Electronic Supplementary Information

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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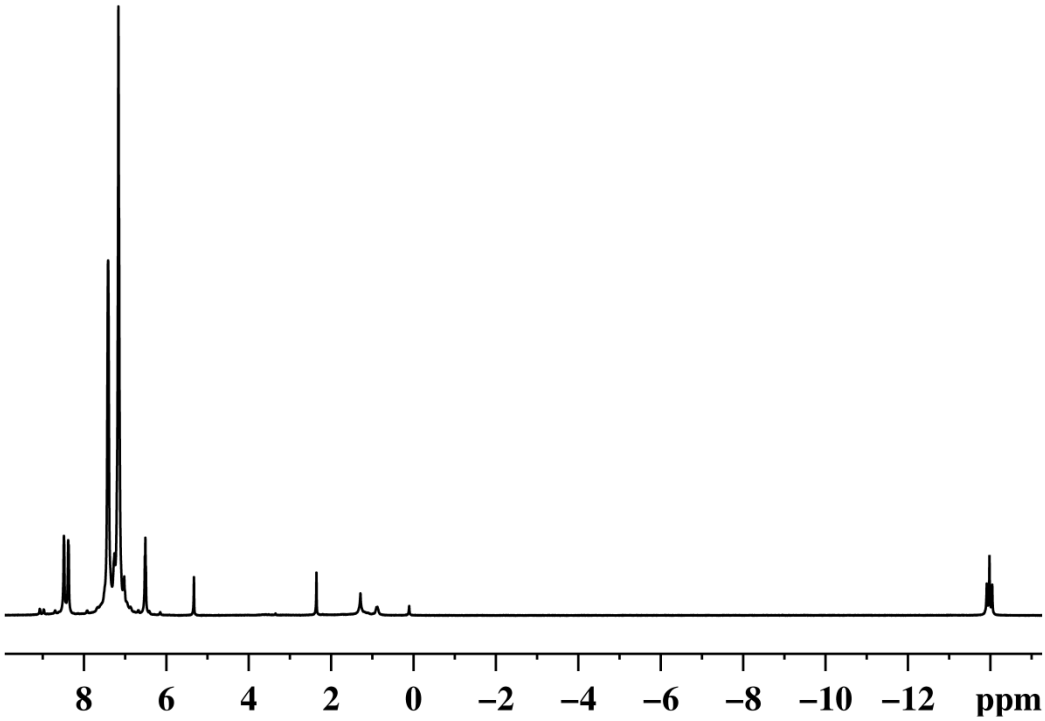

Figure 1. ^{1}H NMR spectrum of *cis, trans*-[$RuH_2(PPh_3)_2(bpm)$] (**2**) in CD_2Cl_2 at room temperature

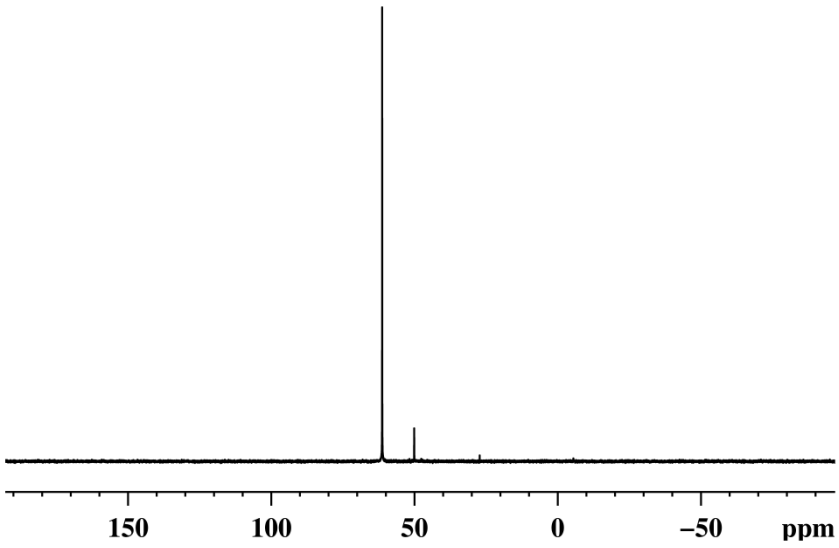

Figure 2. $^{31}P\{^{1}H\}$ NMR spectrum of *cis, trans*-[$RuH_2(PPh_3)_2(bpm)$] (**2**) in CD_2Cl_2 at room temperature

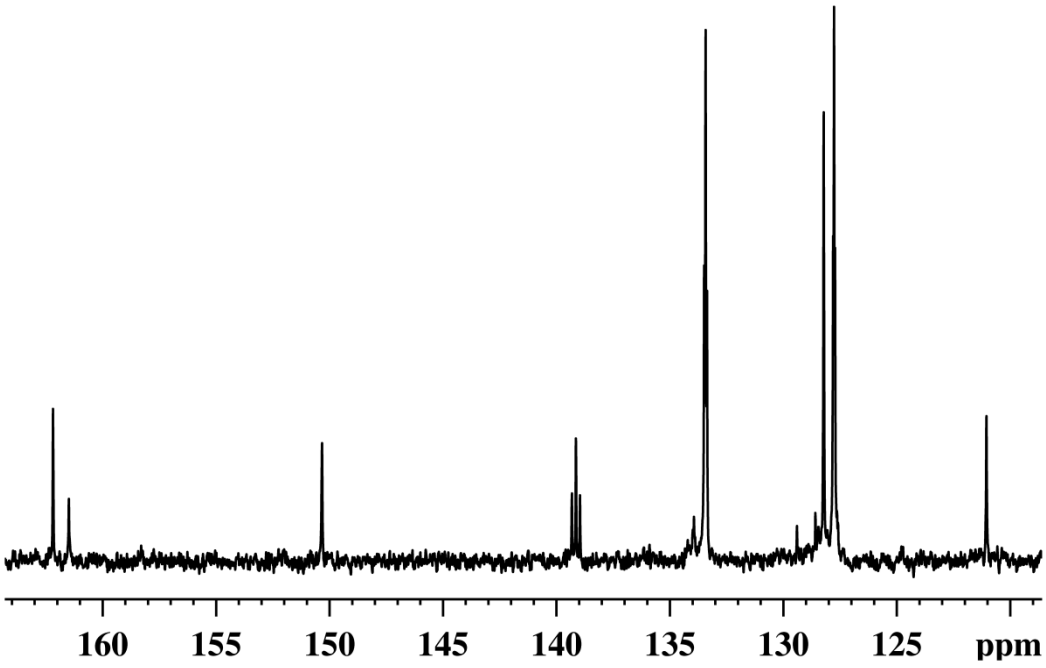

Figure 3. $^{13}C\{^{1}H\}$ NMR spectrum of *cis, trans*-$[RuH_2(PPh_3)_2(bpm)]$ (**2**) in CD_2Cl_2 at room temperature

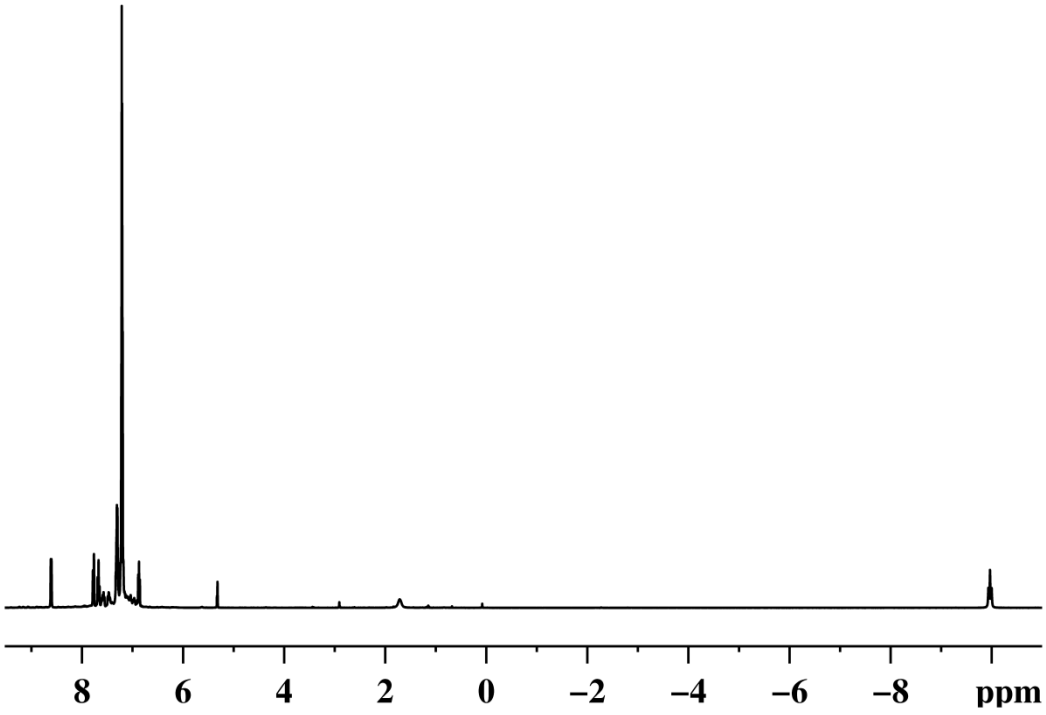

Figure 4. ^{1}H NMR spectrum of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpy)][OTf] (**1a**) in CD_2Cl_2 at room temperature

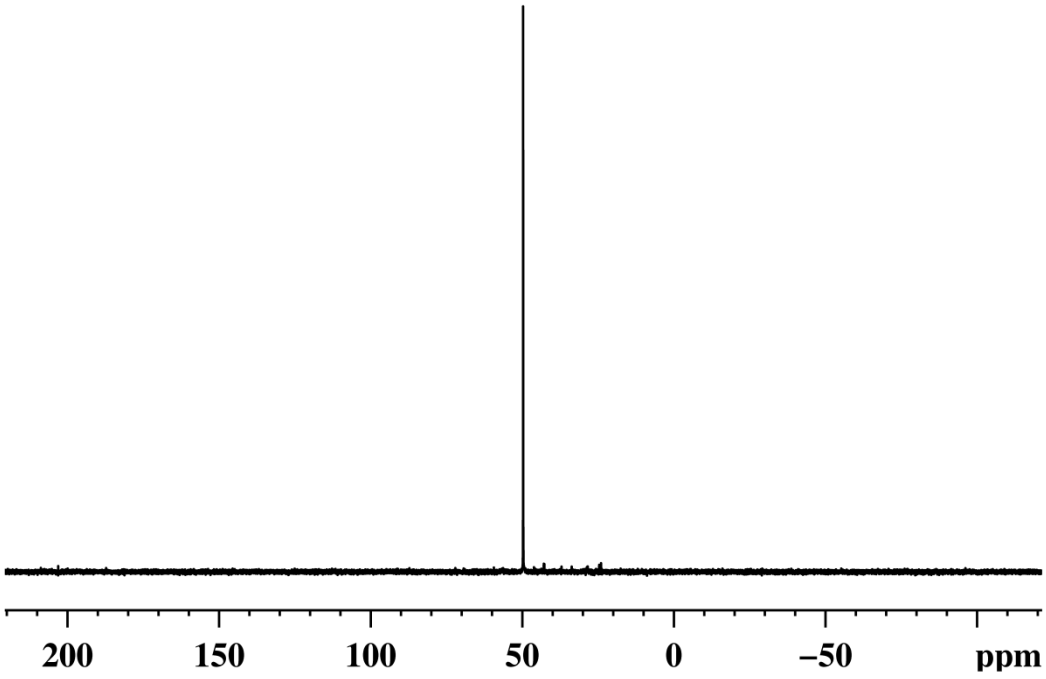

Figure 5. $^{31}P\{^{1}H\}$ NMR spectrum of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpy)][OTf] (**1a**) in CD_2Cl_2 at room temperature

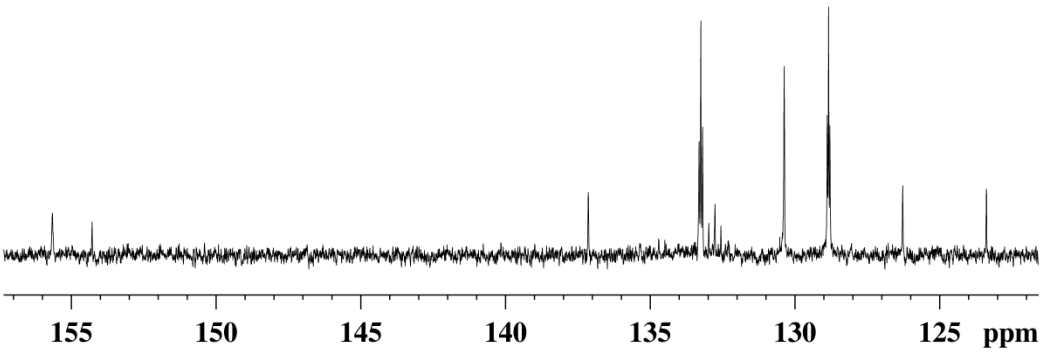

Figure 6. $^{13}C\{^{1}H\}$ NMR spectrum of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpy)][OTf] (**1a**) in CD_2Cl_2 at room temperature

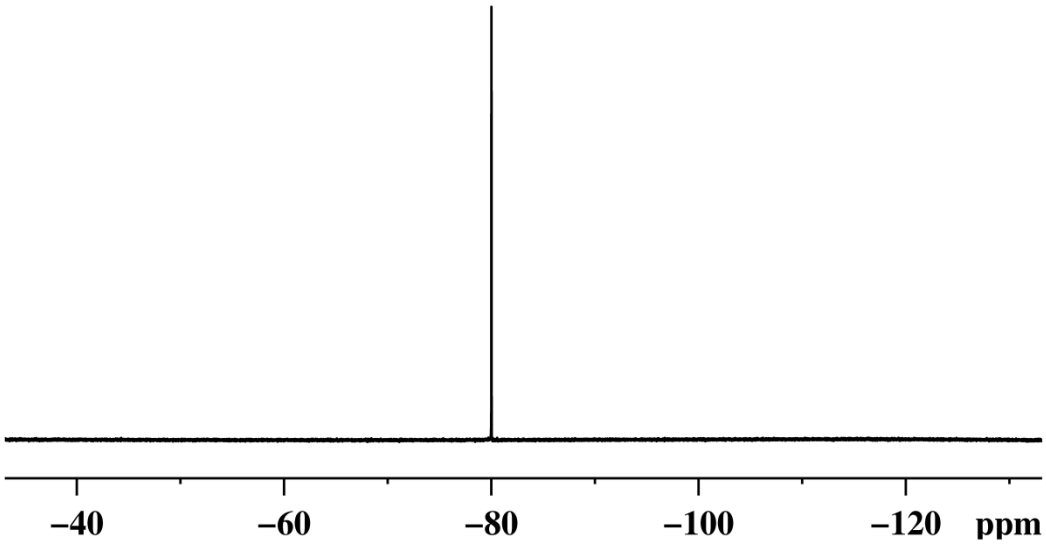

Figure 7. ^{19}F NMR spectrum of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpy)][OTf] (**1a**) in CD_2Cl_2 at room temperature

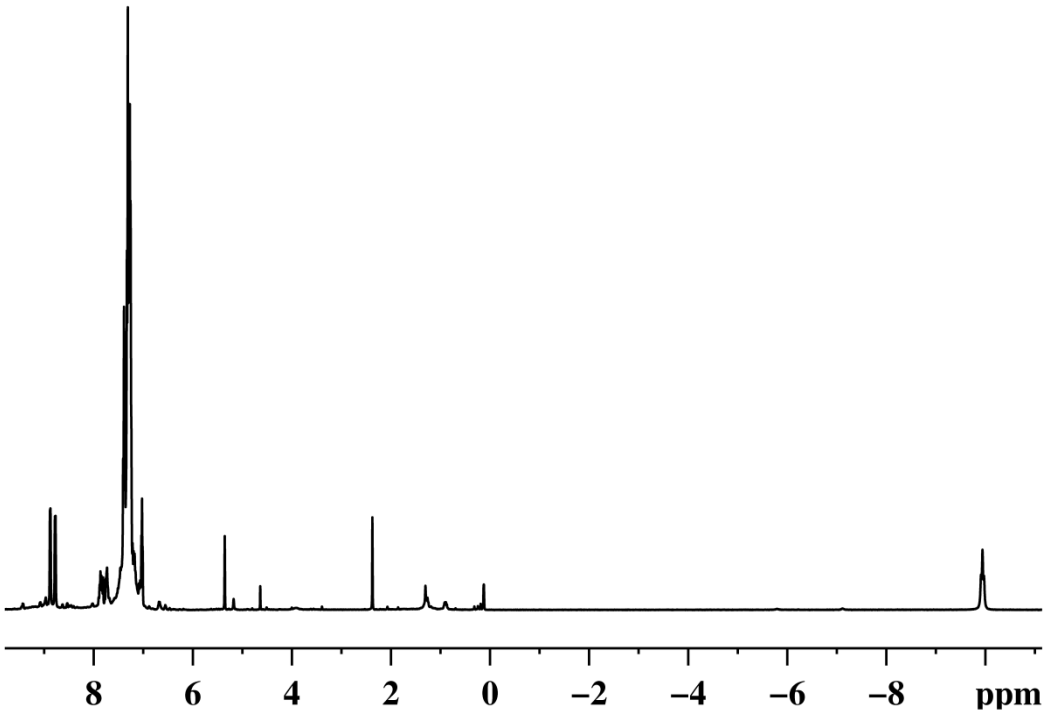

Figure 8. ^{1}H NMR spectrum of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpm)][OTf] (**2a**) in CD_2Cl_2 at room temperature

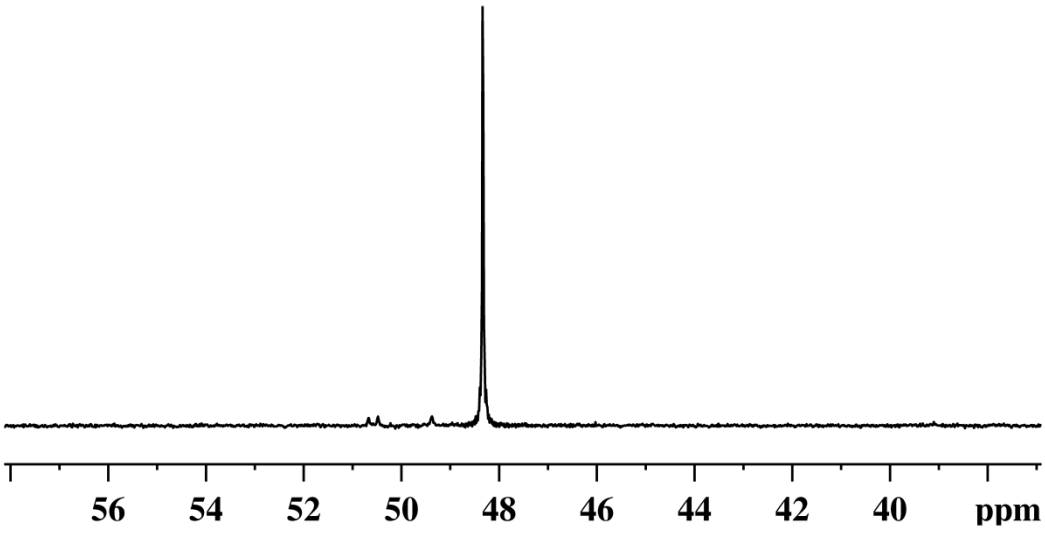

Figure 9. $^{31}P\{^{1}H\}$ NMR spectrum of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpm)][OTf] (**2a**) in CD_2Cl_2 at room temperature

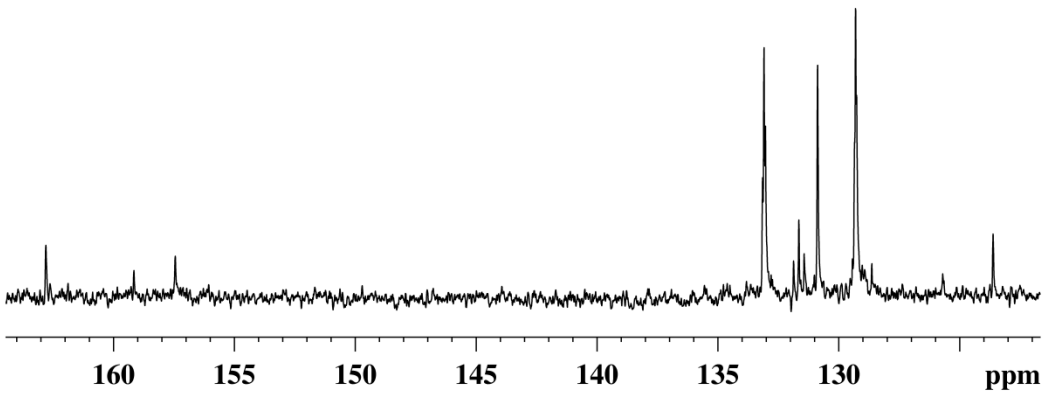

Figure 10. $^{13}C\{^{1}H\}$ NMR spectrum of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpm)][OTf] (**2a**) in CD_2Cl_2 at room temperature

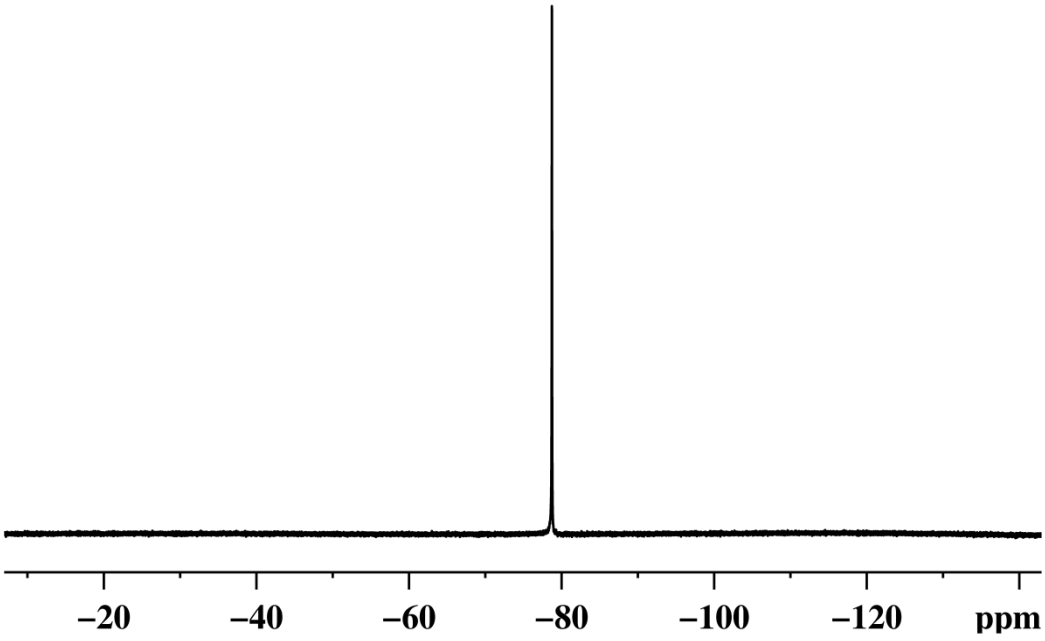

Figure 11. ^{19}F NMR spectrum of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpm)][OTf] (**2a**) in CD_2Cl_2 at room temperature

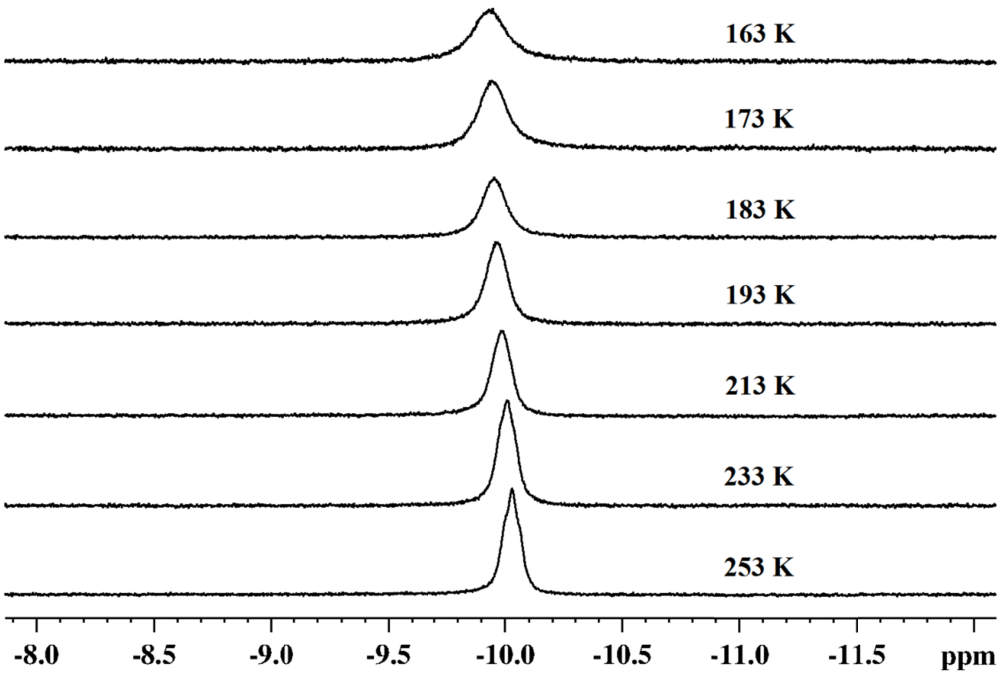

Figure 12. Variable temperature ^{1}H NMR spectral stack plot (hydride region) of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpy)][OTf] (**1a**) in $CDCl_2F/CDClF_2$.

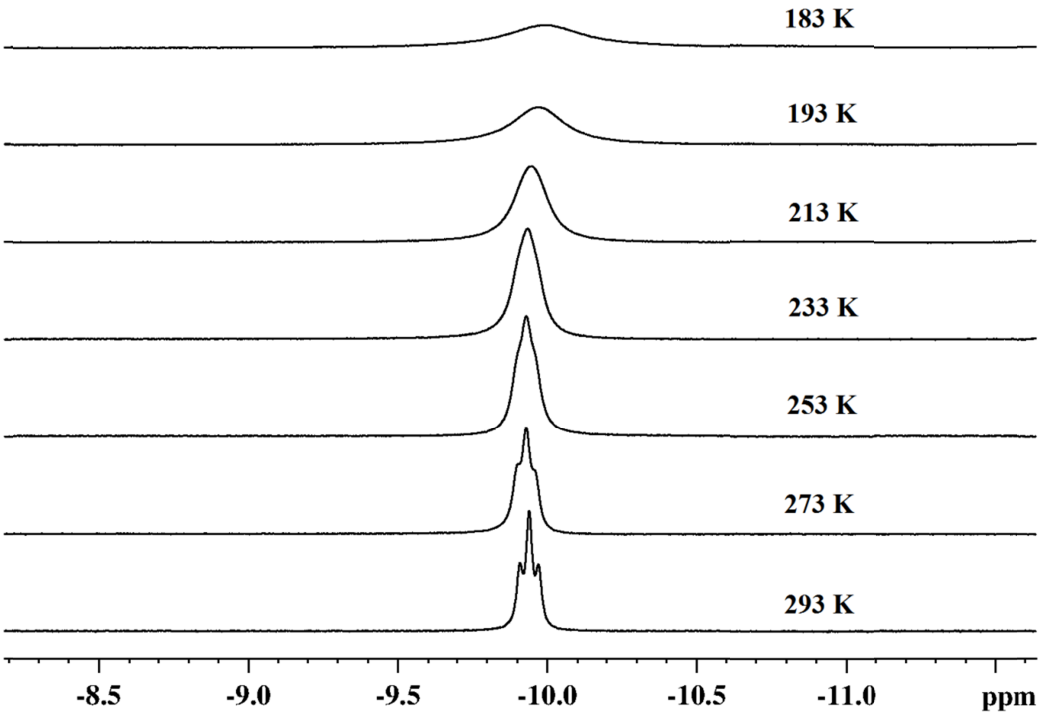

Figure 13. Variable temperature ^{1}H NMR spectral stack plot (hydride region) of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpm)][OTf] (**2a**) in CD_2Cl_2.

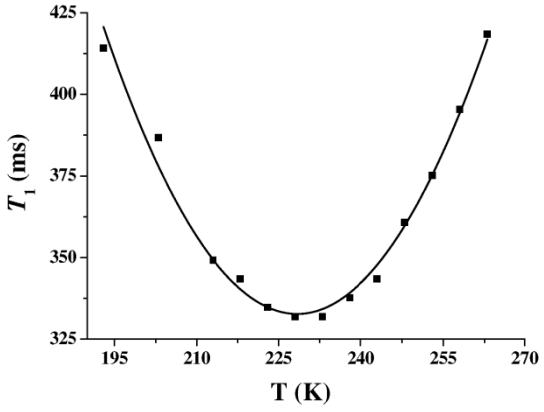

Figure 14. Variable temperature T_1 measurements of *cis, trans*-[RuH_2(**P**Ph_3)$_2$(bpy)] (**1**) in CD_2Cl_2 at 400 MHz.

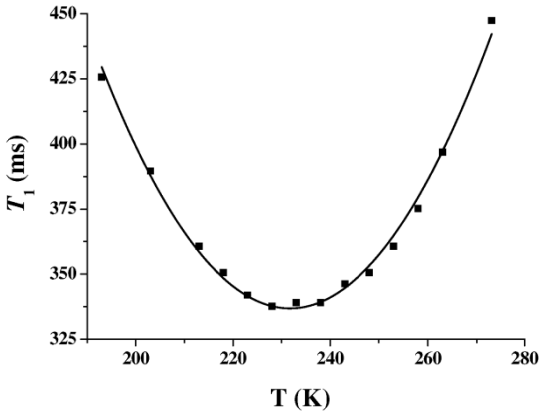

Figure 15. Variable temperature T_1 measurements of *cis, trans*-[$RuH_2(PPh_3)_2(bpm)$] (**2**) (right) in CD_2Cl_2 at 400 MHz.

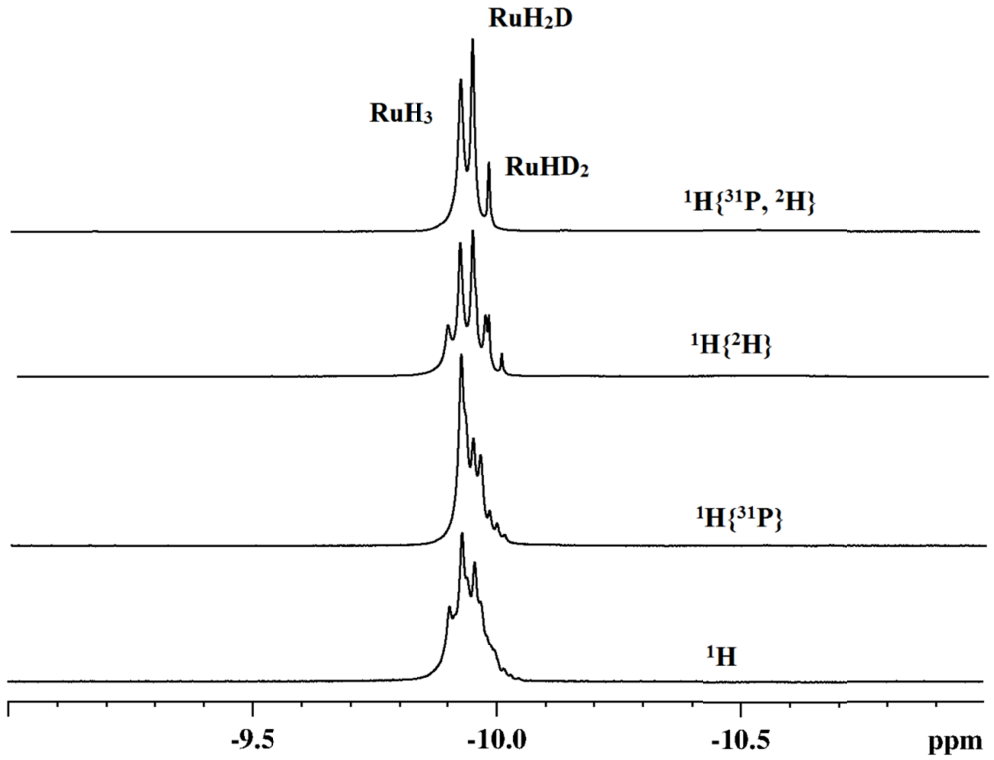

Figure 16. ^1H NMR spectra (hydride region) of the isotopomers of *cis, trans*-[$RuH(\eta^2\text{-}H_2)(PPh_3)_2(bpy)$][OTf] (**1a**) in CD_2Cl_2 at 296 K; acquired using a 500 MHz instrument.

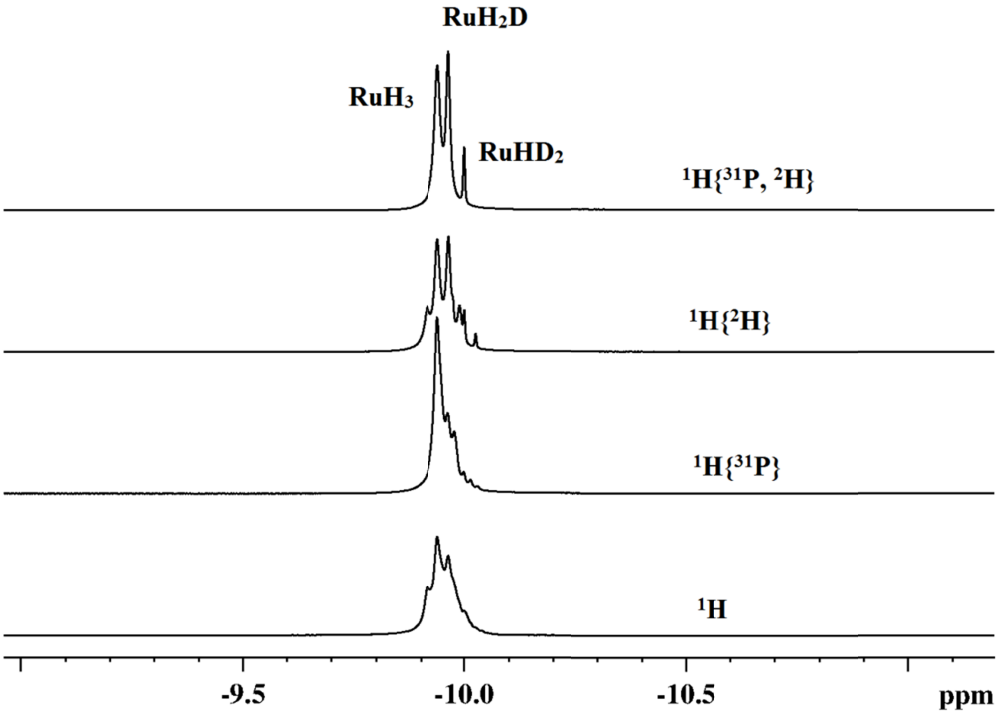

Figure 17. ^{1}H NMR spectra (hydride region) of the isotopomers of *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpm)][OTf] (**2a**) in CD_2Cl_2 at 296 K; acquired using a 500 MHz instrument.

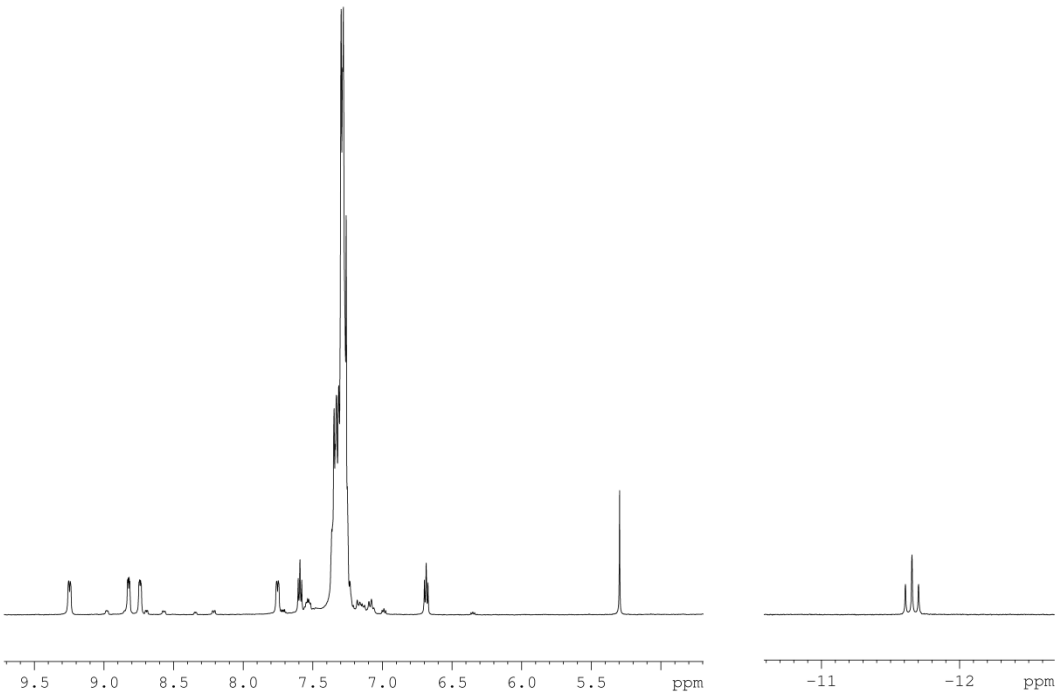

Figure 18. ^{1}H NMR spectrum of *cis, trans*-[RuH(CO)(PPh_3)$_2$(bpm)][OTf] (**2b**) in $CDCl_3$ at room temperature

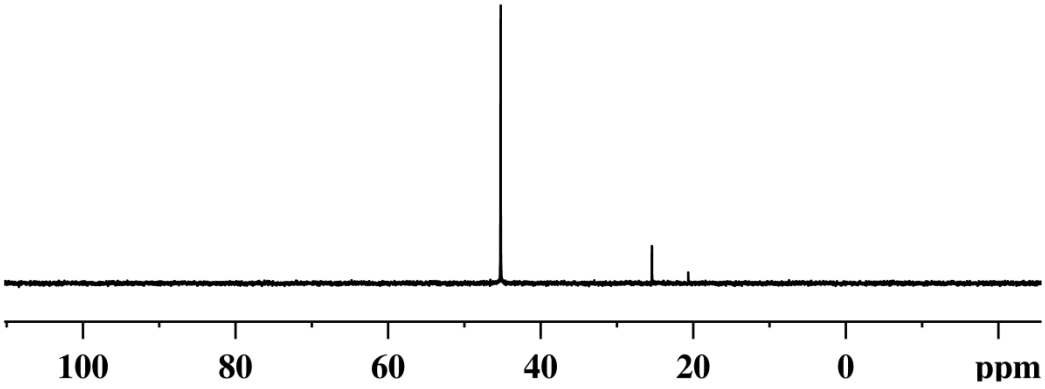

Figure 19. $^{31}P\{^{1}H\}$ NMR spectrum of *cis, trans*-[RuH(CO)(PPh_3)$_2$(bpm)][OTf] (**2b**) in $CDCl_3$ at room temperature

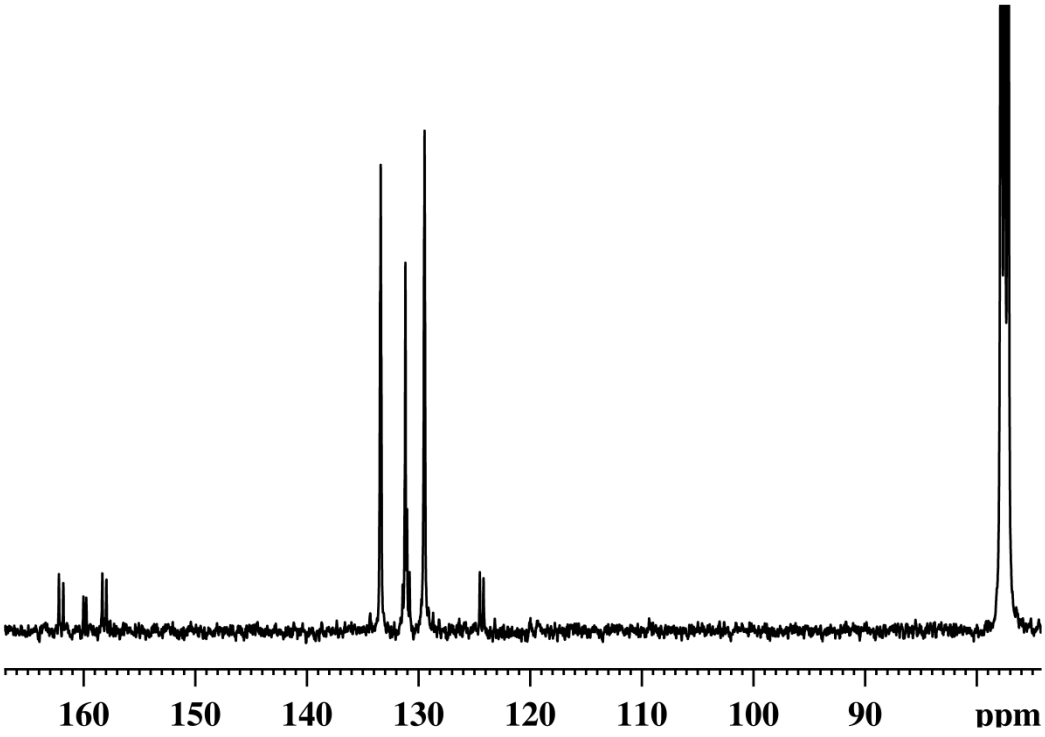

Figure 20. $^{13}C\{^{1}H\}$ NMR spectrum of *cis, trans*-[RuH(CO)(PPh_3)$_2$(bpm)][OTf] (**2b**) in $CDCl_3$ at room temperature

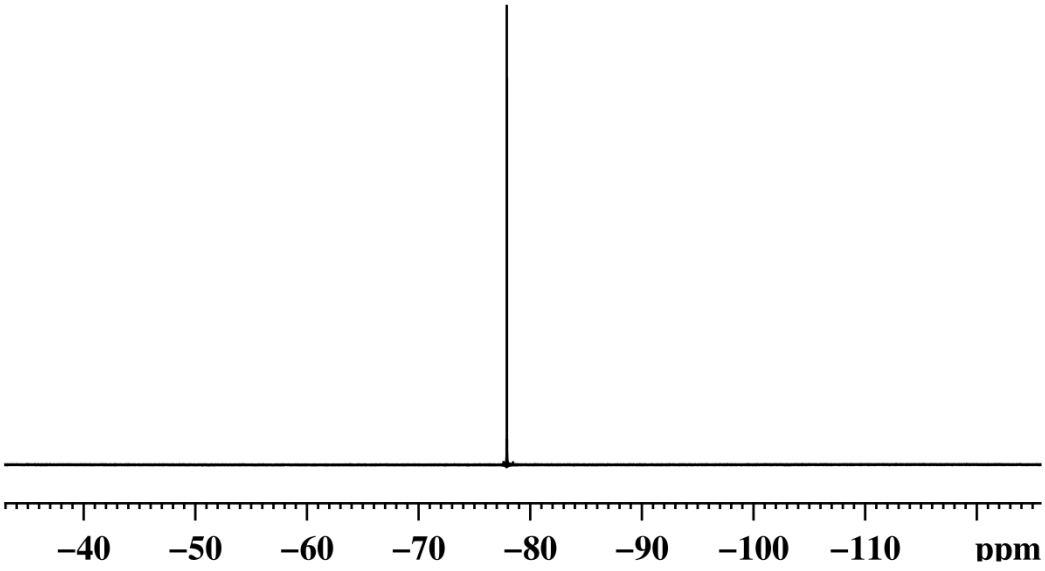

Figure 21. ^{19}F NMR spectrum of *cis, trans*-[RuH(CO)(PPh_3)$_2$(bpm)][OTf] (**2b**) in $CDCl_3$ at room temperature

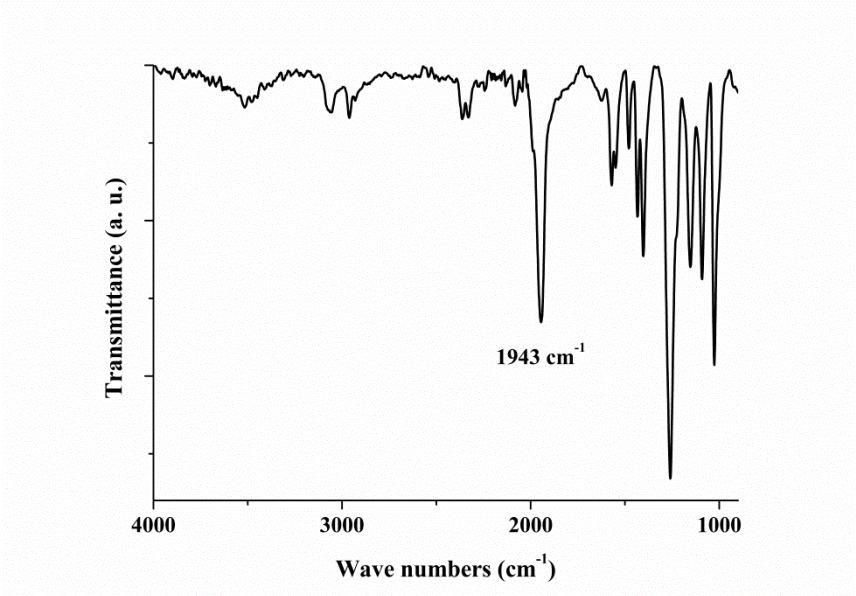

Figure 22. IR spectrum of *cis, trans*-[RuH(CO)(PPh_3)$_2$(bpm)][OTf] (**2b**)

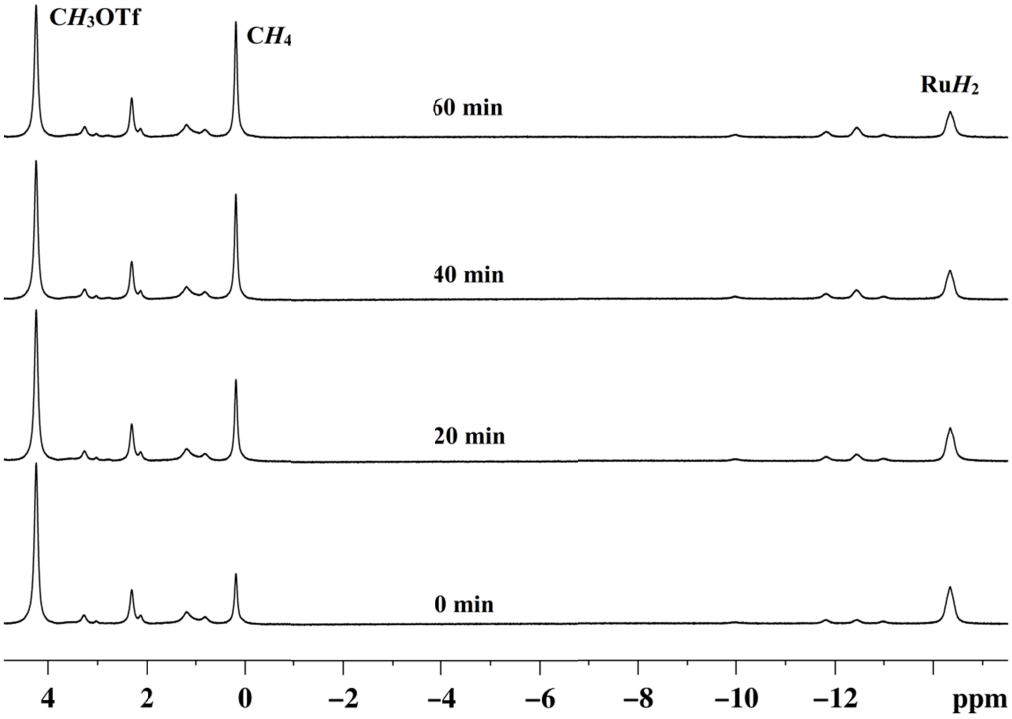

Figure 23. ^{1}H NMR spectral stack plot of the reaction between *cis, trans*-$[RuH_2(PPh_3)_2(bpm)][OTf]$ (**2**) and CH_3OTf in CD_2Cl_2 at 203 K.

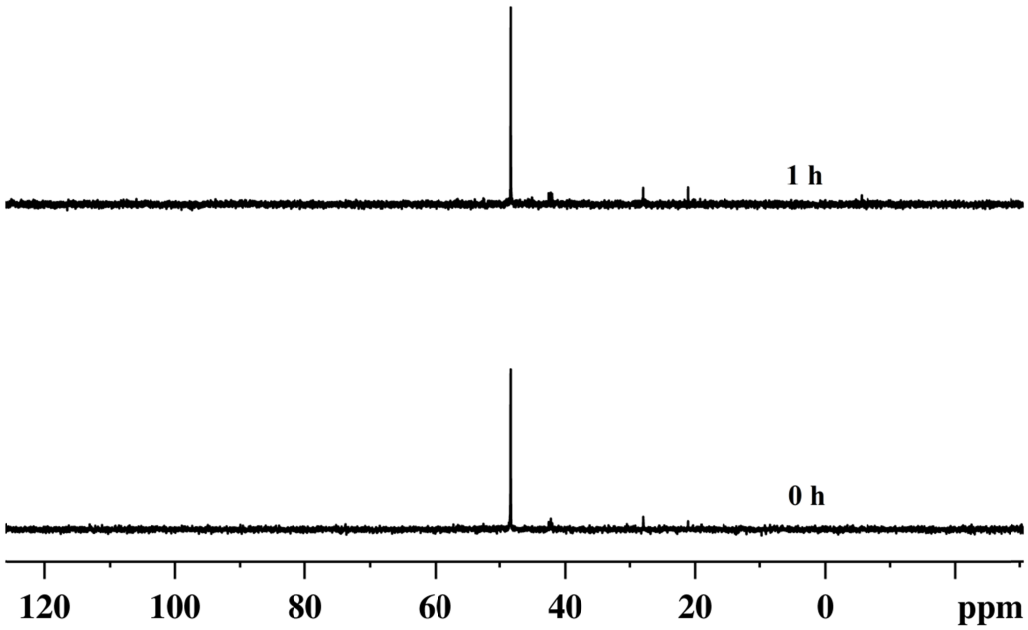

Figure 24. $^{31}P\{^{1}H\}$ NMR spectral stack plot of the reaction between *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpm)][OTf] (**2a**) and Et_3N (2 equiv) in CH_2Cl_2 ($CDCl_3$ external lock) at room temperature

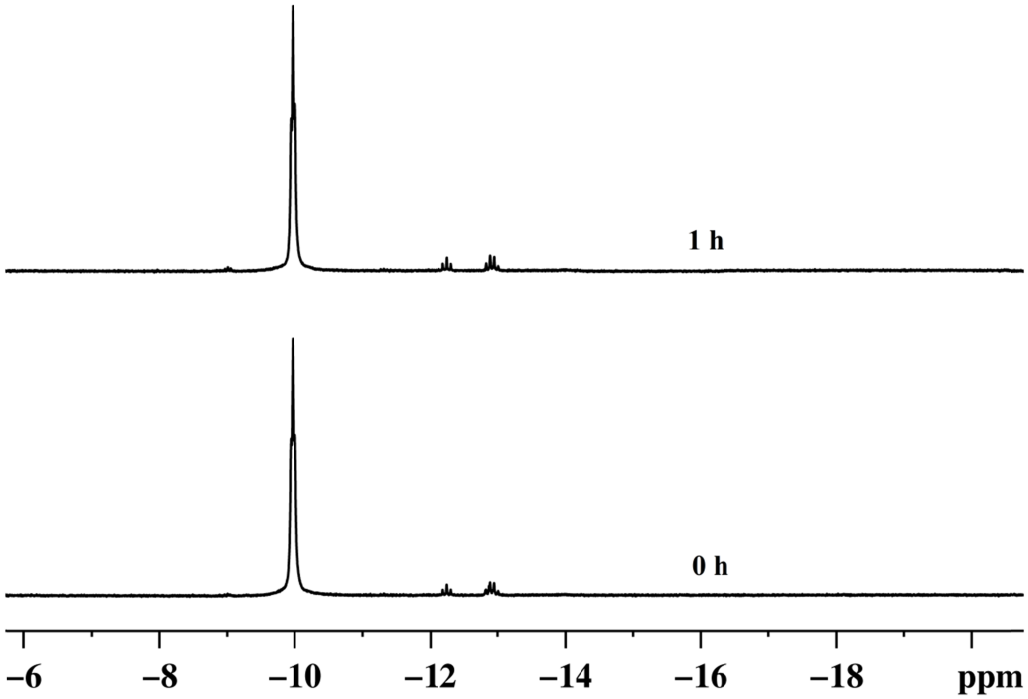

Figure 25. ^{1}H NMR spectral stack plot of the reaction between *cis, trans*-[RuH(η^2-H_2)(PPh_3)$_2$(bpm)][OTf] (**2a**) and Et_3N (2 equiv) in CH_2Cl_2 ($CDCl_3$ external lock) at room temperature

Calculation of $\Delta G^{\neq}$ of the exchange process in 1a and 2a

Rate constant of the exchange process above T_C is written as

$K_a = [\pi (\Delta v)^2] / 2 (W_{½} - W^0_{½})$

Ref: Belci, M. *Basic ^{1}H and ^{13}C NMR Spectroscopy*, Elsevier **2005**, p213.

where,

K = Rate constant of the scrambling process

Δv = Chemical shift difference between dihydrogen and hydride in Hz

$W_{½}$ = Full width at half maxima of the scrambling system

$W^0_{½} = W_{½}$ when there is no scrambling (reference)

T_C = Coalescence temperature

$K_a = [\pi (\Delta v)^2] / 2 (W_{½} - W^0_{½})$

$= A\ e^{-(\Delta G^{\neq})/RT}$ [Arrhenius equation, A = Frequency factor]

Simplification gives

$\ln (W_{½} - W^{0}_{½}) = (\Delta G^{\neq}/R)(1/T) + C$ [C = Constant]

We assume that $W^{0}_{1/2}$ of the hydride signal of **1a** and **2a** are same as that of **1** and **2** respectively in their ^{1}H NMR spectrum.

$W^{0}_{½}$= 30 Hz (FWHM of hydride signal of **1** or **2**)

The above assumption is required since we did not observe decoalescence of the RuH_3 signal of **1a** and **2a**.

$\ln (W_{½} - 30) = [\Delta G^{\neq}\ (\text{approx})/R][1/T] + C$

Slope of $\ln (W_{½} - 30)$ vs $1/T$ plot will give $\Delta G^{\neq}$(approx)

Assumptions:

1. Free energy of activation does not change with temperature
2. Change in line broadening is a measure of change in rate of the exchange process

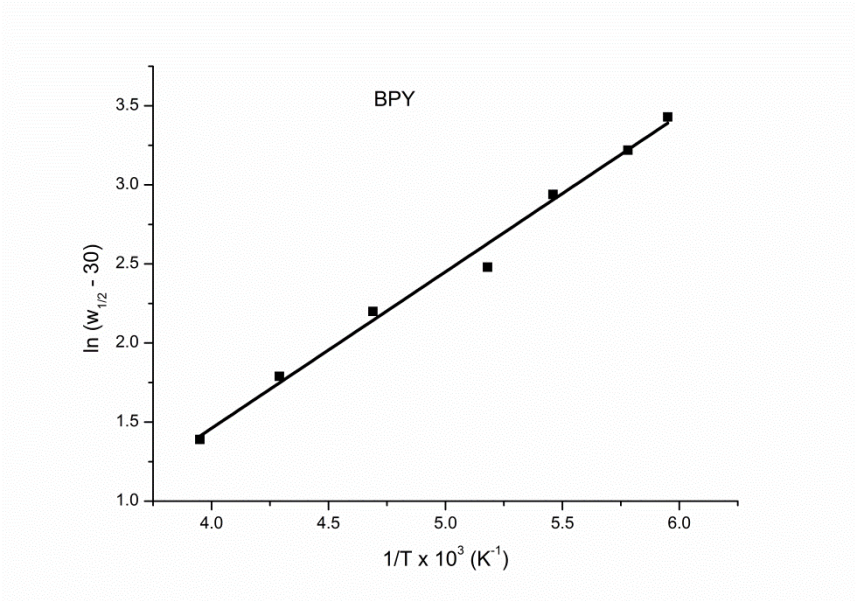

Figure 26. $\ln (W_{½} - 30)$ vs $1/T$ plot of **1a**

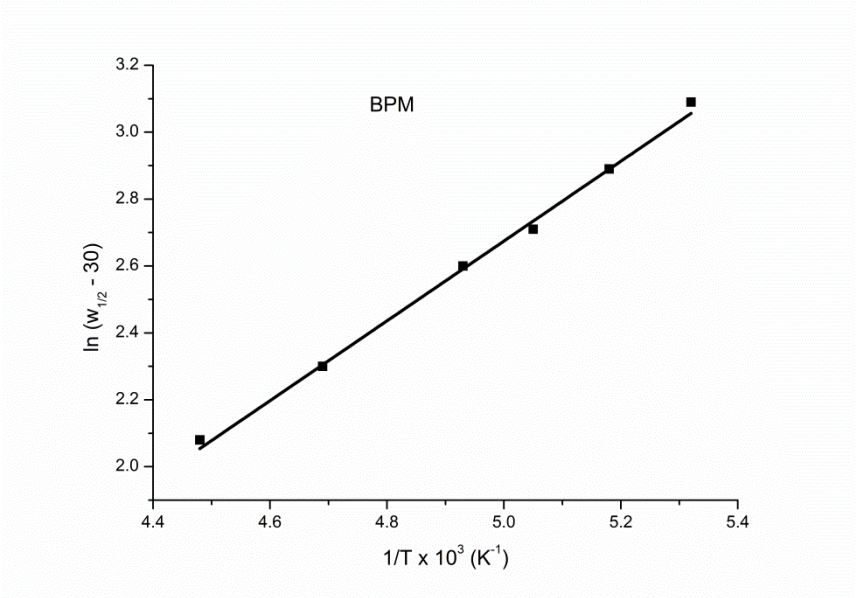

Figure 27. ln ($W_{½}$ – 30) vs 1/T plot of **2a**

Calculation of T_1(min) of the H_2 ligand of 1a and 2a

The relaxation rate (R_{H3}) of the RuH_3 moieties of complexes **1a** and **2a** could be written as the weighted average of that of the individual hydride and η^2-H_2 ligands i.e.,

$R_{H3} = (R_H + 2R_{H2})/3$

where, R_H = relaxation rate of the hydride ligand caused by rest of the molecule, and R_{H2} = relaxation rate of the η^2-H_2 ligand. R_{H2} has two components: (i) R_M i.e., mutual relaxation of the two H-atoms of the η^2-H_2 ligand and (ii) R_R i.e., relaxation of the η^2-H_2 ligand caused by rest of the molecule. Among these two components, R_M is actually related to T_1(min) of the η^2-H_2 ligand, i.e., $T_1(H_2)$.

Therefore, $R_{H3} = \{R_H + 2(R_M + R_R)\}/3$

Or, $R_{H3} = (3R_H + 2R_M)/3$ [since, $R_R \sim R_H$]

Now, we know that $T_1 = (1/R)$, therefore, the above equation can be written in terms of T_1(min) of the η^2-H_2 ligand as,

$1/T_1(H_2) = (3/2)\{1/T_1(RuH_3) - 1/T_1(RuH_2)\}$

where, $T_1(RuH_3)$ is the T_1(min) of complexes **1a** and **2a**, $T_1(RuH_2)$ is the T_1 of complexes **1** and **2** at respective temperatures (183 K for **1a** and 191 K for **2a**).