimum) and $^1J$(H,D) and are found to be 1.07 Å (slow) and 0.95 Å for **1a** and 1.04 Å (slow) and 0.94 Å for **2a**, respectively. The molecular structure of **1a** was determined by X-ray crystallography.

## Introduction

The binding and activation of molecular hydrogen on a metal center continue to attract the attention of researchers from the standpoint of the very interesting structural and dynamical features and catalysis, apart from the interesting reactivity patterns that they exhibit.[1] Complexes possessing dihydrogen and hydride ligands in *cis* conformation exhibit extremely rapid dynamics of exchange of hydrogen atoms between the $\eta^2$-$H_2$ and the hydride ligands in solution (Chart 1). This dynamic exchange is facilitated by a *cis*-interaction which is like a weak hydrogen bonding interaction between dihydrogen and hydride ligands observable in the solid state.[2] Although inelastic neutron scattering could provide important evidence for this interaction, the requirement of large crystals limits its utility to a certain extent. The solution NMR spectral method is rather a very useful tool to study such interactions and processes. However, in certain cases, the dynamics of the exchange is extremely rapid and cannot be frozen in the NMR time scale even at very low temperatures making it difficult to detect the $\eta^2$-$H_2$ ligands in, for example, polyhydride complexes. The dynamic process in *cis*-dihydrogen/hydride complexes could be considered as a type of σ-bond metathesis analogous to olefin metathesis (Chart 1).

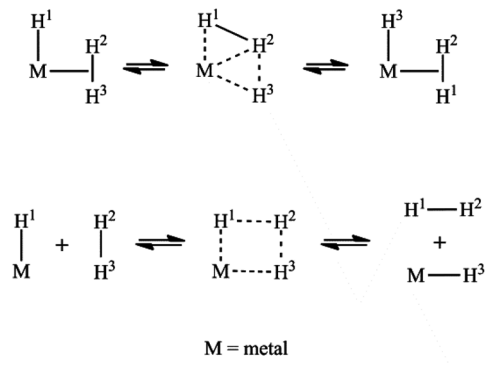


**Chart 1** *Cis*-interaction (top) and σ-bond metathesis (bottom).

Previously, *cis*-dihydrogen/hydride complexes of Mo(II), Ru(II), Os(II), Rh(III), and Ir(III) have been reported.[3] A classical dihydride complex with the two hydride ligands in *cis* conformation related by a $C_2$ axis could be protonated to give the corresponding *cis*-dihydrogen/hydride complex which would render the two ligands in a dynamic exchange process requiring very limited movement of the ancillary ligands around the metal center. Examples of such systems include *cis,trans*-[RuH($\eta^2$-$H_2$)($PCy_3$)$_2$(bpy)][OTf] reported by Heinekey and his co-workers[3d] and *cis,trans*-[IrH($\eta^2$-$H_2$)($PCy_3$)$_2$($\eta^2$-$S_2CH$)][$BF_4$] reported by us.[3b] Heinekey's ruthenium complex was characterized by spin–lattice relaxation time ($T_1$) measurements and partial deuteration studies. However, structural characterization of this complex was not established. Properties of these complexes are slightly different from the true σ-dihydrogen complexes. The adjacent hydride ligand spaced close (~2 Å in the solid state structure)[3e] to the $\eta^2$-$H_2$ ligand has a large

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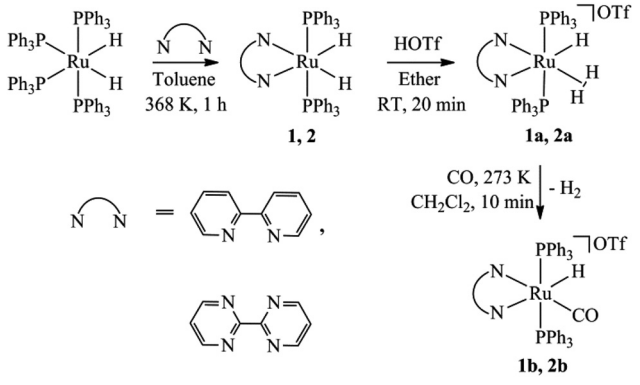
influence on $H_2$ coordination. In solution, all the three H-atoms behave as magnetically equivalent nuclei at ambient temperatures due to fast exchange between the dihydrogen and hydride ligands. Only in a few cases, low temperature NMR spectral studies enabled the observation of the $\eta^2$-$H_2$ and hydride ligands separately in the $^1$H NMR spectrum since this dynamic process has a rather low free energy of activation.[3e]

In continuation of our studies on the H-atom site exchange in *cis*-dihydrogen/hydride complexes, in order to understand the factors that determine their structures and dynamics, we undertook to examine the case of *cis*,*trans*-[RuH($\eta^2$-$H_2$)-($PPh_3$)$_2$(N–N)][OTf] (N–N = 2,2′-bipyridyl (bpy), 2,2′-bipyrimidine (bpm); OTf = trifluoromethane sulfonate ($CF_3SO_3$)) complexes. Since the bulky $PPh_3$ ligands and the rigid chelating N–N ligand will render the system rather sterically rigid thereby minimizing the movement of the ancillary ligands around the metal center, we chose to study the H-atom site exchange between the dihydrogen and hydride ligands in these complexes. The analogous *cis*-$H_2$/hydride derivative *cis*,*trans*-[RuH($\eta^2$-$H_2$)($PCy_3$)$_2$(bpy)][OTf] reported earlier has not been structurally characterized as noted before. Herein, we report the synthesis and spectroscopic characterization of *cis*,*trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(N–N)][OTf] complexes together with the dynamics studies. We also report the X-ray crystal structure of the *cis*,*trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(bpy)][OTf] (**1a**) complex.

## Results and discussion

### Synthesis, characterization, and protonation reaction of *cis*,*trans*-[$RuH_2(PPh_3)_2$(N–N)] (N–N = bpy, 1; bpm, 2)

The starting dihydride complexes *cis*,*trans*-[$RuH_2(PPh_3)_2$(N–N)] (N–N = bpy, **1**; bpm, **2**) were synthesized from the reaction of [$RuH_2(PPh_3)_4$][4] and N–N bidentate ligands (Scheme 1). The bipyridyl complex **1** was reported earlier by Morris and his co-workers.[5] The $^1$H NMR spectra of complexes **1** and **2** are comprised of high field signal at around $\delta$ −14 ppm which could be attributed to the hydride ligands. A suspension of these complexes in diethyl ether reacts instantaneously with HOTf to afford the corresponding *cis*-dihydrogen/hydride complexes, *cis*,*trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, **1a**; bpm, **2a**) (Scheme 1).




Scheme 1

A high field triplet signal around $\delta$ −10 ppm (**1a**, $\delta$ −9.93 ppm; **2a**, $\delta$ −9.94 ppm) integrating to three H-atoms points to the presence of a Ru$H_3$ moiety in these derivatives. Three H-atoms of complexes **1a** and **2a** resonate at a weighted average position between those of the individual chemical shifts of the dihydrogen and hydride ligands due to a fast exchange process that the $^1$H NMR spectroscopy at room temperature cannot arrest. Even at 163 K (in $CDCl_2F$–$CDClF_2$ solvent),[6] no decoalescence of the single resonance was noted. We, however, noted line broadening of the Ru$H_3$ signal due to slowing down of the exchange process.[7] The $\Delta G^{\neq}$ for the exchange process in these complexes were calculated to be around 8 to 13 kJ mol$^{-1}$ (see ESI†).[8]

Presence of an $\eta^2$-$H_2$ ligand in **1a** and **2a** was established by variable temperature spin–lattice relaxation time ($T_1$, ms) measurements, partial deuteration studies, and X-ray crystallography, and confirmed by reacting these two dihydrogen complexes with CO gas, which resulted in $H_2$ evolution accompanied by the formation of the hydride carbonyl derivatives, *cis*,*trans*-[RuH(CO)($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, **1b**; bpm, **2b**) (Scheme 1). Complexes **1b**[9] and **2b** showed spectral signals at around $\delta$ −12 ppm for the Ru*H* moiety and $\delta$ 45 ppm for the *P*$Ph_3$ ligands, respectively, in the $^1$H and $^{31}$P NMR spectra. Additionally, the IR spectrum of **2b** showed a distinct $\nu$(CO) band at 1943 cm$^{-1}$.

### Variable temperature spin–lattice relaxation time ($T_1$, ms) measurements of *cis*,*trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, 1a; bpm, 2a)

We carried out variable temperature NMR spectral studies with a view to obtain limiting spectra that would allow us to observe two distinct signals for the $\eta^2$-$H_2$ and hydride ligands of *cis*,*trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, **1a**; bpm **2a**) complexes. In turn, this could enable us to carry out spin–lattice relaxation time ($T_1$, ms) measurements for the $\eta^2$-$H_2$ and hydride ligands. However, VT $^1$H NMR spectral studies revealed only one signal at all accessible temperatures for both the ligands. Nevertheless, we carried out $T_1$ measurements for the $RuH_3$ moiety of complexes **1a** and **2a** in the temperature range of 293 K to 183 K. Just like in the previously reported dihydrogen complexes,[10] we noted unusually short $T_1$ values for complexes **1a** and **2a**. The $T_1$(minimum) ($CD_2Cl_2$, 400 MHz) observed for complexes **1a** and **2a** are 21.60 ± 0.06 ms (183 K) and 18.80 ± 0.04 ms (191 K), respectively. The VT $^1$H $T_1$ data for complexes **1a** and **2a** are shown in Fig. 1.

It has been reported in the literature that among the $T_1$ values of the entire temperature range measured, the $T_1$(minimum) is the one that is related to the distance between the two dipolar H-atoms of the $\eta^2$-$H_2$ ligands.[10a] However, in the case of complexes **1a** and **2a**, the observed $T_1$(minimum) values cannot be directly correlated with the H–H distance, $d_{HH}$ (Å), of the $\eta^2$-$H_2$ ligand since the adjacent hydride ligand has some contribution to the measured $T_1$. If we assume that the $T_1$ of only the hydride ligand of **1a** and **2a** are the same as

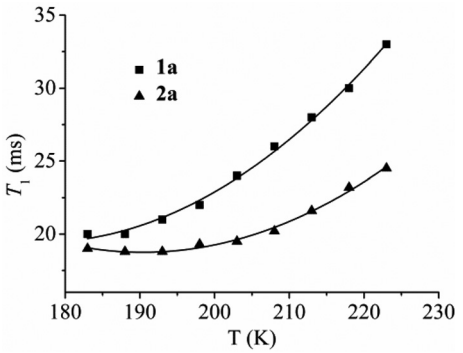



Fig. 1 Variable temperature $T_1$ measurements of *cis,trans*-[RuH($\eta^2$-$H_2$)-($PPh_3$)$_2$(bpy)][OTf] (**1a**) in $CDCl_2F$–$CDClF_2$ and *cis,trans*-[RuH($\eta^2$-$H_2$)-($PPh_3$)$_2$(bpm)][OTf] (**2a**) in $CD_2Cl_2$ at 400 MHz.

that of the $RuH_2$ moiety of **1** and **2**, it is possible to calculate the H–H distance ($d_{HH}$, Å) for the $\eta^2$-$H_2$ ligand of the former complexes.[11] For this purpose, we also carried out VT $T_1$ measurements of complexes **1** and **2** (see ESI†). The $T_1$ ($CD_2Cl_2$, 400 MHz) values for complexes **1** and **2** were found to be 477.0 ± 0.2 ms (183 K) and 439.0 ± 0.1 ms (191 K), respectively. The H–H distance ($d_{HH}$, Å) in the $\eta^2$-$H_2$ ligand of complexes **1a** and **2a** could then be calculated to be ~1.0 Å and ~0.8 Å, considering the slow and the fast rotation regimes of the bound $H_2$ molecule, respectively.[12] This calculation was done by following a modified method (see ESI†) established by Heinekey and co-workers.[11] Both the dihydrogen complexes exhibit the $d_{HH}$ values that are quite close to one another. Complex **2a** ($d_{HH}$ 1.04 Å, slow; 0.82 Å, fast) has a slightly shorter $\eta^2$-$H_2$ ligand in comparison to **1a** (1.07 Å, slow; 0.84 Å, fast). This is rather reasonable because complex **2a** possesses a slightly more electron deficient Ru(II) center which results in less back-bonding from the filled d orbital of the metal center to the σ* MO of the $\eta^2$-$H_2$ ligand.

### Partial deuteration studies of *cis,trans*-[RuH($\eta^2$-$H_2$)-($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, 1a; bpm, 2a) complexes

Treatment of *cis,trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, **1a**; bpm, **2a**) complexes with HD gas resulted in a slow incorporation of deuterium. Two isotopomers, $RuH_2D$ and $RuHD_2$, together with the original $RuH_3$ species were observed in the $^1$H NMR spectrum of the partially deuterated samples (Fig. 2 and 3). The distinct quintet signal expected for $RuHD_2$ species in the $^1H\{^{31}P\}$ NMR spectrum was not observed due to its partial superimposition on the intense 1 : 1 : 1 triplet pattern of the $RuH_2D$ isotopomer. Three chemical shift values are closely spaced ($\Delta\delta_H$ = 20–40 ppb), which is evident from the $^1H\{^{31}P, ^2H\}$ NMR spectrum (Fig. 2 and 3). The isotopic perturbation of resonance (IPR)[13] resulted in an upfield isotopic shift in **1a** and **2a** and the distribution of the deuterium atom is statistical since we noted nearly equal $J(H_2D)$ and $J(HD_2)$ values (Table 1). The coupling constant $^1J$(H,D) and H–H distances ($d_{HH}$, Å) were calculated to be ~30 Hz and ~0.95 Å, respectively.[11]

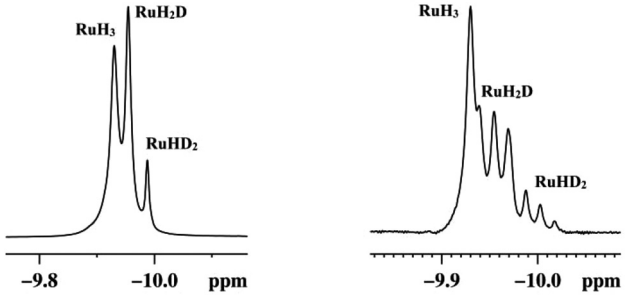



Fig. 2 Hydride regions of the $^1H\{^{31}P, ^2H\}$ (left) and $^1H\{^{31}P\}$ (right) NMR spectra of *cis,trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(bpy)][OTf] (**1a**) ($CD_2Cl_2$, 296 K) acquired at 500 MHz.

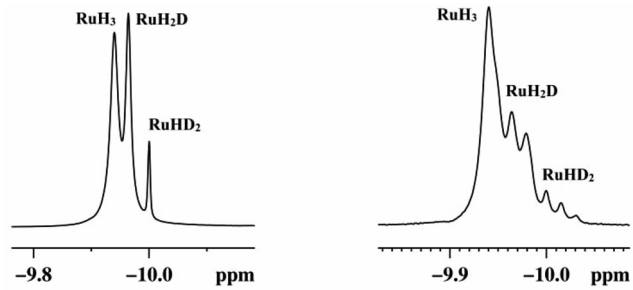



Fig. 3 Hydride regions of the $^1H\{^{31}P, ^2H\}$ (left) and $^1H\{^{31}P\}$ (right) NMR spectra of *cis,trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(bpm)][OTf] (**2a**) ($CD_2Cl_2$, 296 K) acquired at 500 MHz.

Table 1 H–H distances ($d_{HH}$) in the $\eta^2$-$H_2$ ligand of *cis,trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, **1a**; bpm, **2a**), calculated from $T_1$ measurements and partial deuteration studies

| Complex | $d_{HH}$ (slow, Å) | $d_{HH}$ (fast, Å) | $J(H_2D)$ (Hz) | $J(HD_2)$ (Hz) | $^1J_{HD}/d_{HH}$ (Hz/Å) |
|---|---|---|---|---|---|
| **1a** | 1.07 (183 K) | 0.84 | 7.3 (293 K) | 7.5 | 29.6/0.95 |
| **2a** | 1.04 (191 K) | 0.82 | 7.5 (293 K) | 7.7 | 30.4/0.94 |

### Hydride dynamics and stability of *cis,trans*-[RuH($\eta^2$-$H_2$)-($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, 1a; bpm, 2a) complexes

We carried out VT $^1$H NMR spectral studies down to 163 K and 183 K for complexes **1a** and **2a** respectively. Even at those temperatures, the three H-atoms were quite dynamic. No decoalescence of the single resonance for the $RuH_3$ moiety took place except that the signal underwent line broadening at low temperatures. The mechanism that renders the three H-atoms highly dynamic is not well understood in similar systems reported in the literature owing to the difficulty in controlling such a fast dynamic process by using a suitable ligand environment in the coordination sphere of the metal center. This fast exchange makes the three H-atoms chemically equivalent on the NMR time scale.

Three plausible pathways that facilitate the exchange process could be envisioned: (a) oxidative addition of the $\eta^2$-$H_2$ ligand, followed by reductive elimination of a $H_2$ molecule involving the hydride ligand, (b) fast proton transfer (heterolysis) from the dihydrogen to hydride ligand, and (c) through a

concerted trihydrogen anionic species. Oxidative addition of the bound $H_2$ ligand resulting in the formation of a trihydride species followed by the re-formation of a dihydrogen ligand involving the hydride moiety is known to require a large $\Delta G^{\neq}$ and thus is less likely.[3h,j] Free energy barriers required for the H-atom exchange between the dihydrogen and hydride ligands *via* heterolysis of $H_2$ vary in the range of 20–50 kJ mol$^{-1}$.[3d,i,7] Therefore, these two pathways of H-atom site exchange are less favored in our case. Next, we carried out reactions of **1a** and **2a** with certain Lewis bases such as CO, $NMe_3$, $C_5H_5N$, $CH_3CN$, $C_6H_5CN$, $PPh_3$, and $Ph_2PCH_2CH_2PPh_2$ to evaluate the heterolytic behaviour of the bound $H_2$ ligand. Whereas no deprotonation took place in any of these reactions, the bound $H_2$ ligand was substituted by CO, $C_5H_5N$, $CH_3CN$, and $C_6H_5CN$ ligands. Here as well, we rule out the H-atom site exchange *via* heterolysis of $H_2$ followed by the formation of a new dihydrogen ligand involving the hydride ligand and the proton (abstracted from the $H_2$ ligand), which is captured by the Lewis base. The third plausible pathway rendering the three H-atoms equivalent *via* the involvement of a trihydrogen species would mean the requirement of a $\Delta G^{\neq}$ of ~17 kJ mol$^{-1}$ (theoretical).[14] Since we did not observe decoalescence of the $RuH_3$ signal in the $^1$H NMR spectrum up to a temperature of 163 K, it is reasonable to expect that the $\Delta G^{\neq}$ for the exchange process in our case is ≤17 kJ mol$^{-1}$ (approximate $\Delta G^{\neq}$ values were calculated to be 8 and 13 kJ mol$^{-1}$ for **1a** and **2a**, respectively) which points to the involvement of a trihydrogen species.

A closely related *cis*-dihydrogen/hydride complex *cis*,*trans*-[RuH($\eta^2$-$H_2$)$(PCy_3)_2$(bpy)][OTf] reported by Heinekey and his co-workers[3d] exhibits a $d_{HH}$ of ~1.1 Å, which is longer than that in **1a** and **2a**. This is due to the presence of an electron rich $PCy_3$ ligand. In this species as well, no decoalescence of the single resonance for the Ru$H_3$ could be detected even at low temperature. However, another similar system *cis*,*trans*-[RuH($\eta^2$-$H_2$)$(PCy_3)_2(CO)_2$][OTf] showed a low temperature limiting spectrum in the $^{13}$C NMR spectrum at 120 K.[3d] The $\Delta G^{\neq}$ (23.1 kJ mol$^{-1}$) measured for this system is the lowest among the related complexes known. The presence of the π-acceptor, CO ligand in the *trans* position to the $\eta^2$-$H_2$ moiety is responsible for the short H–H bond in this complex, ~0.9 Å. The idea in this case was to have an $\eta^2$-$H_2$ ligand with a large H–H bond energy, which in turn could result in a relatively large and thus measurable $\Delta G^{\neq}$ required for the exchange process.[3d]

It is rather intriguing to note that *cis*,*trans*-[RuH($\eta^2$-$H_2$)-$(PPh_3)_2$(bpy)][OTf] (**1a**) is isolable and is quite stable in the solid state. This observation prompted us to crystallize it and explore its structure (see below). Stability of a dihydrogen complex depends mainly on two bonding components: (i) σ-donation from the filled MO of $H_2$ to an empty d orbital of metal and (ii) back donation of electron density from a filled d orbital of metal to the empty σ* MO of $H_2$. In our case, the unusual stability of **1a** and **2a** could be explained as follows. First, the nitrogen donor present *trans* to the $\eta^2$-$H_2$ ligand optimizes both the components of the M–$H_2$ interaction resulting in a substantially large M–$H_2$ bond energy.[15] Second, the steric bulkiness and suitable arrangement of the phenyl rings of the $PPh_3$ ligands create a specific coordination pocket for the $\eta^2$-$H_2$ ligand. Thus, the $\eta^2$-$H_2$ ligand is protected from substitution by an external nucleophile. The bound $H_2$ ligand, as mentioned above, could not be substituted by sterically bulky ligands such as $PPh_3$ and $Ph_2PCH_2CH_2PPh_2$. However, sterically less demanding ligands were found to substitute the $\eta^2$-$H_2$ ligand.

On the other hand, in an effort to prepare a σ-methane complex of the type *cis*,*trans*-[RuH($\eta^2$-H–$CH_3$)$(PPh_3)_2$(N–N)]-[OTf], we treated the starting dihydride complex *cis*,*trans*-[$RuH_2(PPh_3)_2$(N–N)] (N–N = bpy, **1**; bpm, **2**) with $CH_3OTf$ in the temperature range of 188–203 K. This reaction resulted in methane evolution ($^1$H NMR spectrum: $\delta$ 0.2 ppm, singlet). The spectral details have been deposited in the ESI.† The reaction presumably proceeds through the intermediacy of an $\eta^2$-H–$CH_3$ species which could not be observed; the reason could be that the M–H–C interaction energy falls below the typical range, *i.e.*, 37–63 kJ mol$^{-1}$.[16]

## X-ray crystal structure of *cis*,*trans*-[RuH($\eta^2$-$H_2$)$(PPh_3)_2$(bpy)]-[OTf] (1a)

We obtained single crystals of complex **1a** from a dilute $CH_2Cl_2$ solution by layer diffusion of $Et_2O$ at 273 K under a $H_2$ atmosphere over a period of several days. X-ray diffraction data were collected at 130 K. Selected bond lengths and angles have been summarized in Table 2 and the ORTEP diagram is shown in Fig. 4. The $RuH_3$ fragment and the bpy ligand occupy a

**Table 2** Selected bond lengths (Å) and angles (°) of *cis*,*trans*-[RuH($\eta^2$-$H_2$)$(PPh_3)_2$(bpy)][OTf] (**1a**)

| | | | |
|---|---|---|---|
| H(1a)–H(1b) | 0.99(4) | H(1a)–Ru(1)–H(1b) | 36.6(13) |
| Ru(1)–H(1b) | 1.54(3) | H(1b)–Ru(1)–H(1c) | 62.3(15) |
| Ru(1)–H(1a) | 1.61(3) | H(1c)–Ru(1)–H(1a) | 99.0(14) |
| Ru(1)–H(1c) | 1.55(3) | P(1)–Ru(1)–P(2) | 169.1(1) |
| Ru(1)–N(1) | 2.10(1) | N(1)–Ru(1)–N(2) | 76.31(6) |
| Ru(1)–P(1) | 2.33(1) | | |

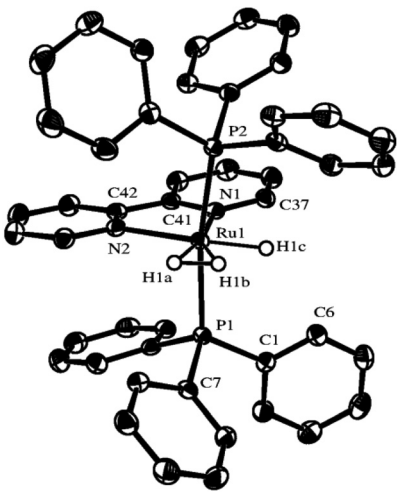



**Fig. 4** ORTEP view of *cis*,*trans*-[RuH($\eta^2$-$H_2$)$(PPh_3)_2$(bpy)][OTf] (**1a**) (thermal ellipsoids are shown at the 50% probability level); counter-ions, solvent molecules, and H-atoms of the bpy and $PPh_3$ ligands are not shown in the diagram for clarity.

single plane around the metal center. The two $PPh_3$ ligands are perpendicular to this plane with a slightly bent conformation (P(1)–Ru(1)–P(2) = 169.1(1)°) towards the $\eta^2$-$H_2$ and hydride ligands. This arrangement creates a sterically encumbered environment around the dihydrogen ligand. The H–H bond length, *d*(H(1a)–H(1b)), is 0.99(4) Å and the H(1a)–Ru(1)–H(1b) angle is about 36.6(13)°, which implies that **1a** is a true $\eta^2$-$H_2$ complex; this is also supported by the partial deuteration studies.[17] The H–H distance in free $H_2$ is 0.74 Å from which it could be calculated that $H_2$ underwent about 34% elongation upon coordination in **1a**. The H(1b) atom of the $H_2$ ligand is about 1.60 Å away from the H(1c) atom, which, in the solid state structure, stays as an isolated hydride ligand with a Ru(1)–H(1c) distance of 1.55(3) Å. Instead of being in linear arrangement, the H(1c)–Ru(1)–N(2) angle is sufficiently bent (168°) away from the coordination site *trans* to the N(1) atom thus creating enough space for accommodating the $\eta^2$-$H_2$ ligand. A straight line is drawn along N(1) and Ru(1) and extrapolated through the mid-point of H(1a)–H(1b) bond, confirming an $\eta^2$ coordination mode of the dihydrogen ligand.

X-ray crystal structure and computational studies of related complexes *cis*,*trans*-[RuH($\eta^2$-$H_2$)($PiPr_3$)$_2$(X)] (X = 2-phenylpyridine (ph-py), benzoquinoline (bq), phenylpyrazole (ph-pz)) have been reported recently.[3e] The $\eta^2$-$H_2$ ligand in those complexes occupies the coordination site that is *trans* to the negatively charged carbon ligand (a strong σ-donor). This typical situation intensifies the back donation effect. Consequently, those complexes were found to be stable under ambient conditions. The H–H distances, $d_{HH}$, in those cases were ~0.9 Å (X-ray).

Earlier, a 16-electron system *cis*,*trans*-[Ru(H)($\eta^2$-$H_2$)($PCy_3$)$_2$(I)] showed unusual geometry around the metal center.[3k] The structural features of the $RuH_3$ moiety of that complex are quite similar to that of **1a**. In general, the hydride and $\eta^2$-$H_2$ ligands of a *cis*-dihydrogen/hydride complex are found to be present in the same plane, mainly due to weak interaction between the hydride ligand and one hydrogen atom of the $\eta^2$-$H_2$ ligand as mentioned earlier. From the structural data of **1a**, it is difficult to say that there is an interaction between the hydride and $\eta^2$-$H_2$ ligands. However, the reason behind all three hydrogen atoms (of **1a**) being in a plane could be the presence of such a kind of weak interaction.

## Conclusions

Protonation of *cis*,*trans*-[$RuH_2(PPh_3)_2$(N–N)] (N–N = bpy, **1**; bpm, **2**) complexes using HOTf resulted in the corresponding dihydrogen complexes *cis*,*trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, **1a**; bpm, **2a**). These derivatives are stable under ambient conditions and, in fact, **1a** was isolable and could be crystallized. The X-ray crystal structure of *cis*,*trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(bpy)][OTf] (**1a**) was established and all the hydrogen atoms were located unambiguously which revealed the presence of a planar $RuH_3$ moiety. In solution, the H-atoms in these two complexes undergo site exchange between the dihydrogen and the hydride ligands with a free energy of activation of ≤17 kJ mol$^{-1}$ and are thought to proceed through the intermediacy of a trihydrogen species. Reaction of *cis*,*trans*-[$RuH_2(PPh_3)_2$(N–N)] complexes with $CH_3OTf$ resulted in methane evolution, and presumably proceeds through the intermediacy of an $\eta^2$-$CH_4$ species, *cis*,*trans*-[RuH($\eta^2$-H–$CH_3$)($PPh_3$)$_2$(N–N)][OTf], which could not be observed spectroscopically.

## Experimental section

### General procedures

All reactions and manipulations were performed under a dry argon or nitrogen atmosphere using standard Schlenk line techniques. Solvents were distilled over respective drying agents prior to use.[18] 2,2′-Bipyridyl (bpy) (Spectrochem), 2,2′-bipyrimidine (bpm), HOTf and $CH_3OTf$ (Aldrich) were used as received. The $^1$H, $^{13}$C (100 MHz), $^{19}$F (376 MHz) and $^{31}$P (160 MHz) NMR spectral data were acquired using an Avance Bruker 400 MHz instrument. The NMR spectral studies of the H/D isotopomers were carried out at the NMR Research Centre, Indian Institute of Science, Bangalore by using an Avance Bruker 500 MHz instrument. All $^1$H and $^{13}$C NMR spectral values noted herein are relative to the signals of the respective deuterated solvents used.[19] The $^{31}$P and $^{19}$F NMR spectral signals are calibrated, respectively, to 85% $H_3PO_4$ (aqueous solution) and $CFCl_3$ as external references at $\delta$ 0.0 ppm. IR spectra of the neat powder samples were recorded using a Bruker ALPHA-P spectrometer working in the 400–4500 cm$^{-1}$ range with a 4 cm$^{-1}$ resolution.

### Synthesis of *cis*,*trans*-[$RuH_2(PPh_3)_2$(N–N)] (N–N = bpy, 1; bpm, 2)

A toluene solution (15 mL) of [$RuH_2(PPh_3)_4$] (800 mg, 0.70 mmol) and N–N bidentate ligand (160 mg, 1.03 mmol bpy; 160 mg, 1.01 mmol bpm) was heated at 368 K for 1 h in an oil bath. The resulting dark green (bpy) or dark black (bpm) colored solution was cooled to room temperature and then diethyl ether (50 mL) was added to cause precipitation. After the mixture was stirred for 10 min (to allow complete dissolution of $PPh_3$), the resulting precipitate was filtered and washed with diethyl ether (3 × 10 mL) to afford *cis*,*trans*-[$RuH_2(PPh_3)_2$(bpy)] (**1**) as dark violet powder and *cis*,*trans*-[$RuH_2(PPh_3)_2$(bpm)] (**2**) as a dark black solid. Yield: complex **1**, 460 mg (84%); complex **2**, 390 mg (70%). Complex **1** was reported previously by Morris and his co-workers.[5] Characterization details of complex **2**: $^1$H NMR (400 MHz, $CD_2Cl_2$, 293 K, $\delta$ ppm): −13.98 (t, *J*(H, P) = 27.0 Hz, 2H, Ru*H*$_2$), 6.51 (t, *J*(H, H) = 5.0 Hz, 2H, bpm: 5,5′-*H*), 7.16–7.41 (m, 30H, P*Ph*$_3$), 8.38 (d, *J*(H, H) = 5.0 Hz, 2H, bpm: 6,6′-*H*), 8.48 (s, 2H, bpm: 4,4′-*H*); $^{13}$C{$^1$H} NMR (100 MHz, $CD_2Cl_2$, 293 K, $\delta$ ppm): 121.1 (s, bpm: 5,5′-*C*), 127.8 (t, *J*(C, P) = 4.0 Hz, $PPh_3$: *meta*-*C*), 128.2 (s, $PPh_3$: *para*-*C*), 133.4 (t, *J*(C, P) = 6.0 Hz, $PPh_3$: *ortho*-*C*), 139.1 (t, *J*(C, P) = 22.0 Hz, $PPh_3$: *ipso*-*C*), 150.3 (s, bpm: 4,4′-*C*), 161.5 (s, bpm: 2,2′-*C*), 162.2 (s, bpm: 6,6′-*C*) (for atomic numbering of the

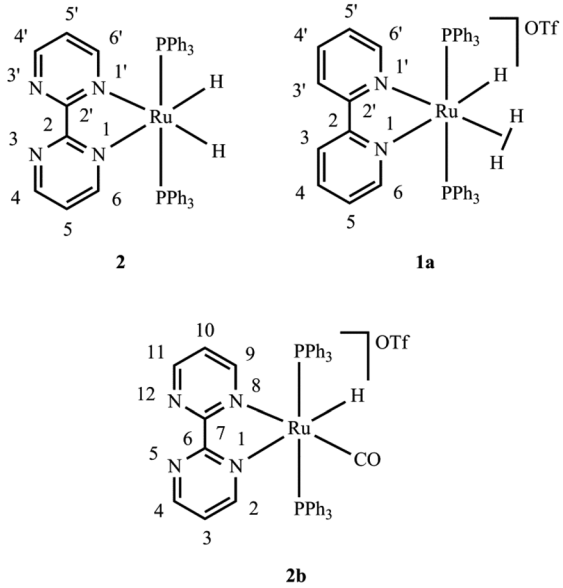



Chart 2

bpm ligand, see Chart 2); $^{31}P\{^1H\}$ NMR (160 MHz, $CD_2Cl_2$, 293 K, $\delta$ ppm): 61.3 (s, *P*$Ph_3$); IR (neat, $cm^{-1}$): 1920 ($\nu_{RuH}$); ESI-MS ($CH_3CN$): *m*/*z* 785 ($M^+$ − H); Anal. Calc. for $C_{44}H_{38}N_4P_2Ru$: C 67.25, H 4.87, N 7.13%; Found: C 67.43, H 4.50, N 6.80%.

### Synthesis of *cis*,*trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, 1a; bpm, 2a)

To a suspension of *cis*,*trans*-[$RuH_2(PPh_3)_2$(N–N)] (100 mg, 0.12 mmol **1**; 100 mg, 0.11 mmol **2**) in $Et_2O$ (10 mL) was added HOTf (12 μL, 0.12 mmol) in an atmosphere of $H_2$ or $N_2$ or Ar. The dark violet (**1**) or dark black (**2**) colored suspension turned yellow (**1a**) or brown (**2a**) within 20 min of stirring. The reaction mixture was left undisturbed for the precipitate to settle down at the bottom of the Schlenk tube. Unreacted HOTf (if any) was removed by washing the resulting solid of complexes **1a** and **2a** with $Et_2O$ (2 × 10 mL). Yield: complex **1a**, 100 mg (90%); complex **2a**, 60 mg (51%).

Characterization details of complex **1a**: $^1H$ NMR (400 MHz, $CD_2Cl_2$, 293 K, $\delta$ ppm): −9.93 (t, *J*(H, P) = 13.0 Hz, 3H, Ru*H*$_3$), 6.91 (t, *J*(H, H) = 5.0 Hz, 2H, bpy: 5,5′-*H*), 7.22–7.36 (m, P*Ph*$_3$), 7.80 (t, *J*(H, H) = 5.0 Hz, 2H, bpy: 4,4′-*H*), 7.81 (d, *J*(H, H) = 5.0 Hz, 2H, bpy: 3,3′-*H*), 8.65 (d, *J*(H, H) = 5.0 Hz, 2H, bpy: 6,6′-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$, 293 K, $\delta$ ppm): 123.4 (s, bpy: 3,3′-*C*), 126.3 (s, bpy: 5,5′-*C*), 128.8 (t, *J*(C, P) = 4.0 Hz, $PPh_3$: *meta*-*C*), 130.4 (s, $PPh_3$: *para*-*C*), 132.8 (t, *J*(C, P) = 21.0 Hz, $PPh_3$: *ipso*-*C*), 133.3 (t, *J*(C, P) = 6.0 Hz, $PPh_3$: *ortho*-*C*), 137.1 (s, bpy: 4,4′-*C*), 154.3 (s, bpy: 2,2′-*C*), 155.7 (s, bpy: 6,6′-*C*) (for atomic numbering of the bpy ligand, see Chart 2); $^{31}P\{^1H\}$ NMR (160 MHz, $CD_2Cl_2$, 293 K, $\delta$ ppm): 48.9 (s, *P*$Ph_3$); $^{19}F$ NMR (376 MHz, $CD_2Cl_2$, 293 K, $\delta$ ppm): −80 (s, C*F*$_3$).

Characterization details of complex **2a**: $^1H$ NMR (400 MHz, $CD_2Cl_2$, 293 K, $\delta$ ppm): −9.94 (t, *J*(H, P) = 12.0 Hz, 3H, Ru*H*$_3$), 7.03 (t, *J*(H, H) = 5.0 Hz, 2H, bpm: 5,5′-*H*), 7.23–7.42 (m, P*Ph*$_3$), 8.78 (d, *J*(H, H) = 5.0 Hz, 2H, bpm: 6,6′-*H*), 8.88 (d, *J*(H, H) = 4.0 Hz, 2H, bpm: 4,4′-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CD_2Cl_2$, 273 K, $\delta$ ppm): 123.6 (s, bpm: 5,5′-*C*), 129.3 (t, *J*(C, P) = 4.0 Hz, $PPh_3$: *meta*-*C*), 130.9 (s, $PPh_3$: *para*-*C*), 131.7 (t, *J*(C, P) = 22.0 Hz, $PPh_3$: *ipso*-*C*), 133.1 (t, *J*(C, P) = 6.0 Hz, $PPh_3$: *ortho*-*C*), 157.4 (s, bpm: 4,4′-*C*), 159.2 (s, bpm: 2,2′-*C*), 162.8 (s, bpm: 6,6′-*C*) (atomic numbering of the bpm ligand of **2a** is the same as that of bpy of **2**); $^{31}P\{^1H\}$ NMR (160 MHz, $CD_2Cl_2$, 293 K, $\delta$ ppm): 48.3 (s, *P*$Ph_3$); $^{19}F$ NMR (376 MHz, $CD_2Cl_2$, 293 K, $\delta$ ppm): −78.7 (s, C*F*$_3$).

### Spin–lattice relaxation time ($T_1$, ms; 400 MHz) measurements

Variable temperature $T_1$ data were obtained for complexes **1a** and **2a** using the standard inversion recovery method at 400 MHz by applying a 180–$\tau$–90° pulse sequence with a 5 K or 10 K temperature interval.[20] Errors in the $T_1$ data were calculated from the fitting of delay time ($\tau$) *vs.* intensity plot. The error in the $T_1$(minimum) was calculated from fitting of the *T vs.* $T_1$ curve.

### Partial deuteration experiments

Partial deuteration of complexes **1a** and **2a** was achieved by bubbling HD gas (generated by a reaction between NaH and $D_2O$) through their $CH_2Cl_2$ solutions for 1 h at 213 K, 273 K, and 288 K. The extent of incorporation of deuterium into the *cis*-$H_2$/hydride complexes was found to be maximum at 288 K.

### Synthesis of *cis*,*trans*-[RuH(CO)($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, 1b; bpm, 2b)

CO gas was bubbled through $CH_2Cl_2$ (10 mL) solutions of *cis*, *trans*-[RuH($\eta^2$-$H_2$)($PPh_3$)$_2$(N–N)][OTf] (N–N = bpy, **1a**; bpm, **2a**) complexes (120 mg, 0.13 mmol **1a**; 120 mg, 0.12 mmol **2a**) at 273 K for 10 min. The solutions were then stirred at room temperature for 30 min to allow for completion of the reaction and then filtered through Celite. The resulting filtrates were concentrated to 1 mL and *cis*,*trans*-[RuH(CO)($PPh_3$)$_2$(N–N)]-[OTf] (N–N = bpy, **1b**; bpm, **2b**) complexes were precipitated by addition of $Et_2O$ (10 mL). Yield, **1b**: 80 mg (64%); **2b**: 62 mg (50%). Complex **1b** was reported by Luther and Heinekey previously.[9c]

Characterization details of *cis*,*trans*-[RuH(CO)($PPh_3$)$_2$(bpm)]-[OTf] complex **2b**: $^1H$ NMR (400 MHz, $CDCl_3$, 293 K, $\delta$ ppm): −11.65 (t, *J*(H, P) = 19.0 Hz, 1H, Ru*H*), 6.67 (t, *J*(H, H) = 5.0 Hz, 1H, bpm: 3-*H*), 7.27–7.39 (m, P*Ph*$_3$), 7.57 (t, *J*(H, H) = 5.0 Hz, 1H, bpm: 10-*H*), 7.75 (d, *J*(H, H) = 5.0 Hz, 1H, bpm: 2-*H*), 8.74 (d, *J*(H, H) = 5.0 Hz, 1H, bpm: 4-*H*), 8.83 (d, *J*(H, H) = 5.0 Hz, 1H, bpm: 11-*H*), 9.24 (d, *J*(H, H) = 5.0 Hz, 1H, bpm: 9-*H*); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$, 293 K, $\delta$ ppm): 124.2 (s, bpm: 3-*C*), 124.5 (s, bpm: 10-*C*), 129.5 (t, *J*(C, P) = 4.0 Hz, $PPh_3$: *meta*-*C*), 131.0 (t, *J*(C, P) = 22.0 Hz, $PPh_3$: *ipso*-*C*), 131.2 (s, $PPh_3$: *para*-*C*), 133.4 (t, *J*(C, P) = 6.0 Hz, $PPh_3$: *ortho*-*C*), 158.0 (s, bpm: 4-*C*), 158.3 (s, bpm: 11-*C*), 159.8 (s, bpm: 6-*C*), 160.0 (s, bpm: 7-*C*), 161.8 (s, bpm: 2-*C*), 162.2 (s, bpm: 9-*C*), 203.5 (t, *J*(C, P) = 14.0 Hz, *C*O) (for atomic numbering of the bpy ligand, see Chart 2); $^{31}P\{^1H\}$ NMR (160 MHz, $CDCl_3$, 293 K, $\delta$ ppm): 45.2 (s, *P*$Ph_3$); $^{19}F$ NMR (376 MHz, $CDCl_3$, 293 K, $\delta$ ppm): −77.9 (s, C*F*$_3$); IR (neat, $cm^{-1}$): 1943 ($\nu_{CO}$); ESI-MS ($CH_3CN$): *m*/*z* 813

(0.3, M − OTf), 590 (0.7, M − OTf − $PPh_3$ + $K^+$), 521 (1.0, M − OTf − $PPh_3$ − H − CO), 364 (0.5, M − OTf − $PPh_3$ − CO − bpm); Anal. Calc. for $C_{46}H_{47}F_3N_4O_9P_2RuS$: C 52.98, H 3.67, N 5.37%; Found: C 52.34, H 3.87, N 6.28%.

### Reaction of *cis*,*trans*-[$RuH_2(PPh_3)_2$(N–N)] (N–N = bpy, 1; bpm, 2) with $CH_3OTf$

A NMR tube provided with a high vacuum stopcock was charged with *cis*,*trans*-[$RuH_2(PPh_3)_2$(N–N)] (20 mg, 0.03 mmol **1**; 20 mg, 0.025 mmol **2**) and $CD_2Cl_2$ (0.5 mL) inside a glove box. $CH_3OTf$ (2.4 μL, 0.04 mmol) was added to the solution under frozen conditions. Then, the NMR tube was evacuated for 30 min before flame sealing. The frozen solid was melted slowly in a low temperature slush bath (183 K, mixture of $Et_2O$ and liq. $N_2$). The sample was then inserted into a NMR probe that was precooled and maintained at 183 K before acquiring the $^1H$ and $^{31}P$ NMR spectral data at that temperature.

### X-ray crystal structure determination of *cis*,*trans*-[$RuH(\eta^2\text{-}H_2)(PPh_3)_2$(bpy)][OTf] (1a)

A single crystal of *cis*,*trans*-[$RuH(\eta^2\text{-}H_2)(PPh_3)_2$(bpy)][OTf] (**1a**) suitable for X-ray diffraction study was chosen carefully under a microscope and coated with paraffin oil to avoid direct exposure to air. The unit cell parameters and the intensity data were collected at 130 K on a Bruker KAPPA APEX II CCD diffractometer equipped with a fine focus Mo Kα X-ray source. The SMART software was used for data acquisition and the SAINT software for data reduction. Absorption corrections were made using the SADABS program. The structure was solved by direct methods and refined using the SHELX programs.[21] All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by difference Fourier synthesis and refined isotropically. Complex **1a** crystallized in $P2_1/n$ space group with four molecules in the unit cell. The complete crystallographic data of complex **1a** are summarized in Table 3.

Table 3 Crystallographic data of *cis*,*trans*-[$RuH(\eta^2\text{-}H_2)(PPh_3)_2$(bpy)]-[OTf] (**1a**)

| | |
|---|---|
| CCDC number | 951511 |
| Formula | $C_{47}H_{41}N_2P_2SO_3F_3Ru{\cdot}CH_2Cl_2$ |
| Formula weight | 1018.81 |
| Colour of crystal | Yellow |
| Temperature (K) | 130(2) |
| Crystal system | Monoclinic |
| Space group | $P2_1/n$ |
| $a$ (Å) | 9.5167(5) |
| $b$ (Å) | 22.4523(12) |
| $c$ (Å) | 21.4491(12) |
| $\beta$ (°) | 96.349(2) |
| $V$ (Å$^3$) | 4555.0(4) |
| $Z$ | 4 |
| $\mu$ (Mo Kα) (cm$^{-1}$) | 6.34 |
| $F$(000) | 2080 |
| Crystal size (mm) | 0.31 × 0.15 × 0.01 |
| Radiation | Mo Kα ($\lambda$ = 0.71073 cm$^{-1}$) |
| Limiting indices | $-11 \le h \le 11$, $-27 \le k \le 27$, $-26 \le l \le 26$ |
| $\theta$ (°) range | 1.81–25.99 |
| Absorption correction | Empirical |
| Refinement method | Full-matrix least squares on $F^2$ |
| Number of data/unique data | 79482/8954 |
| Maximum and minimum transmission | 0.9937 and 0.8277 |
| $R_{int}$ | 0.0362 |
| Number of parameters refined | 731 |
| $R$ (final) [$I > 2\sigma(I)$] | $R_1$ = 0.0265, w$R_2$ = 0.0640 |
| $R$ (all) | $R_1$ = 0.0331, w$R_2$ = 0.0698 |
| GOF | 1.073 |

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