

Supporting information

Competing pathways in the photochemistry of $\text{Ru}(\text{H})_2(\text{CO})(\text{PPh}_3)_3$

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Table of Contents

Figure S1.	^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of 1 in C_6D_6 .	S3
Figure S2.	Pulse sequences used in the laser pump-NMR probe experiments.	S3
	$T_{1(\text{min})}$ relaxation	S4
Figure S3.	$^1\text{H}\{^{31}\text{P}\}$ EXSY experiments of a solution of 1 in C_6D_6 under H_2 pressure.	S5
Figure S4.	$^{31}\text{P}\{^1\text{H}\}$ EXSY experiments of a solution of 1 in C_6D_6 .	S6
Figure S5.	Hydride region of the ^1H spectrum of 1 in C_6D_6 after <i>in-situ</i> photolysis under 4 bar of H_2 at 298 K.	S6
Figure S6.	Hydride region of the ^1H NMR spectrum of 1 after broadband photolysis in neat $\text{C}_5\text{H}_5\text{N}$.	S7
Figure S7.	Hydride region of the ^1H NMR spectrum of 1 after broadband photolysis in neat $\text{C}_5\text{H}_5\text{N}$.	S7
Figure S8.	^1H NMR spectrum of a solution of 1 in C_6D_6 in the presence of excess pyridine under $p\text{-H}_2$ pressure after 16 laser shots.	S8
Figure S9.	^1H - ^1H 2D-COSY NMR spectrum of the hydride region of a C_6D_6	S9

	solution of 1 with 10 folds excess pyridine under <i>p</i> -H ₂ pressure.	
Figure S10.	¹ H- ¹⁵ N 2D-HMQC NMR spectrum of the hydride region of a C ₆ D ₆ solution of 1 with 10 folds excess ¹⁵ N-pyridine under <i>p</i> -H ₂ pressure.	S9
	AsPh ₃ experiments with multiple laser shots	S10
Figure S11.	Hydride region of the hyperpolarised ¹ H and { ³¹ P} ¹ H spectrum of a C ₆ D ₆ solution of 1 under <i>p</i> -H ₂ in the presence of excess AsPh ₃ .	S11
Figure S12.	Schemes for possible mechanisms of isomerization.	S12
Figure S13.	FTIR spectrum of 1 in toluene at 220 K.	S13
Figure S14.	TRIR difference spectra obtained in the range (a) 1-20 ns and (b) 45 ns - 28 μs after 355 nm laser flash of a solution of 1 in benzene- <i>d</i> ₆ with added pyridine (ca. 10 ⁻² M).	S13
Figure S15.	FTIR spectrum of 1 (1940 cm ⁻¹) and a mixture of 1 and 4-CN in C ₆ D ₆ solution formed by laser photolysis (355 nm) of a solution of 1 with excess pyridine- <i>d</i> ₅ . The product spectrum is presented as a difference with respect to the initial spectrum with peak at 1921 cm ⁻¹ .	S14
Figure S16.	DFT Calculated structures with M06/LACVP(d) functional with principal bond lengths, angles, and CO-stretching frequencies.	S15
Table 1	Calculated and observed ν(CO) values for pyridine complexes	S18

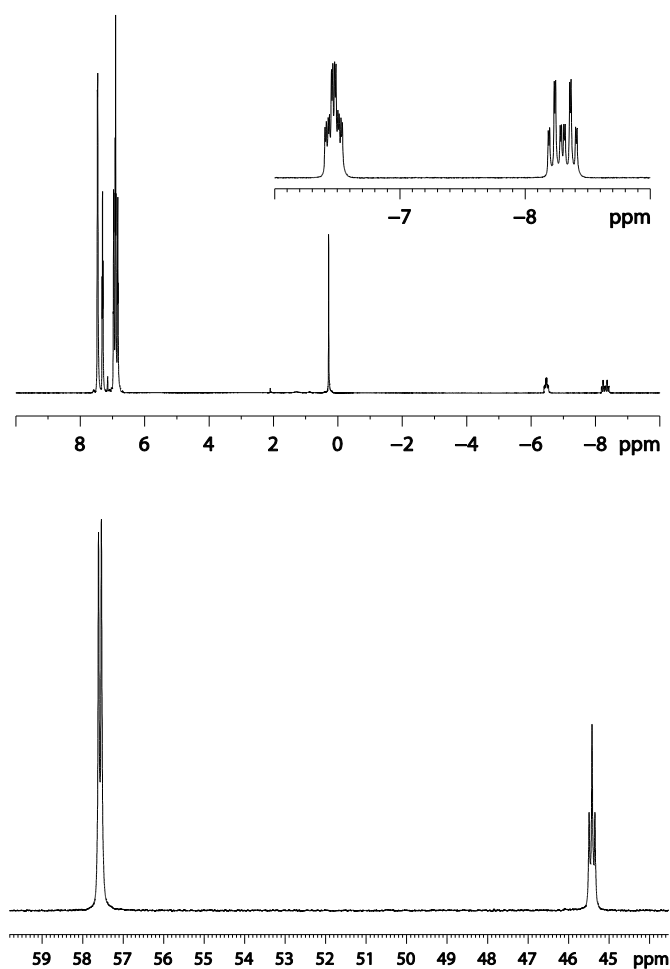


Figure S1. Top: ^1H NMR spectrum of **1** in C_6D_6 . Bottom: $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **1** in C_6D_6 .

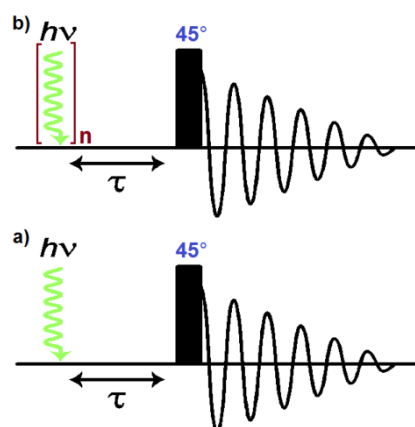


Figure S2. Pulse sequences used in the laser pump-NMR probe experiments. (a) In the single-shot experiments, a single laser pulse (5 ns) is followed by a delay (τ) for evolution of the chemical system before observation is achieved through the application of a *rf* pulse. (b)

The multiple laser pulse experiments apply a train of laser pulses, separated by an additional delay of 100 ms between each of the n pulses

$T_{1(\min)}$ relaxation

$T_{1(\min)}$ was measured by conducting inversion recovery experiments on the dihydrogen resonances over a range of temperatures. At $T_{1(\min)}$, d_{HH} can be calculated from the value of $T_{1(\min)}$, where ν is the spectrometer frequency in MHz and T_1 is in s (equation 1).¹⁻³

$$d_{HH}(\text{\AA}) = 5.815 \sqrt[6]{T_{1\min}/\nu} \quad \text{Equation 1}$$

The relaxation rate of the dihydrogen ligand is affected by all other NMR active nuclei close by. If the system has a dihydrogen ligand that is not exchanging rapidly with any hydride ligands, the bond length can be corrected for the other NMR active species present.¹ If the hydride and dihydrogen ligands are undergoing fast exchange, the observed relaxation rate is a weighted average of the relaxation rates at the different environments.^{2,3} A further complication occurs if the H_2 unit can rotate internally during the molecular tumbling period. In this case the spinning correction cannot distinguish between the rotation of the dihydrogen ligand and the molecular tumbling⁴ and equation 2 should be used.

$$d_{HH}(\text{\AA}) = 5.815 \sqrt[6]{\frac{1}{4}} \sqrt[6]{\frac{T_{1\min}}{\nu}} = 4.611 \sqrt[6]{\frac{T_{1\min}}{\nu}} \quad \text{Equation 2}$$

We corrected for the relaxation of the hydride ligands by assuming that their relaxation time was the same as that for the hydride ligands of **1**, which we measured as 0.39 s at 400 MHz for the resonance at δ -8.19. The measured relaxation time for **2** was 0.035 ± 0.002 s. The relaxation rates R_{hydride} for **1** and R_{obs} for **2** are 2.56 and 28.6 s^{-1} , respectively. The observed relaxation rate is given by:

$$R_{\text{obs}} = 0.5(R_{\text{hydride}} + R_{H_2}) \quad \text{Equation 3}$$

yielding a value of R_{H_2} of 54.6 s^{-1} and a corrected value $T_{1(\text{corr})}$ of 0.018 s. If eq 1 applies, d_{HH} is calculated as 1.1 Å, while if eq 2 applies, d_{HH} is estimated as 0.87 Å.

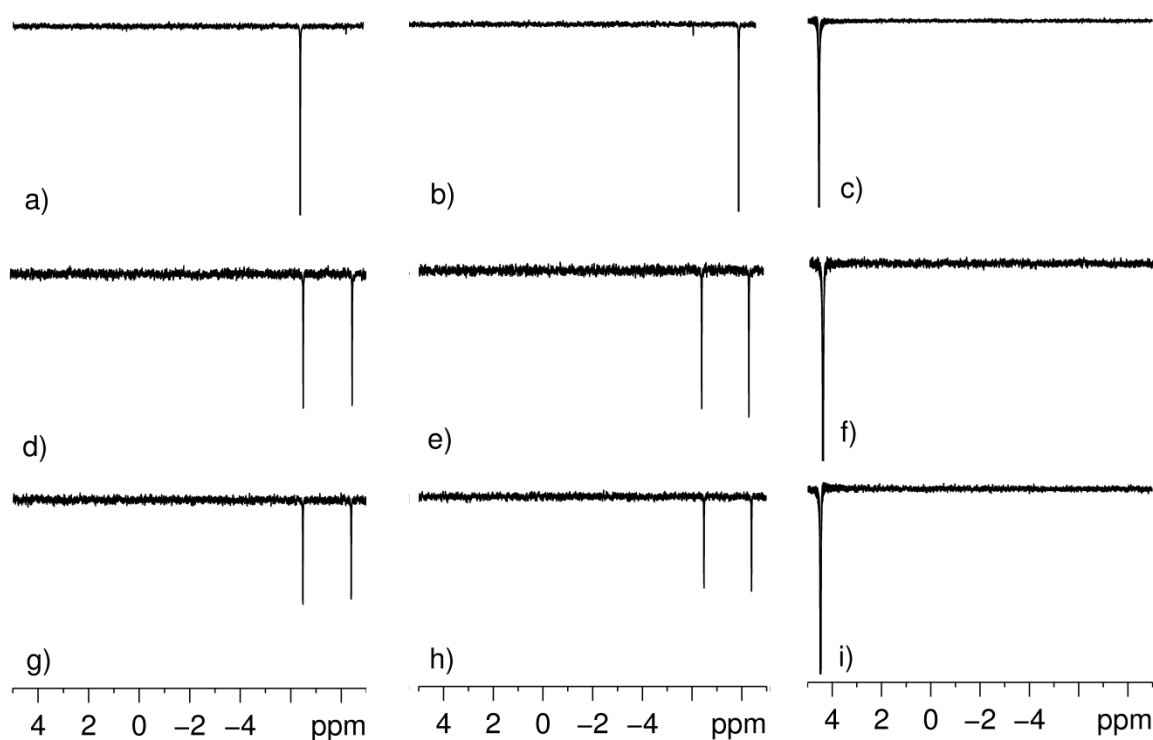


Figure S3: $^1\text{H}\{^{31}\text{P}\}$ EXSY experiments of a solution of **1** in C_6D_6 under H_2 pressure. All the spectra have been recorded at a mixing time of 300 ms. a) Exciting the signal at $\delta - 6.47$ at 298 K; b) Exciting the signal at $\delta - 8.30$ at 298 K; c) Exciting the signal of dissolved H_2 at $\delta 4.46$ at 298 K; d) Exciting the signal at $\delta - 6.47$ at 333 K; e) Exciting the signal at $\delta - 8.30$ at 333 K; f) Exciting the signal at $\delta 4.46$ at 333 K; g) Exciting the signal at $\delta - 6.47$ at 333 K in the presence of 20 eq of PPh_3 ; h) Exciting the signal at $\delta - 8.30$ at 333 K in the presence of 20 eq of PPh_3 ; i) Exciting the signal at $\delta 4.46$ at 333 K in the presence of 20 eq of PPh_3 . The experiments showed intramolecular exchange between the hydrides but no intermolecular exchange with free H_2 .

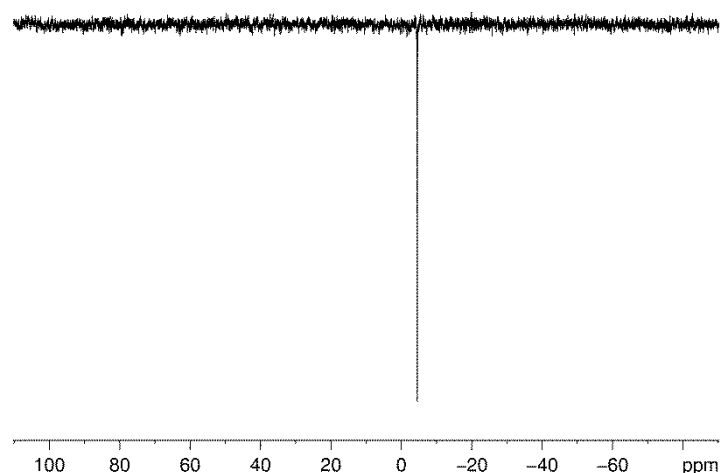


Figure S4: $^{31}\text{P}\{^1\text{H}\}$ EXSY experiments of a solution of **1** in C_6D_6 under H_2 pressure in the presence of 20 equivalents of PPh_3 at 333 K with a mixing time of 300 ms, exciting the free PPh_3 at $\delta -5.6$. No exchange observed with the PPh_3 groups of complex **1**.

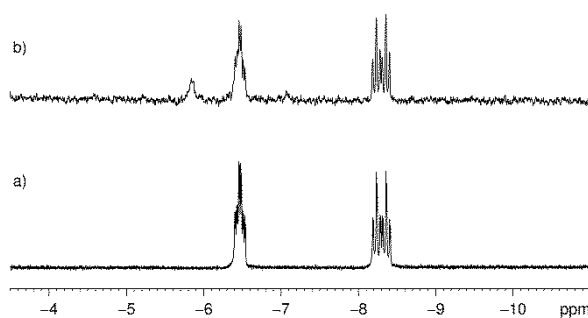


Figure S5. Hydride region of the ^1H spectrum of **1** in C_6D_6 after *in-situ* photolysis under 4 bar of H_2 at 298 K. a) Starting spectrum at $t = 0$ showing resonances for **1**. b) Spectrum of the same solution after 32 laser shots and 1 NMR scan displaying peaks for **1**, and a new broad resonance for **2**. Complex **2** is very unstable at room temperature (it becomes undetectable under the same conditions but with 2 NMR scans) and decays extremely fast.

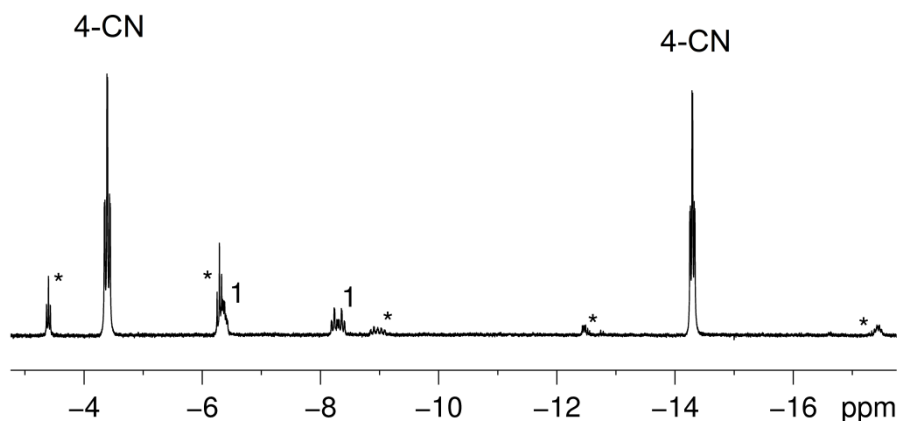


Figure S6. Hydride region of the ^1H spectrum of **1** after broadband photolysis in neat $\text{C}_5\text{H}_5\text{N}$. The main product is complex **4-CN**; asterisks indicate byproducts due to prolonged irradiation.

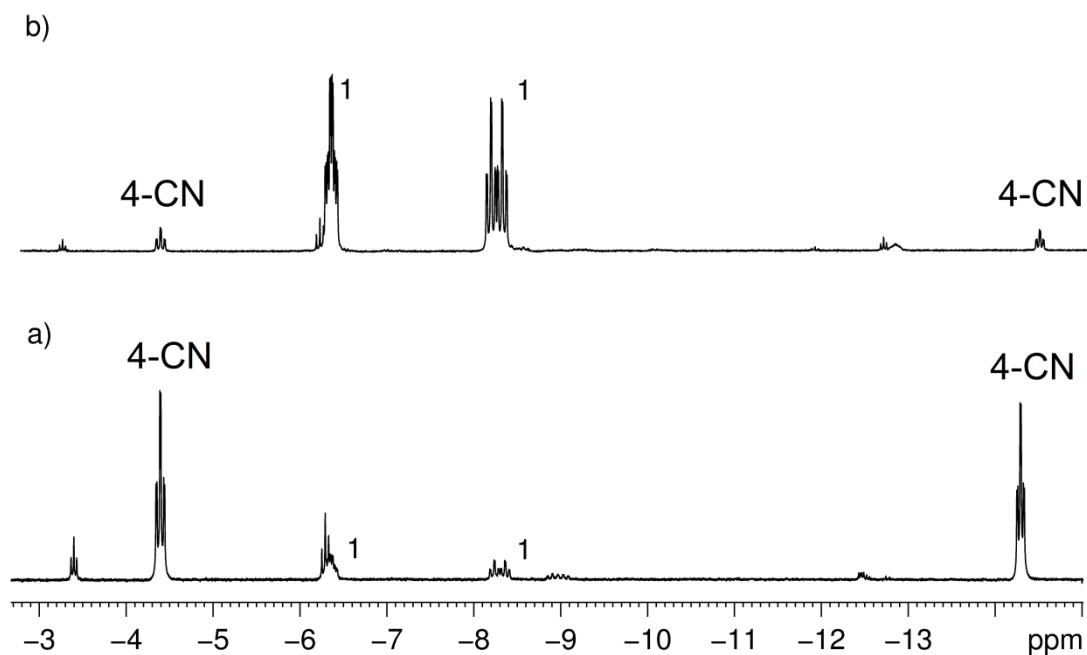


Figure S7. a) Hydride region of the ^1H spectrum of **1** after broadband photolysis in neat $\text{C}_5\text{H}_5\text{N}$. The main product is complex **4-CN**; b) the same solution after pumping off the pyridine and dissolution of the crude in C_6D_6 ; the product has reverted almost quantitatively to starting material **1**.

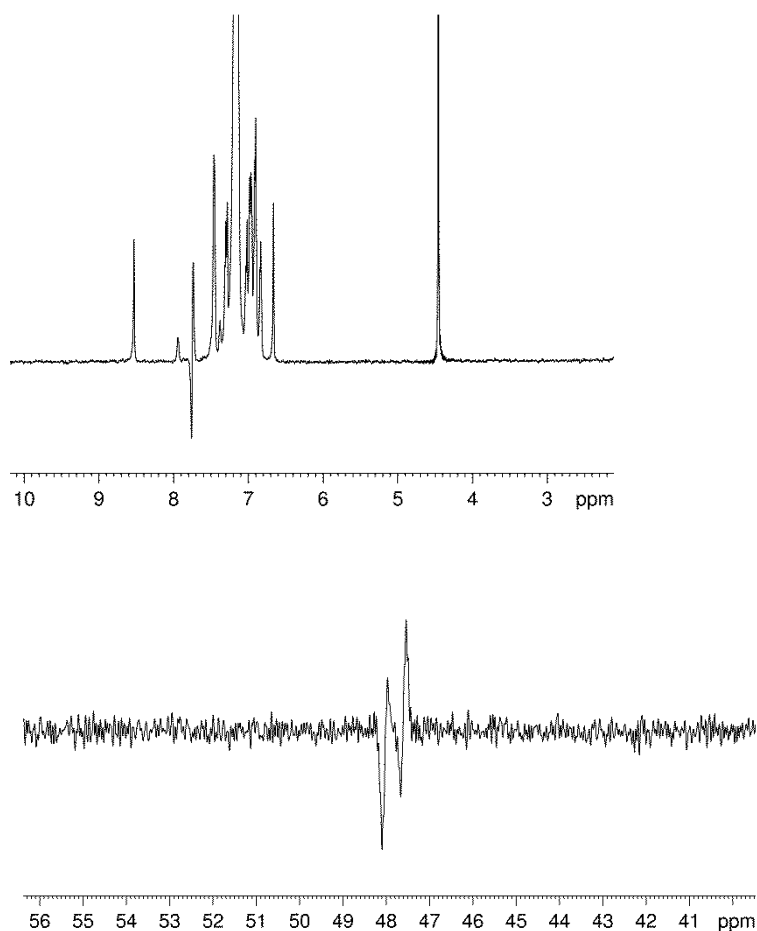


Figure S8. Above: ^1H spectrum of a solution of **1** in C_6D_6 in the presence of excess pyridine under $p\text{-H}_2$ pressure after 16 laser shots showing hyperpolarisation being transferred to the ortho aromatic protons of **4-PP**. Below: ^{31}P spectrum of the same solution displaying hyperpolarization transferred to phosphorus for complex **4-PP**. The spectrum was acquired after 4 laser shots and is 1 NMR scan.

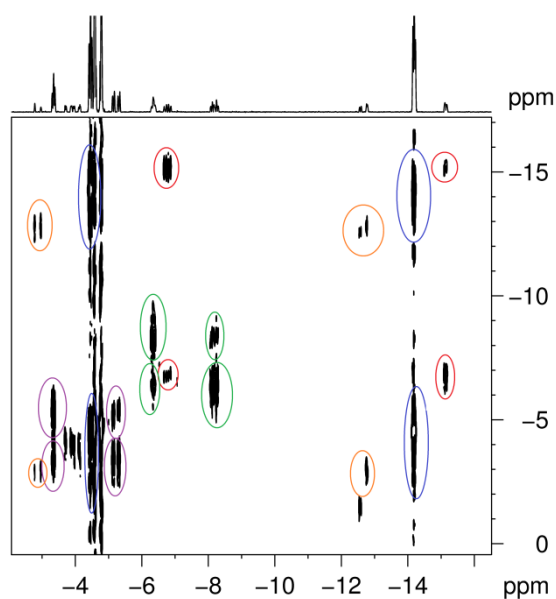
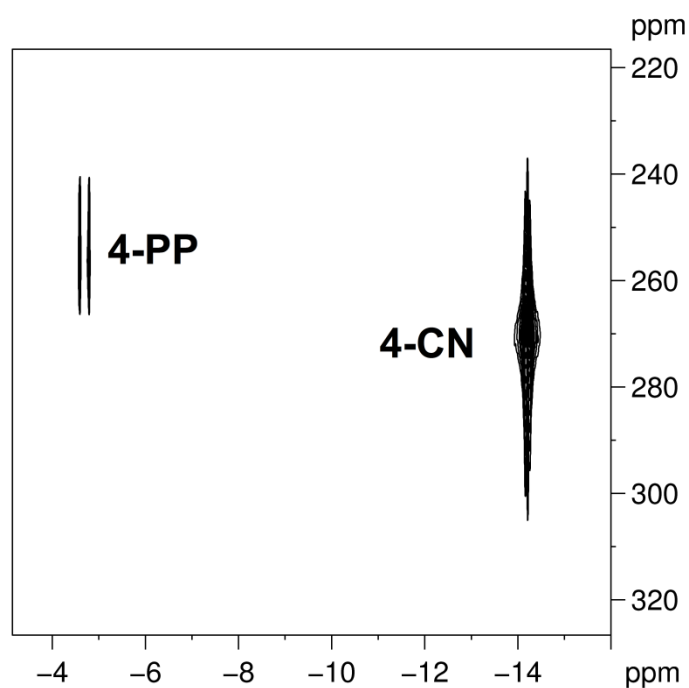


Figure S9. ^1H - ^1H 2D-COSY NMR spectrum of the hydride region of a C_6D_6 solution of **1** with 10 folds excess pyridine under $p\text{-H}_2$ pressure. Each increment was acquired after 4 laser shots in order to build up enough concentration for the detection of the minor species. This 2D-COSY spectrum was acquired using a using a $\pi/4\text{-}t_1\text{-}\pi/4\text{-}t_2$ pulse sequence. Circles of the same colour identify hydrides belonging to the same compound. Green circles: **1**; blue: **4-CN**; red: **4-CP**; purple: **4-NP**. Orange: product not identified.



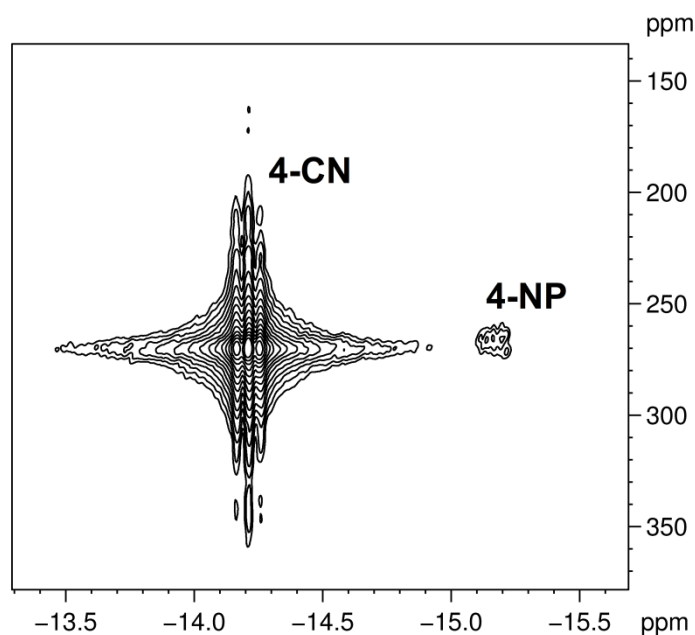


Figure S10. ^1H - ^{15}N 2D-HMQC NMR spectrum of the hydride region of a C_6D_6 solution of **1** with 10 folds excess ^{15}N -pyridine under $p\text{-H}_2$ pressure. Each increment was acquired after 8 laser shots in order to build up enough concentration for the detection of the minor species. The bottom spectrum was scaled x4 in order to see the cross peak for the minor isomer **4-NP**.

AsPh₃ experiments with multiple laser shots. Exposure of a C_6D_6 solution of **1** in the presence of excess AsPh₃ and $p\text{-H}_2$ to multiple laser shots (up to 16) led to the appearance of new species formed as minor products. The analogous complexes to **4-NP** and **4-CP** were observed (**3-NAs** and **3-CAs**) but no peaks for the analogous symmetric species of **4-PP** were detected at room temperature. In order to see if the photochemistry of **1** in the presence of excess AsPh₃ parallels the product distribution in the presence of excess pyridine, an optically dilute solution of **1** and excess AsPh₃ (10 fold) in toluene- d_8 was put under a $p\text{-H}_2$ atmosphere and irradiated at low 220 K. Exposure of the solution to 8 laser shots led to detection of hyperpolarised signal for **1** and **3-CN**; however, when the sample was irradiated for a longer time (30 s), a broad peak corresponding to **2** was observed. The amount of **2** increased with increased photolysis while the resonances for the hydride peaks of **3-CN** increased a very little amount. These observations suggest that at this temperature there is a preference for reaction with H_2 over AsPh₃ after PPh₃ loss; this is probably a consequence of decreased solubility of AsPh₃ at low T. Upon raising the temperature to 240 K the broad resonance for **2** disappeared and a large increase in intensity for the resonances of **3-CN** was observed indicating displacement of the dihydrogen ligand followed

by AsPh_3 coordination to yield **3-CN**. If the photochemistry was restarted with a single laser shot, hyperpolarised peaks for **1**, **3-CN**, **3-NAs** and **3-CAs** were now observed; those species appeared to have built up and to be thermally stable at this temperature (See SI). No resonances for the analogous complex of **4-PP** were observed in these experiments. This observation may be attributed to the H_2 competing with AsPh_3 in occupying the vacant site on the metal centre at low T and fast equilibration to form **4** at higher temperature when AsPh_3 coordination becomes the major process. Nevertheless, the similarity in product distribution between reactions with pyridine and AsPh_3 suggest that the two reactions follow the same photochemical reactivity.

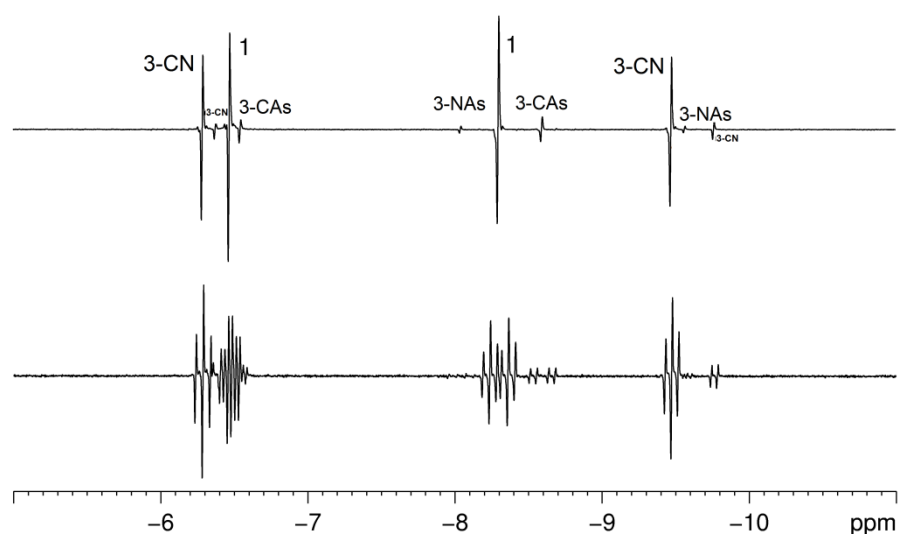
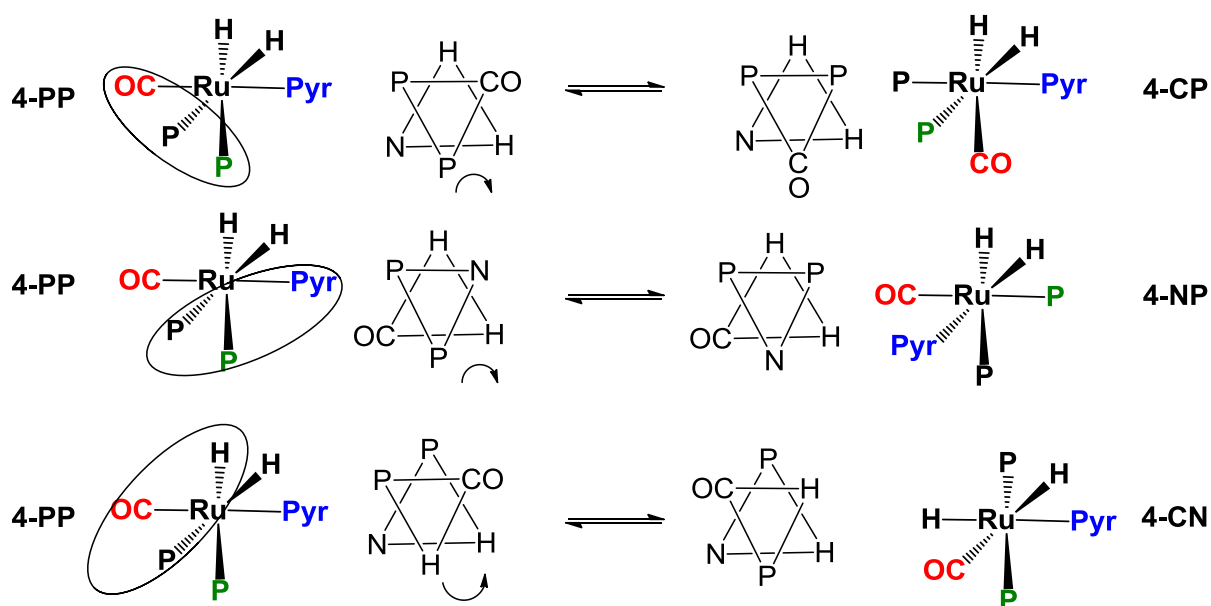


Figure S11. Bottom: Hydride region of the hyperpolarised ^1H spectrum of a C_6D_6 solution of **1** under $p\text{-H}_2$ in the presence of excess AsPh_3 . The solution was exposed to 8 laser shots. **Top:** Hydride region of the $^1\text{H}\{^{31}\text{P}\}$ spectrum acquired in the same conditions. The solution was exposed to 4 laser shots.

TRIGONAL TWIST



Berry pseudorotation of square pyramid viewed down axis of pair of eq ligands

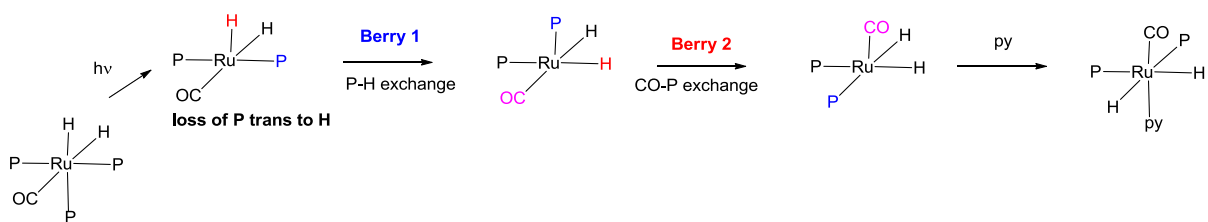
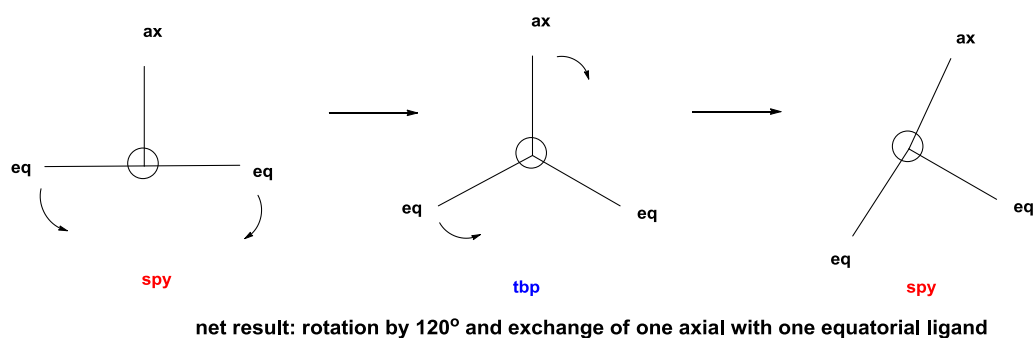


Figure S12. Schemes for possible mechanisms of isomerization. Top: trigonal twist; bottom: Berry pseudorotation.

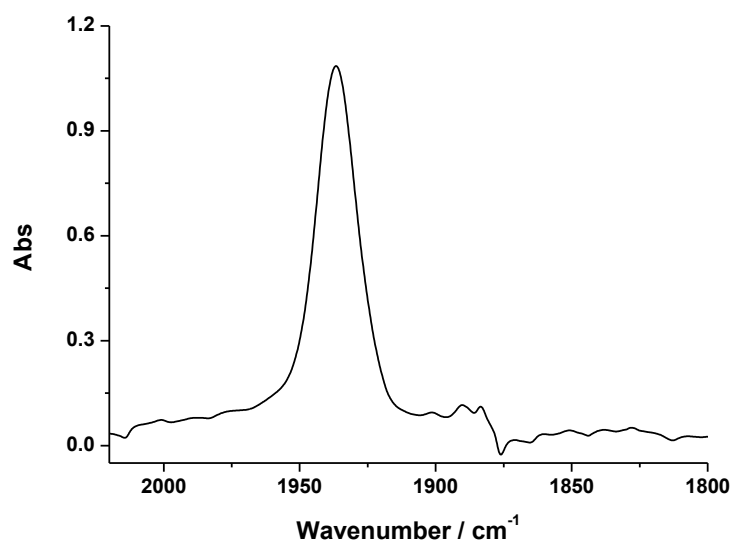


Figure S13. FTIR spectrum of **1** in toluene at 220 K

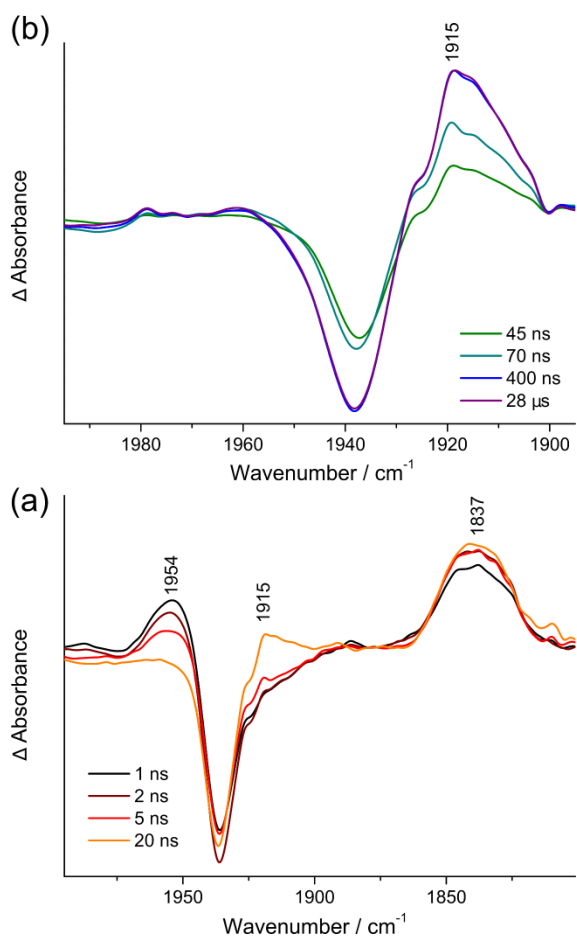


Figure S14. TRIR difference spectra obtained in the range (a) 1-20 ns and (b) 45 ns - 28 μ s after 355 nm laser flash of a solution of **1** in benzene- d_6 with added pyridine (ca. 10^{-2} M).

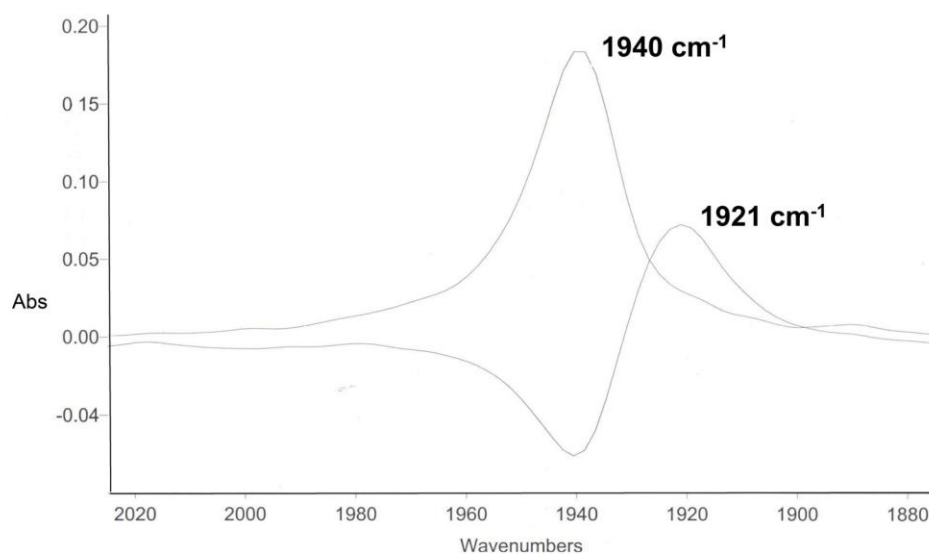


Figure S15. FTIR spectrum of **1** (1940 cm^{-1}) and a mixture of **1** and **4-CN** in C_6D_6 solution formed by laser photolysis (355 nm) of a solution of **1** with excess pyridine- d_5 . The product spectrum is presented as a difference with respect to the initial spectrum with peak at 1921 cm^{-1} .

1

$$\nu(\text{CO}) = 1927 \text{ cm}^{-1}$$

$$\angle \text{H}_{\text{eq}}\text{-Ru-H}_{\text{eq}} = 86.30^\circ$$

$$\angle \text{H}_{\text{eq}}\text{-Ru-C}_{\text{eq}} = 87.99^\circ$$

$$\angle \text{H}_{\text{eq}}\text{-Ru-P}_{\text{eq}} = 92.24^\circ$$

$$\angle \text{P}_{\text{eq}}\text{-Ru-H}_{\text{eq}} = 93.46^\circ$$

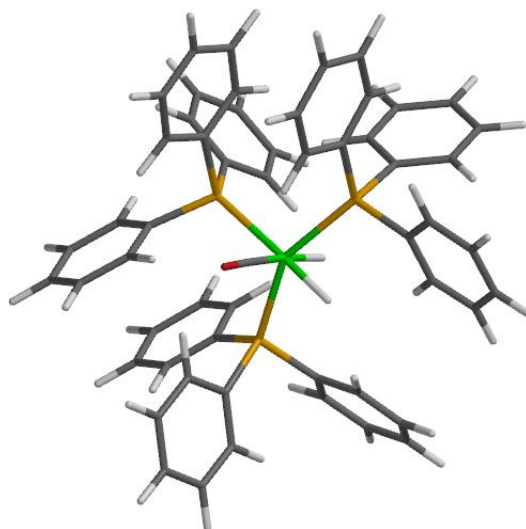
$$\angle \text{P}_{\text{ax}}\text{-Ru-P}_{\text{ax}} = 147.90^\circ$$

$$R(\text{Ru-H}_{\text{eq}}) = 1.63 / 1.70 \text{ \AA}$$

$$R(\text{Ru-C}_{\text{eq}}) = 1.91 \text{ \AA}$$

$$R(\text{Ru-P}_{\text{eq}}) = 2.47 \text{ \AA}$$

$$R(\text{Ru-P}_{\text{ax}}) = 2.37 / 2.40 \text{ \AA}$$



$$\nu(\text{CO}) = 1973 \text{ cm}^{-1}$$

$$\angle \text{H}_{\text{eq}}\text{-Ru-H}_{\text{eq}} = 86.20^\circ$$

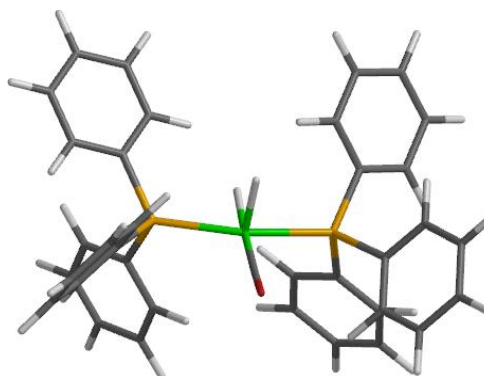
$$\angle \text{H}_{\text{eq}}\text{-Ru-C}_{\text{eq}} = 87.23 / 173.43^\circ$$

$$\angle \text{P}_{\text{ax}}\text{-Ru-P}_{\text{ax}} = 162.90^\circ$$

$$R(\text{Ru-H}_{\text{eq}}) = 1.57 / 1.71 \text{ \AA}$$

$$R(\text{Ru-C}_{\text{eq}}) = 1.92 \text{ \AA}$$

$$R(\text{Ru-P}_{\text{ax}}) = 2.35 / 2.35 \text{ \AA}$$



$$\nu(\text{CO}) = 1903 \text{ cm}^{-1}$$

$$\angle \text{C-Ru-P (trans)} = 24.06^\circ$$

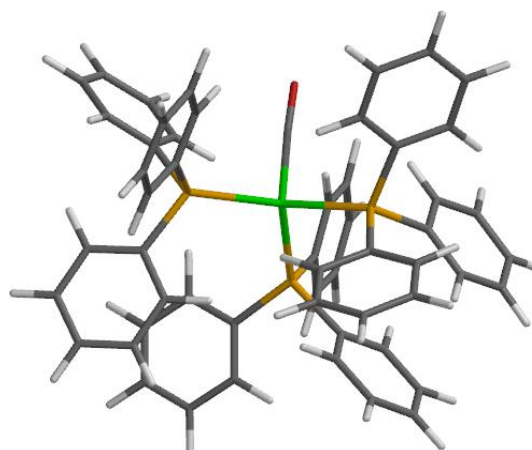
$$\angle \text{P-Ru-P (trans)} = 151.04^\circ$$

$$\angle \text{P-Ru-P (cis)} = 105.10 / 95.66^\circ$$

$$R(\text{Ru-C}) = 1.86 \text{ \AA}$$

$$R(\text{Ru-P (P trans C)}) = 2.41 \text{ \AA}$$

$$R(\text{Ru-P (P trans P)}) = 2.36 / 2.38 \text{ \AA}$$



2

$\nu(\text{CO}) = 1974 \text{ cm}^{-1}$

$\angle \text{H}_{\text{eq}}\text{-Ru-H}_{\text{eq}} = 83.31^\circ$

$\angle \text{H}_{\text{eq}}\text{-Ru-C}_{\text{eq}} = 89.67^\circ$

$\angle \text{H}_{\text{eq}}\text{-Ru-P}_{\text{eq}} = 92.24^\circ$

$\angle \text{H}(\text{H}_2)_{\text{eq}}\text{-Ru-H}_{\text{eq}} = 85.41 / 92.45^\circ$

$\angle \text{P}_{\text{ax}}\text{-Ru-P}_{\text{ax}} = 161.59^\circ$

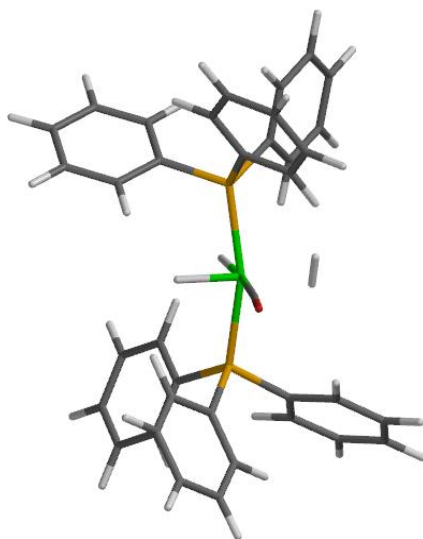
$\text{R}(\text{Ru-H}_{\text{eq}}) = 1.61 / 1.70 \text{ \AA}$

$\text{R}(\text{Ru-C}_{\text{eq}}) = 1.93 \text{ \AA}$

$\text{R}(\text{Ru-H}_2) = 1.93 \text{ \AA}$

$\text{R}(\text{Ru-P}_{\text{ax}}) = 2.37 / 2.37 \text{ \AA}$

$\text{R}(\text{H-H}) = 0.81 \text{ \AA}$



4-CN

$\nu(\text{CO}) = 1946 \text{ cm}^{-1}$

$\angle \text{H}_{\text{eq}}\text{-Ru-H}_{\text{eq}} = 86.25^\circ$

$\angle \text{H}_{\text{eq}}\text{-Ru-C}_{\text{eq}} = 89.85^\circ$

$\angle \text{C}_{\text{eq}}\text{-Ru-N}_{\text{eq}} = 98.36^\circ$

$\angle \text{N}_{\text{eq}}\text{-Ru-H}_{\text{eq}} = 85.56^\circ$

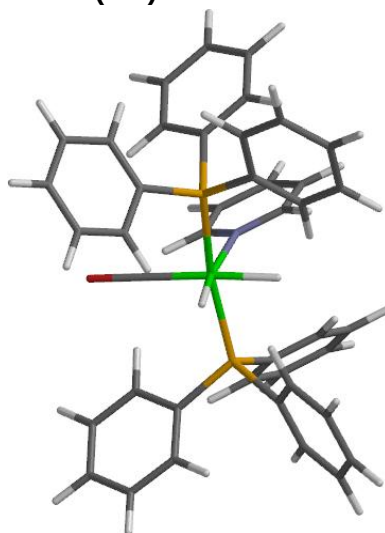
$\angle \text{P}_{\text{ax}}\text{-Ru-P}_{\text{ax}} = 165.74^\circ$

$\text{R}(\text{Ru-H}_{\text{eq}}) = 1.62 / 1.71 \text{ \AA}$

$\text{R}(\text{Ru-C}_{\text{eq}}) = 1.91 \text{ \AA}$

$\text{R}(\text{Ru-N}_{\text{eq}}) = 2.30 \text{ \AA}$

$\text{R}(\text{Ru-P}_{\text{ax}}) = 2.35 / 2.37 \text{ \AA}$



4-PP

$$\nu(\text{CO}) = 1955 \text{ cm}^{-1}$$

$$\angle \text{H}_{\text{eq}}\text{-Ru-H}_{\text{eq}} = 78.73^\circ$$

$$\angle \text{H}_{\text{eq}}\text{-Ru-P}_{\text{eq}} = 87.53 / 90.41^\circ$$

$$\angle \text{P}_{\text{eq}}\text{-Ru-P}_{\text{eq}} = 103.33^\circ$$

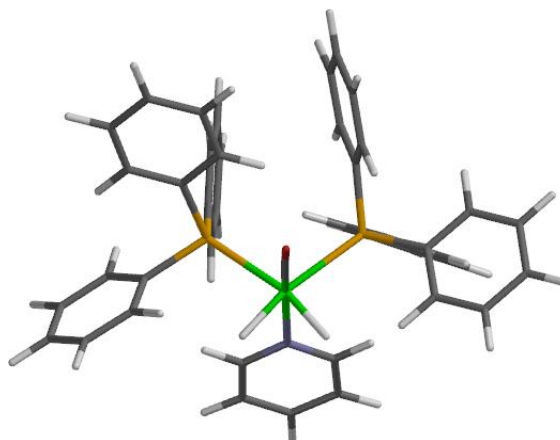
$$\angle \text{N}_{\text{ax}}\text{-Ru-C}_{\text{ax}} = 165.81^\circ$$

$$R(\text{Ru-H}_{\text{eq}}) = 1.63 / 1.64 \text{ \AA}$$

$$R(\text{Ru-P}_{\text{eq}}) = 2.47 / 2.48 \text{ \AA}$$

$$R(\text{Ru-C}_{\text{ax}}) = 1.85 \text{ \AA}$$

$$R(\text{Ru-N}_{\text{ax}}) = 2.25 \text{ \AA}$$



4-HH

$$\nu(\text{CO}) = 1941 \text{ cm}^{-1}$$

$$\angle \text{C}_{\text{eq}}\text{-Ru-H}_{\text{eq}} = 93.25 / 94.86^\circ$$

$$\angle \text{H}_{\text{eq}}\text{-Ru-N}_{\text{eq}} = 85.97 / 86.18^\circ$$

$$\angle \text{P}_{\text{ax}}\text{-Ru-P}_{\text{ax}} = 179.09^\circ$$

$$R(\text{Ru-H}_{\text{eq}}) = 1.72 / 1.73 \text{ \AA}$$

$$R(\text{Ru-C}_{\text{eq}}) = 1.84 \text{ \AA}$$

$$R(\text{Ru-N}_{\text{eq}}) = 2.25 \text{ \AA}$$

$$R(\text{Ru-P}_{\text{ax}}) = 2.38 / 2.40 \text{ \AA}$$

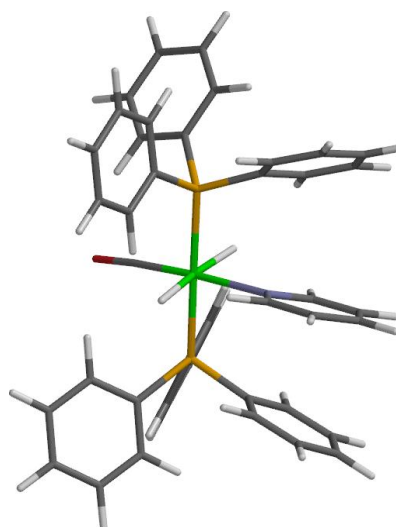


Figure S16. DFT Calculated structures with M06/LACVP(d) functional with principal bond lengths, angles, and CO-stretching frequencies. Note: Coordinated hydrogen atoms are taken to define the equatorial plane.

Table 1. Calculated and observed $\nu(\text{CO})$ values for pyridine complexes
 $\text{Ru}(\text{H})_2(\text{CO})(\text{PPh}_3)_2(\text{pyridine})$

Complex	$\nu(\text{CO})$ exptl in C_6D_6	$\nu(\text{CO})$ calcd by Timney method ^a	$\nu(\text{CO})$ calcd by DFT ^b
4-CN	1921	1941	1946
4-PP	1911	1898	1955
4-NP		1930	
4-CP		1941	

For pyridine, the ligand effect constants for *cis* and *trans* positions are both negative but with much larger values for *trans*. The Timney calculations⁵ predict shifts of -5 and -49 cm^{-1} with respect to **1** whereas the DFT calculations predict shifts of +19 and +28 cm^{-1} , respectively. The experiment shows a peak shifted by -27 cm^{-1} but with shoulders to high and low frequency. We note that the DFT calculations show that **4-PP** is considerably distorted from an octahedron and that the Timney method assumes an octahedral geometry.

1. Desrosiers, P. J.; Cai, L.; Lin, Z.; Richards, R.; Halpern, J.; *J. Am. Chem. Soc.*, **1991**, *113*, 4173.
2. Hamilton, D. G.; Crabtree, R. H., *J. Am. Chem. Soc.*, **1988**, *110*, 4126.
3. Morris, R. H. *Coord. Chem. Rev.*, **2008**, *252*, 2381.
4. Woessner, D. E. *J. Chem. Phys.*, **1962**, *37*, 647.
5. Timney, J. A. *Inorg. Chem.* **1979**, *18*, 2502.