

Electronic Supporting Information

**Heterobimetallic Complexes Stabilized by the P₂N₂ Macrocyclic Ligand System:
Synthesis and Reactivity of a Rhodium-Copper System That Activates Molecular Hydrogen**

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V6T 1Z1

Figure S1: ¹ H NMR (400.2 MHz in C ₆ D ₆) spectrum of Rh(COE)[P ₂ N ₂]Cu at room temperature.	S3
Figure S2: ¹³ C { ¹ H} NMR (100.6 MHz in C ₆ D ₆) spectrum of Rh(COE)[P ₂ N ₂]Cu at room temperature.	S3
Figure S3: ³¹ P { ¹ H} (161.9 MHz in toluene-d ₈) spectra of Rh(COE)[P ₂ N ₂]Cu at a series of temperatures (labelled on the right).	S4
Figure S4: ¹ H NMR (400.2 MHz in C ₆ D ₆) spectrum of ([P ₂ N ₂ H]Rh(H)(μ-H) ₂ Cu) ₂ .	S5
Figure S5: ³¹ P { ¹ H} (161.9 MHz in C ₆ D ₆) spectrum of ([P ₂ N ₂ H]Rh(H)(μ-H) ₂ Cu) ₂ .	S5
Figure S6: ¹³ C { ¹ H} NMR (100.6 MHz in C ₆ D ₆) spectrum of ([P ₂ N ₂ H]Rh(H)(μ-H) ₂ Cu) ₂ at room temperature.	S6
Figure S7: ¹ H NMR (400.2 MHz in C ₆ D ₆) spectrum of (PPh ₃)Cu[P ₂ N ₂]Rh(H) ₂ .	S7
Figure S8: Detailed aliphatic and aromatic regions of the ¹ H NMR (400.2 MHz in C ₆ D ₆) spectrum of (PPh ₃)Cu[P ₂ N ₂]Rh(H) ₂ .	S7
Figure S9: ³¹ P { ¹ H} (161.9 MHz in C ₆ D ₆) spectrum of (PPh ₃)Cu[P ₂ N ₂]Rh(H) ₂ .	S8
Figure S10: ¹³ C { ¹ H} NMR (100.6 MHz in C ₆ D ₆) spectrum of (PPh ₃)Cu[P ₂ N ₂]Rh(H) ₂ .	S9
Figure S11: Detail of the ¹³ C { ¹ H} NMR (100.6 MHz in C ₆ D ₆) spectrum of (PPh ₃)Cu[P ₂ N ₂]Rh(H) ₂ .	S9
Figure S12: Detail of the silyl methyl region of the ¹ H NMR (400.2 MHz in C ₆ D ₆) monitoring experiment of treatment of Rh(COE)[P ₂ N ₂]Cu with excess H ₂ .	S10
Figure S13: Detail of the hydride region of the ¹ H NMR (400.2 MHz in C ₆ D ₆) monitoring experiment of treatment of Rh(COE)[P ₂ N ₂]Cu with excess H ₂ .	S11
Figure S14: Detail of the silyl methyl region of the ¹ H NMR (400.2 MHz in C ₆ D ₆) spectra at select times after Rh(COE)[P ₂ N ₂]Cu was treated with 1 atm of D ₂ in a J-Young tube.	S12
Figure S15: Detail of the hydride region of the ¹ H NMR (400.2 MHz in C ₆ D ₆) spectra at	S13

select times after Rh(COE)[P₂N₂]Cu was treated with 1 atm of D₂ in a J-Young tube.

Figure S16: Detail of the silyl methyl region of the ¹ H NMR (400.2 MHz in C ₆ D ₆) spectra at select times after Rh(COE)[P ₂ N ₂]Cu was treated with excess D ₂ in a Schlenk flask.	S14
Figure S17: Detail of the hydride region of the ¹ H NMR (400.2 MHz in C ₆ D ₆) spectra at select times after Rh(COE)[P ₂ N ₂]Cu was treated with excess D ₂ in a Schlenk flask.	S15
X-ray Crystallographic Analysis, CCDC Identification	S16
Table S1: Crystal data and structure refinement parameters for Rh(COE)[P ₂ N ₂]Cu	S17
Table S2: Crystal data and structure refinement parameters for ([P ₂ N ₂ H]RhH(μ-H) ₂ Cu) ₂	S18
Gas Chromatography-Mass Spectrometry Experiments	S19
Figure S18: Reference mass spectrum of cyclooctane obtained using the GC-MS method outlined.	S19
Table S3: Intensities of major ionic species in the mass spectrum of cyclooctane.	S20
Figure S19: Combined mass spectrum (RT 5.05-5.35 min.) of the collected organic products of the reaction of Rh(COE)[P ₂ N ₂]Cu (0.040 g) with D ₂ (1 atm) at ~20°C.	S20
Figure S20: Combined mass spectrum (RT 5.05-5.35 min.) of the collected organic products of the reaction of Rh(COE)[P ₂ N ₂]Cu (0.031 g) with D ₂ (4 atm) at ~30-35° C.	S21
Figure S21: Combined mass spectrum (RT 5.05-5.35 min.) of the collected organic products of the reaction of Rh(COE)[P ₂ N ₂]Cu (0.032 g) with D ₂ (4 atm) at ~10° C.	S21
Figure S22: Comparison of the isotopomer distributions of the molecular ion in the three GC-MS experiments where Rh(COE)[P ₂ N ₂]Cu was treated with D ₂ .	S22
In-Silico Simulation of Deuteration Experiments	S23
Figure S23: Comparison of simulation and experimental data for isotopomer distribution when Rh(COE)[P ₂ N ₂] (0.041) is exposed to 1 atm of D ₂ .	S30
Figure S24: Simulated mass spectrum of the isotopomers of cyclooctane generated when Rh(COE)[P ₂ N ₂] (0.041) is exposed to 1 atm of D ₂ .	S30
Figure S25: Comparison of simulation and experimental data for isotopomer distribution when Rh(COE)[P ₂ N ₂] (0.032 g) is exposed to 4 atm of D ₂ .	S31
Figure S24: Simulated mass spectrum of the isotopomers of cyclooctane generated when Rh(COE)[P ₂ N ₂] (0.032) is exposed to 4 atm of D ₂ .	S31

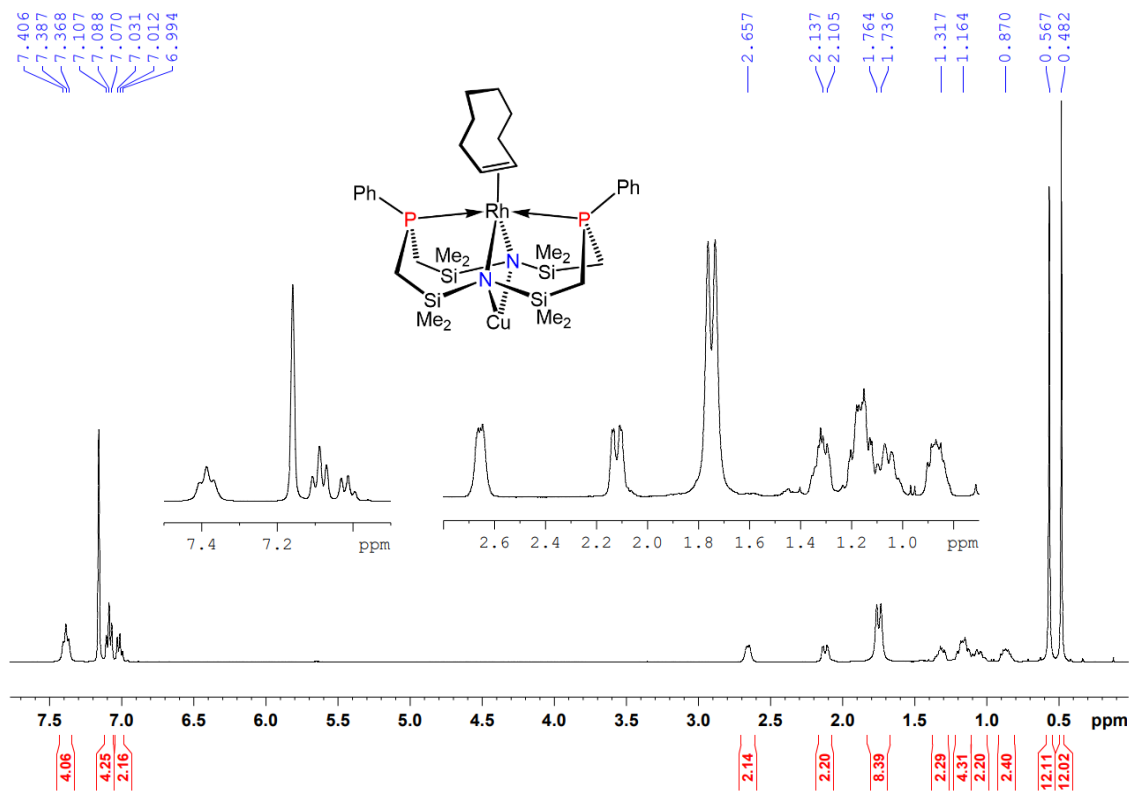


Figure S1: ^1H NMR (400.2 MHz in C_6D_6) spectrum of $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$ at room temperature. The blue peak markers shown at the top are in ppm units and correspond to the bottom full spectrum.

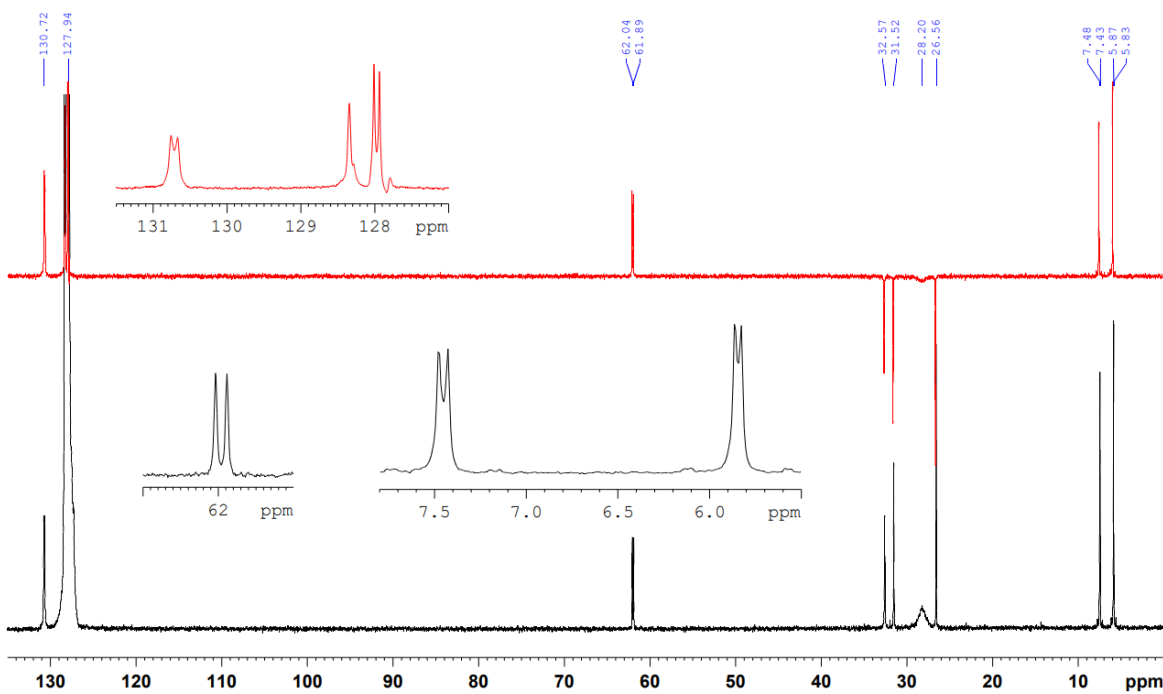


Figure S2: $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz in C_6D_6) spectrum of $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$ at room temperature. The DEPT-135 spectrum is stacked, plotted in red.

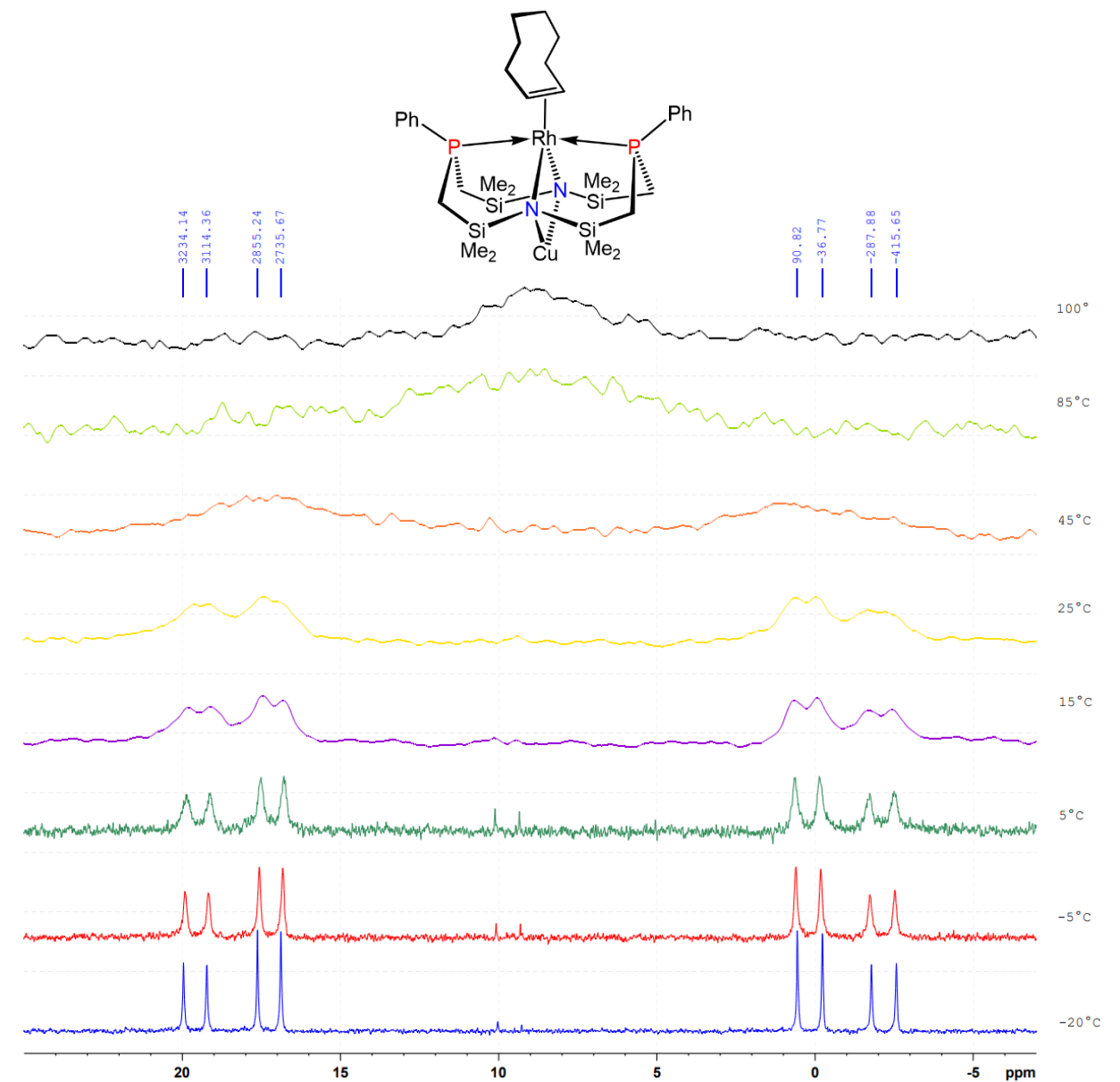


Figure S3: $^{31}\text{P}\{^1\text{H}\}$ (161.9 MHz in toluene- d_8) spectra of $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$ at a series of temperatures (labelled on the right). Line broadening of spectra taken at the five highest temperatures was adjusted to 50.0 for clarity. Peak labels shown in blue correspond to the spectrum taken at -20°C .

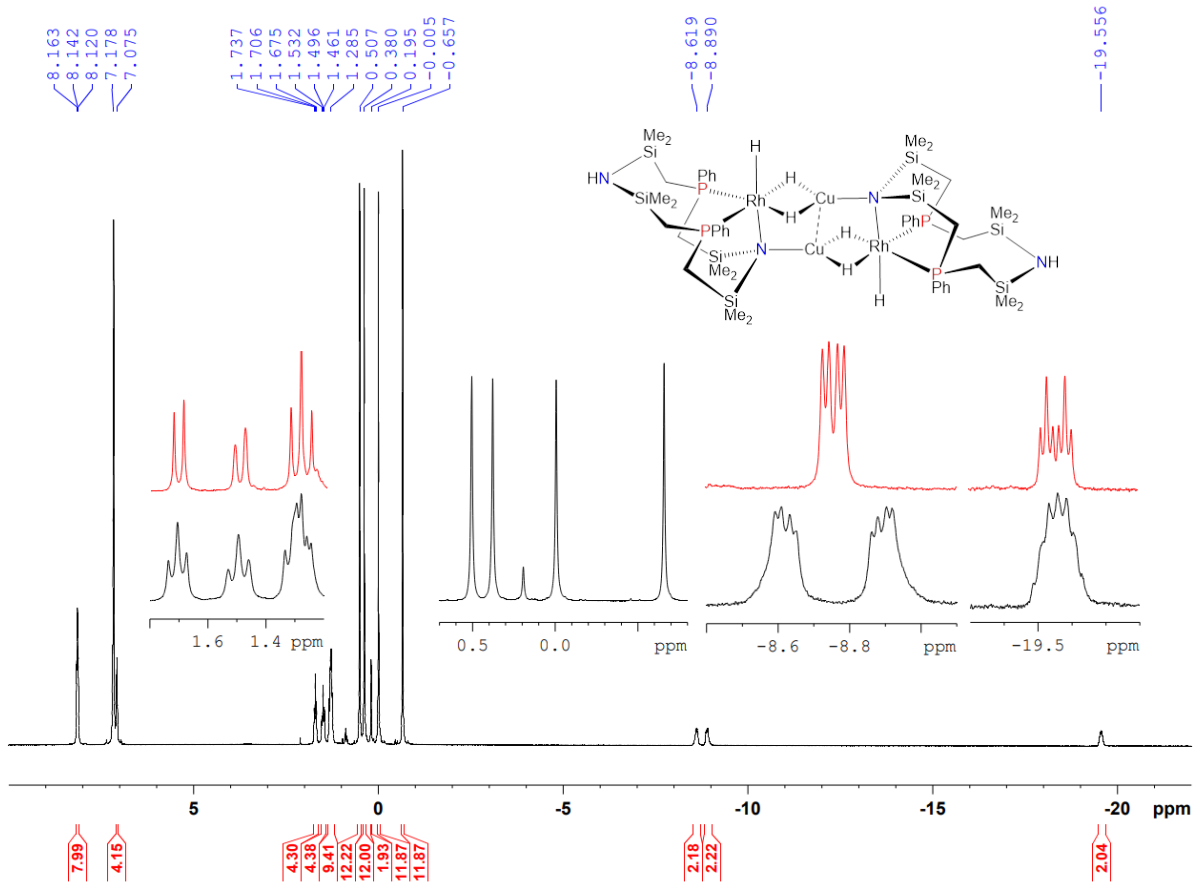


Figure S4: ^1H NMR (400.2 MHz in C_6D_6) spectrum of $([\text{P}_2\text{N}_2\text{H}]\text{Rh}(\text{H})(\mu\text{-H})_2\text{Cu})_2$. Detailed regions inset are stacked with the corresponding $^1\text{H}\{^31\text{P}\}$ spectrum shown in red. The peak labels at the top are in ppm units and correspond to the full spectrum at the bottom.

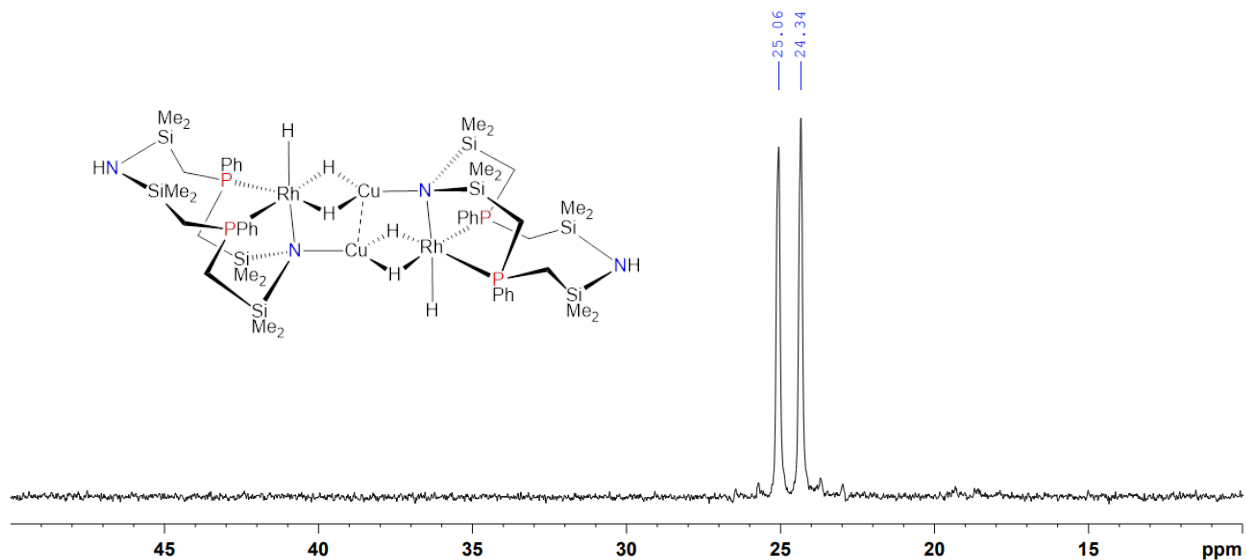


Figure S5: $^{31}\text{P}\{^1\text{H}\}$ (161.9 MHz in C_6D_6) spectrum of $([\text{P}_2\text{N}_2\text{H}]\text{Rh}(\text{H})(\mu\text{-H})_2\text{Cu})_2$.

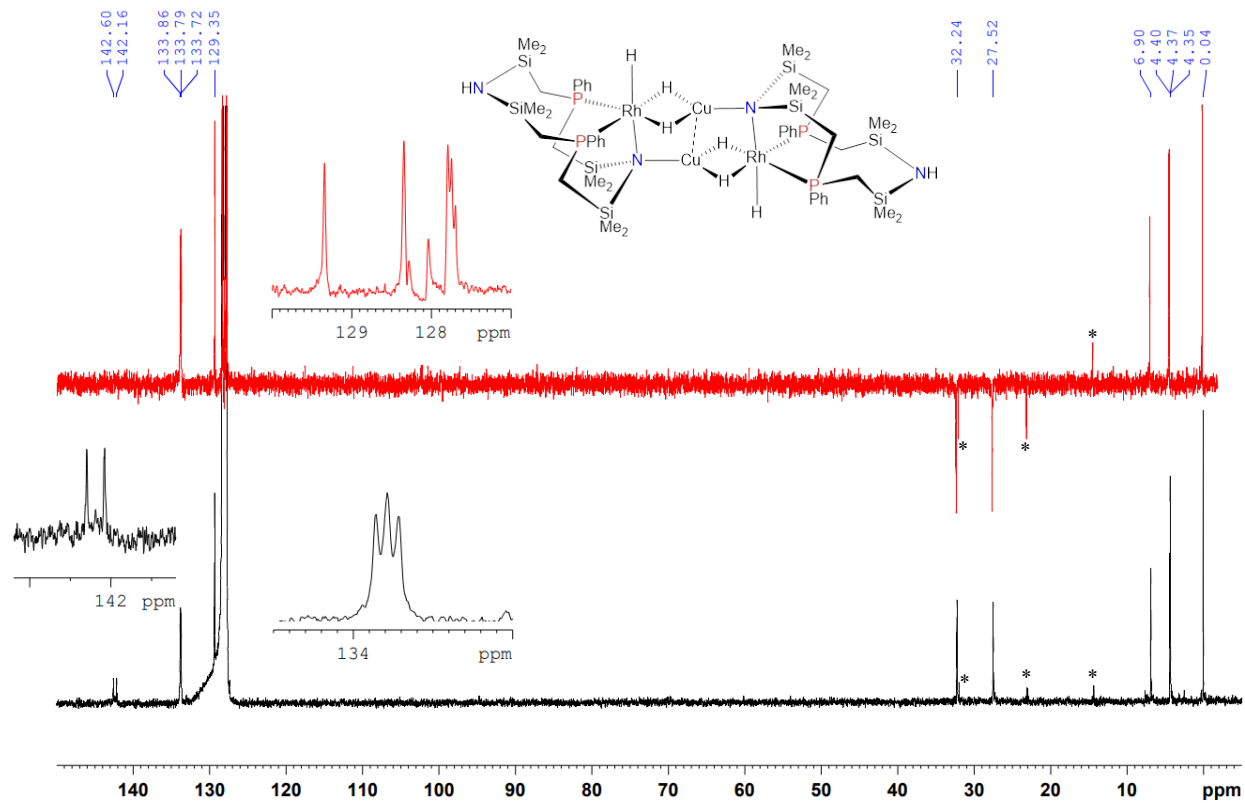


Figure S6: $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz in C_6D_6) spectrum of $[\text{P}_2\text{N}_2\text{H}]\text{Rh}(\text{H})(\mu\text{-H})_2\text{Cu}_2$ at room temperature. The DEPT-135 spectrum is stacked, plotted in red. (Resonances marked with *) correspond to residual hexane solvent).

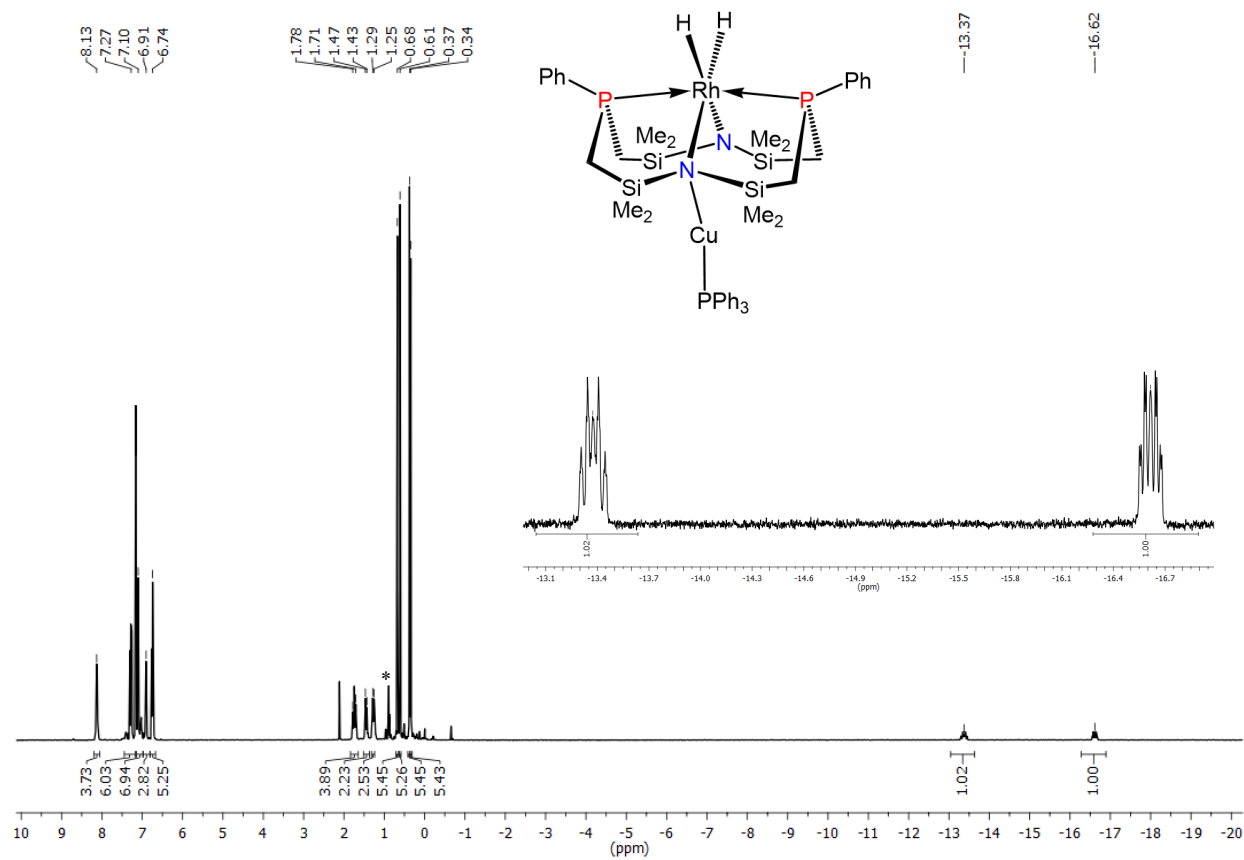


Figure S7: ^1H NMR (400.2 MHz in C_6D_6) spectrum of $(\text{PPh}_3)\text{Cu}[\text{P}_2\text{N}_2]\text{Rh}(\text{H})_2$. Resonances marked with (*) correspond to residual hexanes solvent.

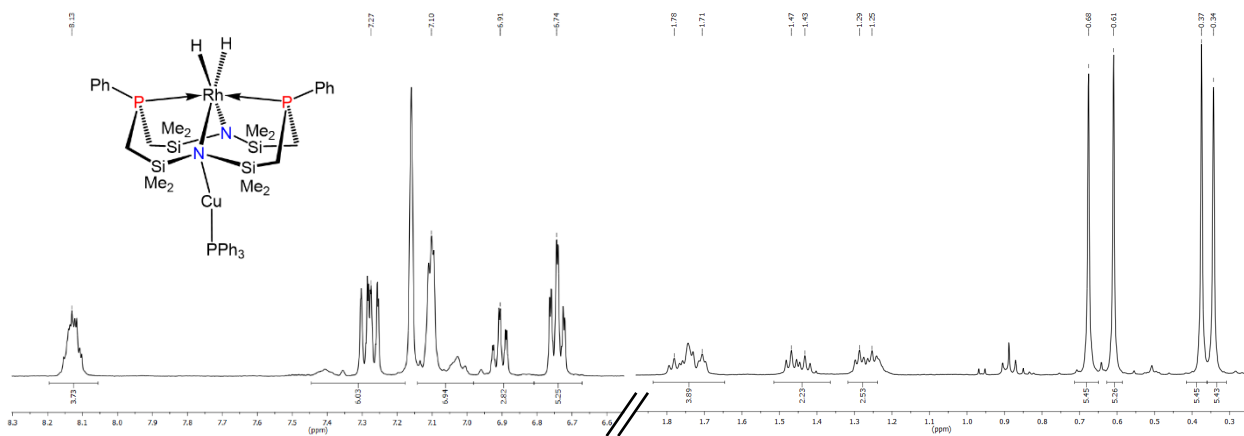


Figure S8: Detailed aliphatic and aromatic regions of the ^1H NMR (400.2 MHz in C_6D_6) spectrum of $(\text{PPh}_3)\text{Cu}[\text{P}_2\text{N}_2]\text{Rh}(\text{H})_2$.

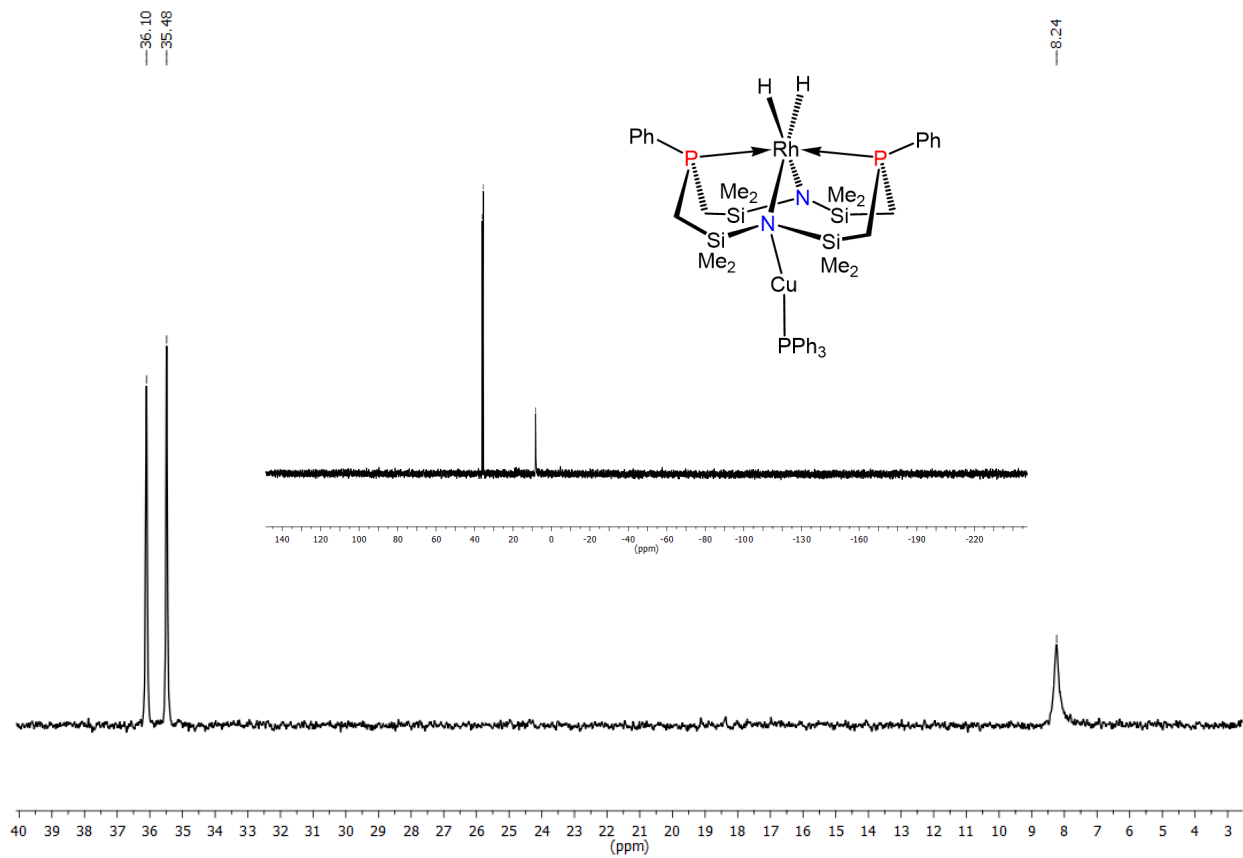


Figure S9: $^{31}\text{P}\{^1\text{H}\}$ (161.9 MHz in C_6D_6) spectrum of $(\text{PPh}_3)\text{Cu}[\text{P}_2\text{N}_2]\text{Rh}(\text{H})_2$.

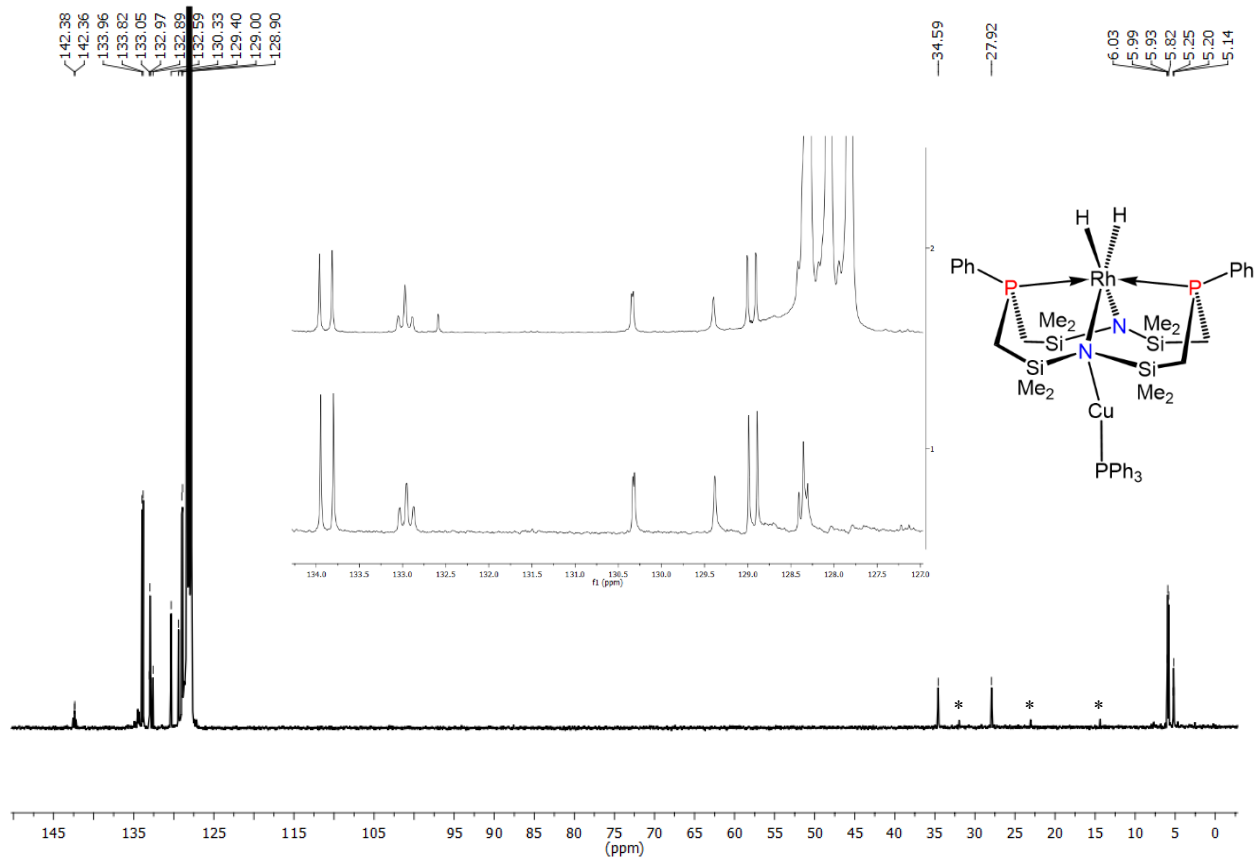


Figure S10: $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz in C_6D_6) spectrum of $(\text{PPh}_3)\text{Cu}[\text{P}_2\text{N}_2]\text{Rh}(\text{H})_2$. The inset detailed aromatic region is stacked with the corresponding DEPT-135 spectrum (bottom). Resonances marked with (*) belong to residual hexanes solvent.

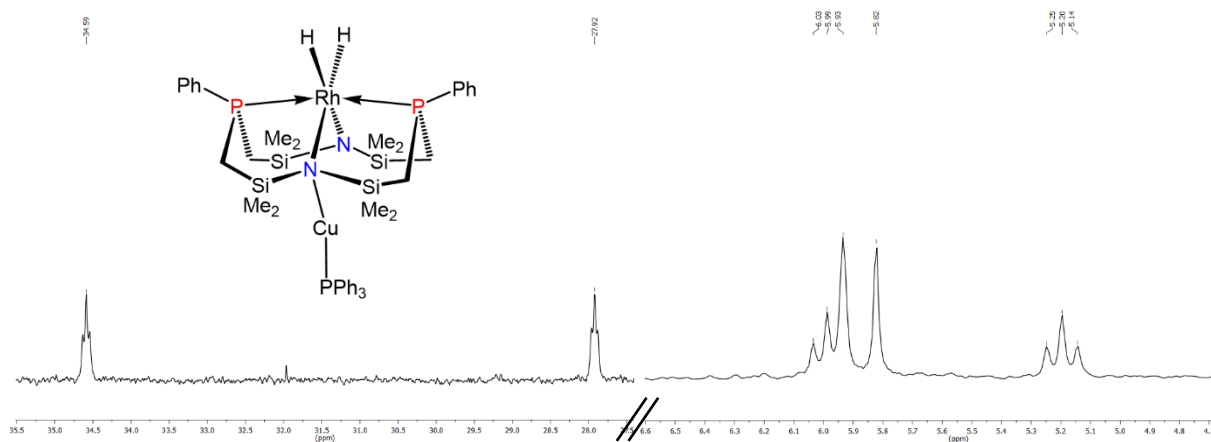


Figure S11: Detail of the $^{13}\text{C}\{^1\text{H}\}$ NMR (100.6 MHz in C_6D_6) spectrum of $(\text{PPh}_3)\text{Cu}[\text{P}_2\text{N}_2]\text{Rh}(\text{H})_2$. Resonances marked with (*) belong to residual hexanes solvent.

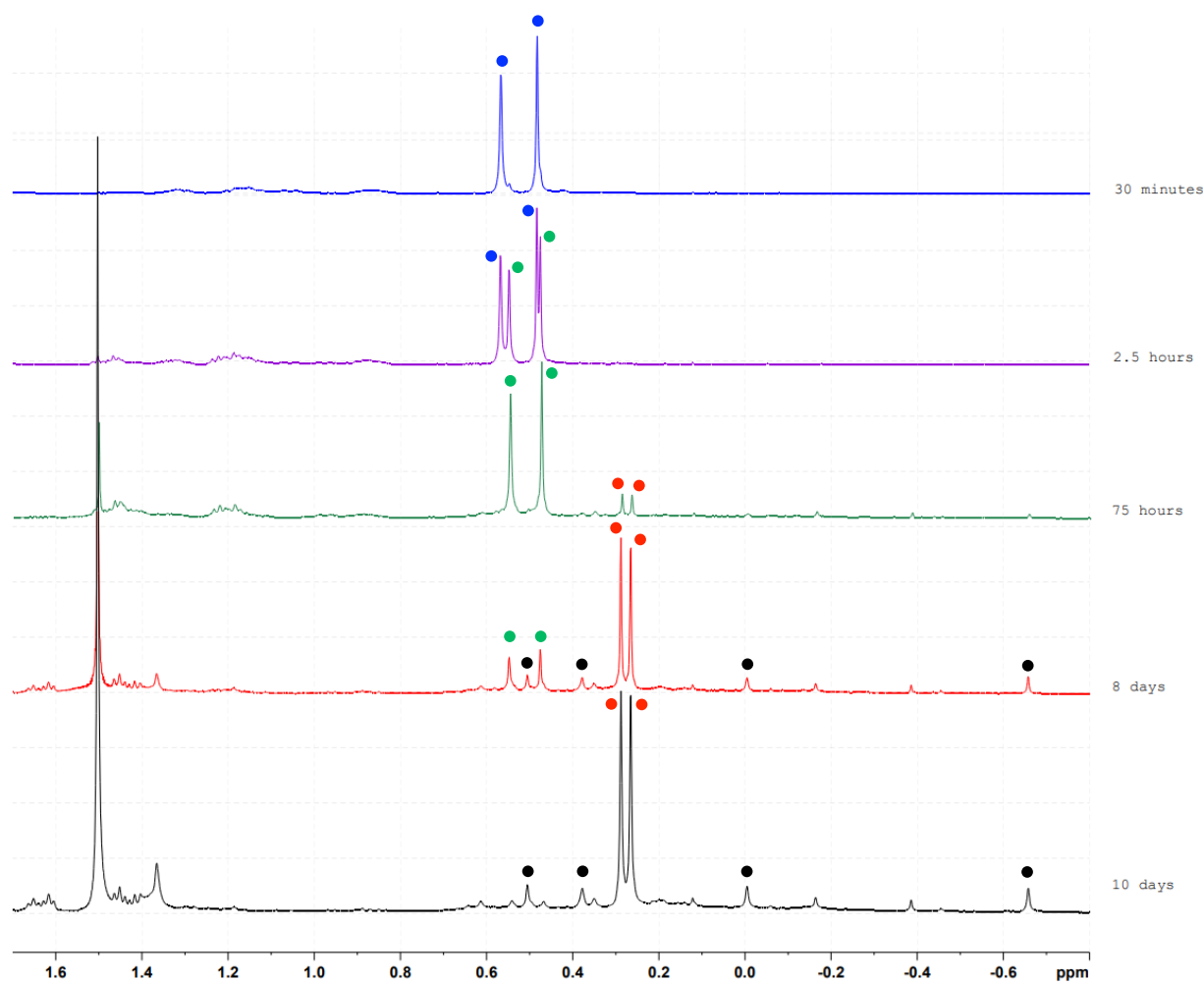
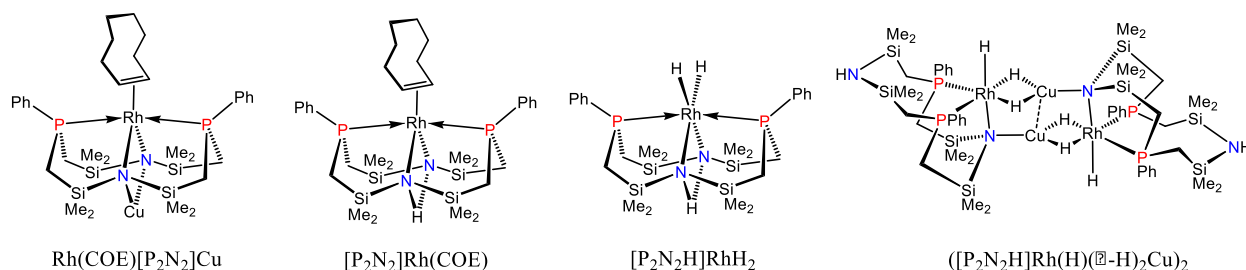


Figure S12: Detail of the silyl methyl region of the ^1H NMR (400.2 MHz in C_6D_6) monitoring experiment of treatment of $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$ with H_2 in a J-Young tube. The labels on the right correspond to the time the spectrum was taken after the initial addition of H_2 . Furthermore, the reaction vessel was refilled with H_2 after 48 hours, and heated on the 9th and 10th days. Resonances marked with a blue dot correspond to $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$, those with a green dot to $[\text{P}_2\text{N}_2\text{H}]\text{Rh}(\text{COE})$, those with a red dot to $[\text{P}_2\text{N}_2\text{H}]\text{RhH}_2$ and those with a black dot to the final product, $([\text{P}_2\text{N}_2\text{H}]\text{Rh}(\text{H})(\mu\text{-H})_2\text{Cu})_2$. The peak at δ 1.50 corresponds to cyclooctane arising from hydrogenation of dissociated syn-cyclooctene.



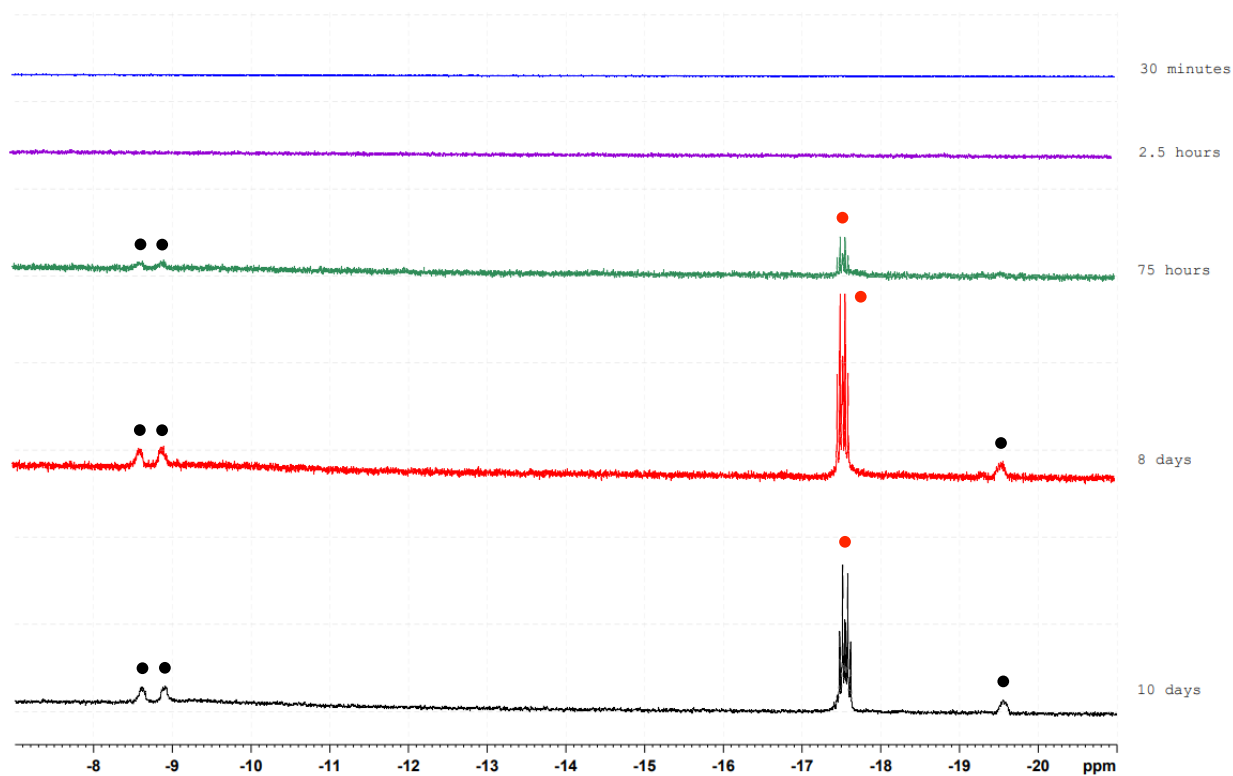


Figure S13: Detail of the hydride region of the ^1H NMR (400.2 MHz in C_6D_6) monitoring experiment of treatment of $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$ with H_2 in a J-Young tube. The labels on the right correspond to the time the spectrum was taken after the initial addition of H_2 . Furthermore, the reaction vessel was refilled with H_2 after 48 hours, and heated on the 9th and 10th days. Resonances marked with a red dot correspond to $[\text{P}_2\text{N}_2\text{H}]\text{RhH}_2$ and those with a black dot to the final product, $([\text{P}_2\text{N}_2\text{H}]\text{Rh}(\text{H})(\mu\text{-H})_2\text{Cu})_2$.

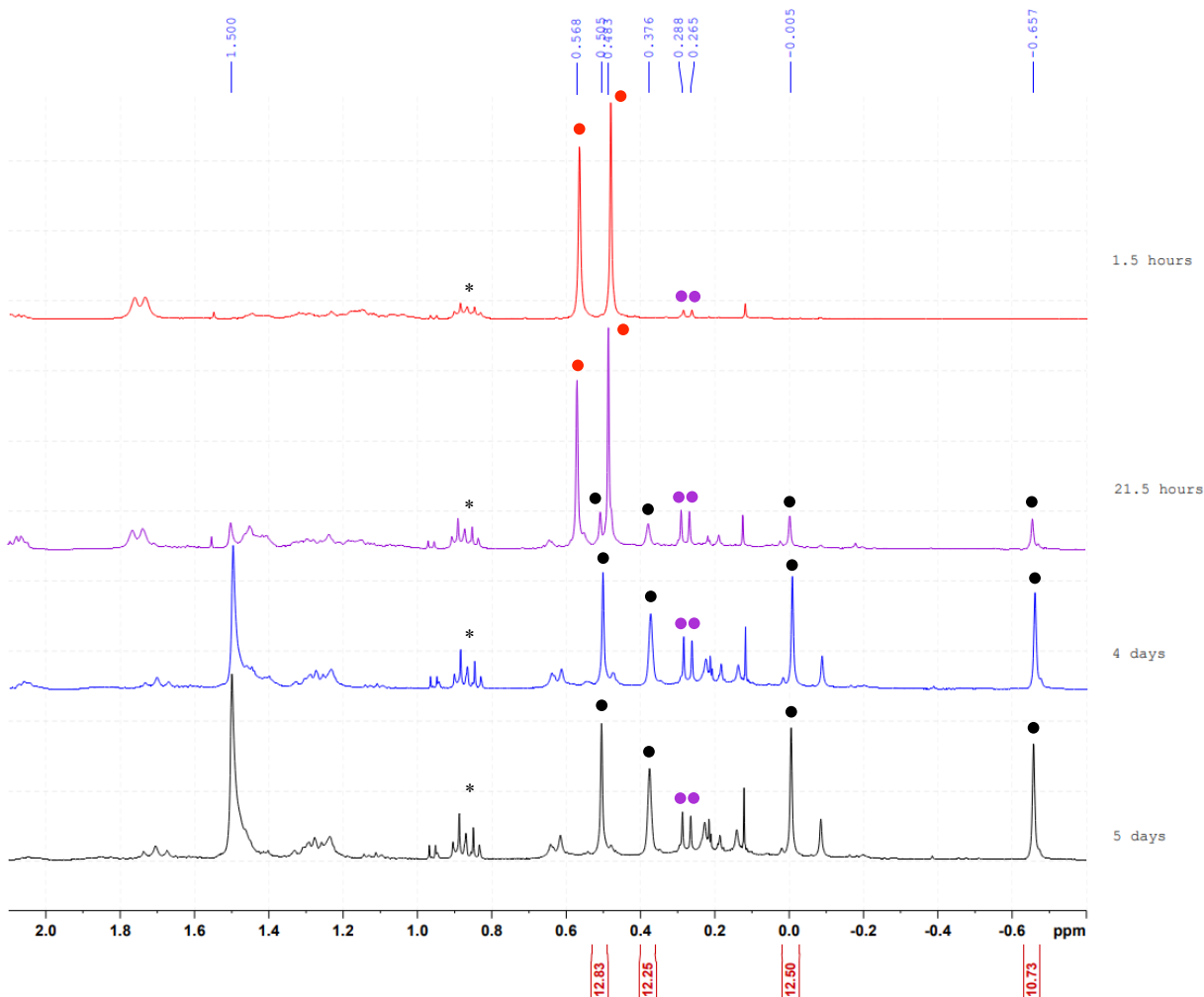


Figure S14: Detail of the silyl methyl region of the ^1H NMR (400.2 MHz in C_6D_6) spectra at select times after $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$ was treated with 1 atm of D_2 in a J-Young tube. The labels on the right correspond to time after the first addition of D_2 . The J-Young tube was recharged with 1 atm of D_2 immediately after the NMR spectrum at 21.5 hours was observed. The resonance at δ 1.50 corresponds to cyclooctane- d_x generated from the deuteration of cyclooctene. The specific degree of deuteration is variable and dependent on the H/D exchange mechanism described in the discussion. Resonances marked with (*) correspond to residual hexanes solvent. Resonances marked with a black dot correspond to $([\text{P}_2\text{N}_2\text{D}]\text{Rh}(\text{H}/\text{D})(\mu\text{-H}/\text{D})_2\text{Cu})_2$, those marked with a purple dot to $[\text{P}_2\text{N}_2\text{D}]\text{RhD}_2$, and those with a red dot to $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$. Contrary to previous experiments with H_2 , $[\text{P}_2\text{N}_2\text{D}]\text{Rh}(\text{COE})$ was not observed throughout this experiment. Note also that a resonances at δ 0.20 corresponding to the N-H moiety of $([\text{P}_2\text{N}_2\text{H}]\text{Rh}(\text{H})(\mu\text{-H})_2\text{Cu})_2$ and at δ 2.00 corresponding to the N-H moiety of $[\text{P}_2\text{N}_2\text{H}]\text{RhH}_2$ were not observed. Integrations shown in red below the horizontal axis correspond to the NMR spectrum taken after 5 days.

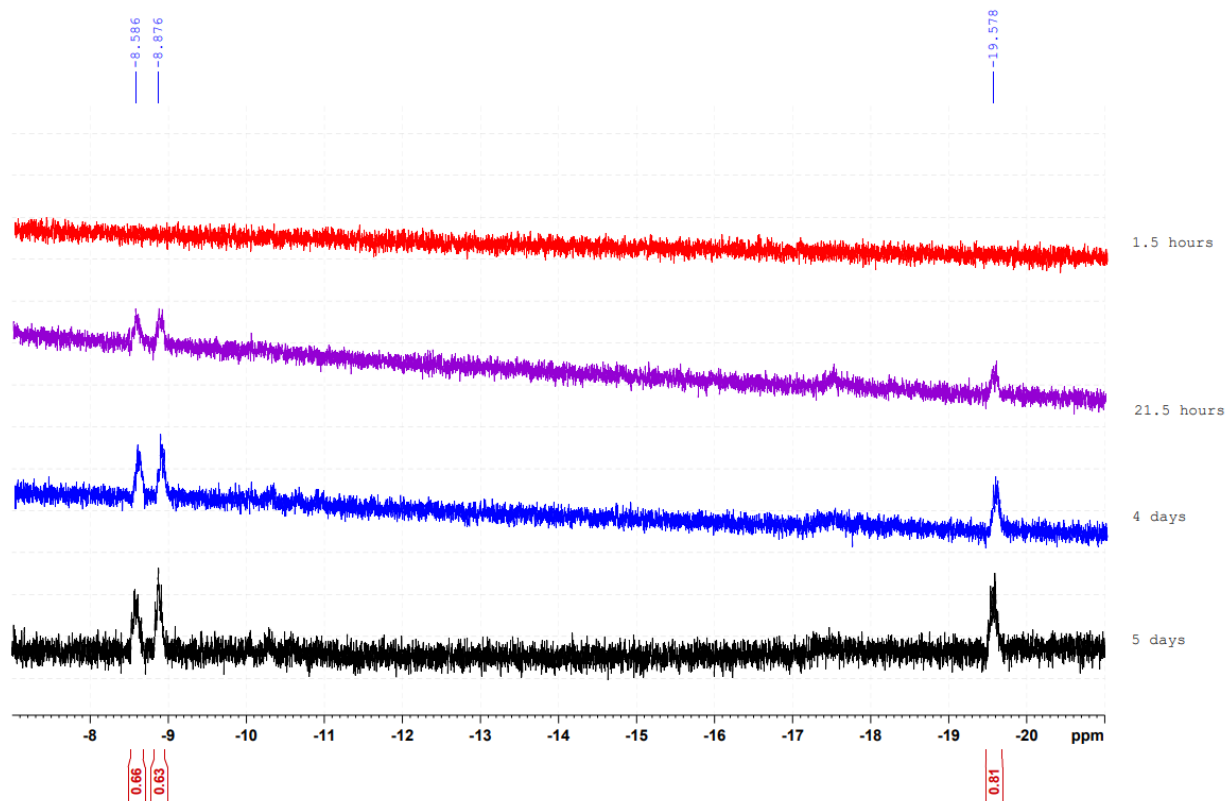


Figure S15: Detail of the hydride region of the ^1H NMR (400.2 MHz in C_6D_6) spectra at select times after $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$ was treated with 1 atm of D_2 in a J-Young tube. The labels on the right correspond to time after the first addition of D_2 . The J-Young tube was recharged with 1 atm of D_2 immediately after the NMR spectrum at 21.5 hours was observed. Resonances shown correspond to the hydrides of $([\text{P}_2\text{N}_2\text{H}]\text{Rh}(\text{H})(\mu\text{-H})_2\text{Cu})_2$ proposed to arise from the H/D exchange process described in the discussion. Integrations shown in red below the horizontal axis correspond to the NMR spectrum taken after 5 days. Each integration region shown theoretically integrates to 2 H in fully-hydrogenated $([\text{P}_2\text{N}_2\text{H}]\text{Rh}(\text{H})(\mu\text{-H})_2\text{Cu})_2$.

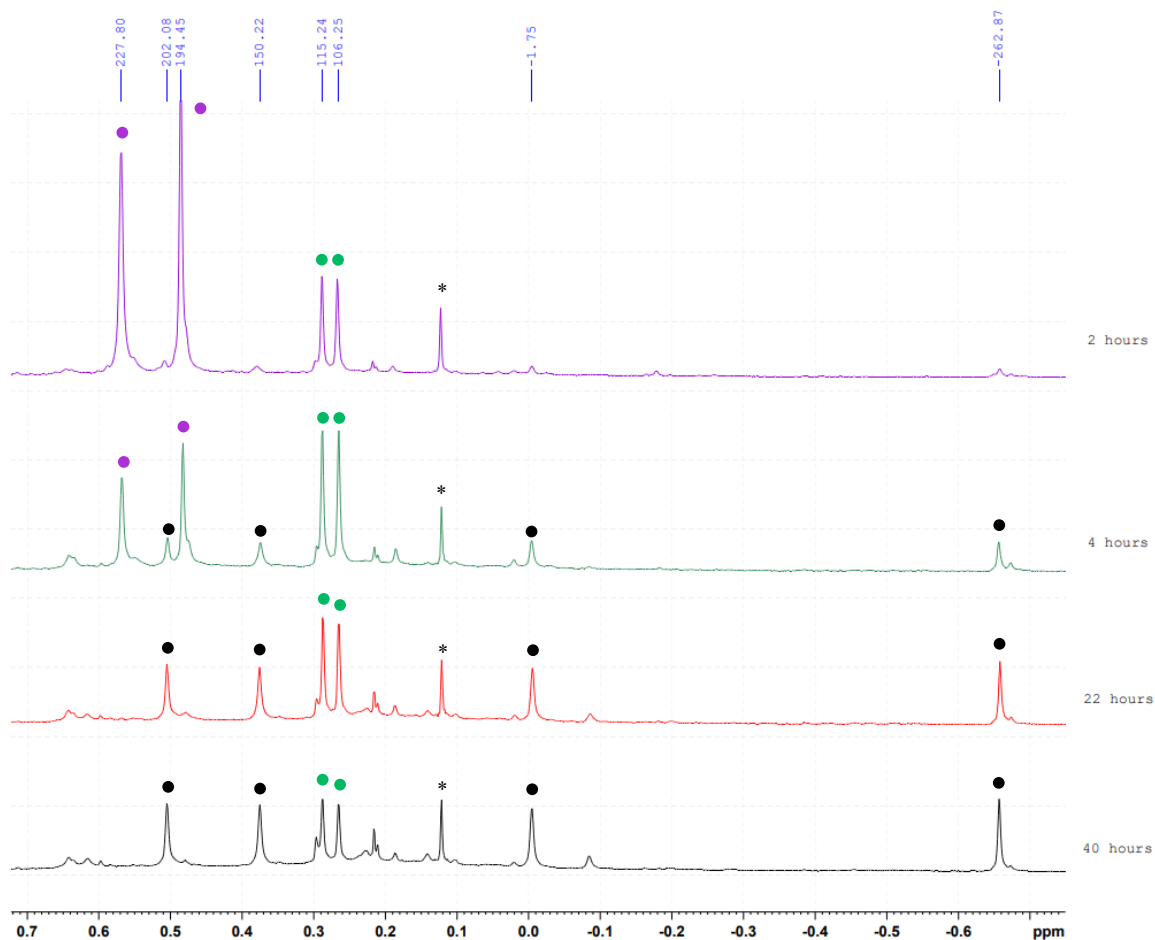


Figure S16: Detail of the silyl methyl region of the ^1H NMR (400.2 MHz in C_6D_6) spectra at select times after $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$ was treated with excess D_2 in a Schlenk flask. The labels on the right correspond to time after the first addition of 4 atm D_2 . After each spectra was taken, the Schlenk flask was re-charged with 4 atm D_2 . Resonances marked with (*) correspond to residual HMDSO solvent. Resonances marked with a black dot correspond to $([\text{P}_2\text{N}_2\text{D}]\text{Rh}(\text{D})(\mu\text{-D})_2\text{Cu})_2$, those marked with a green dot to $[\text{P}_2\text{N}_2\text{D}]\text{RhD}_2$, and those with a purple dot to $\text{Rh}(\text{COE})[\text{P}_2\text{N}_2]\text{Cu}$. Again, no appreciable amount of $[\text{P}_2\text{N}_2\text{D}]\text{Rh}(\text{COE})$ is observed.

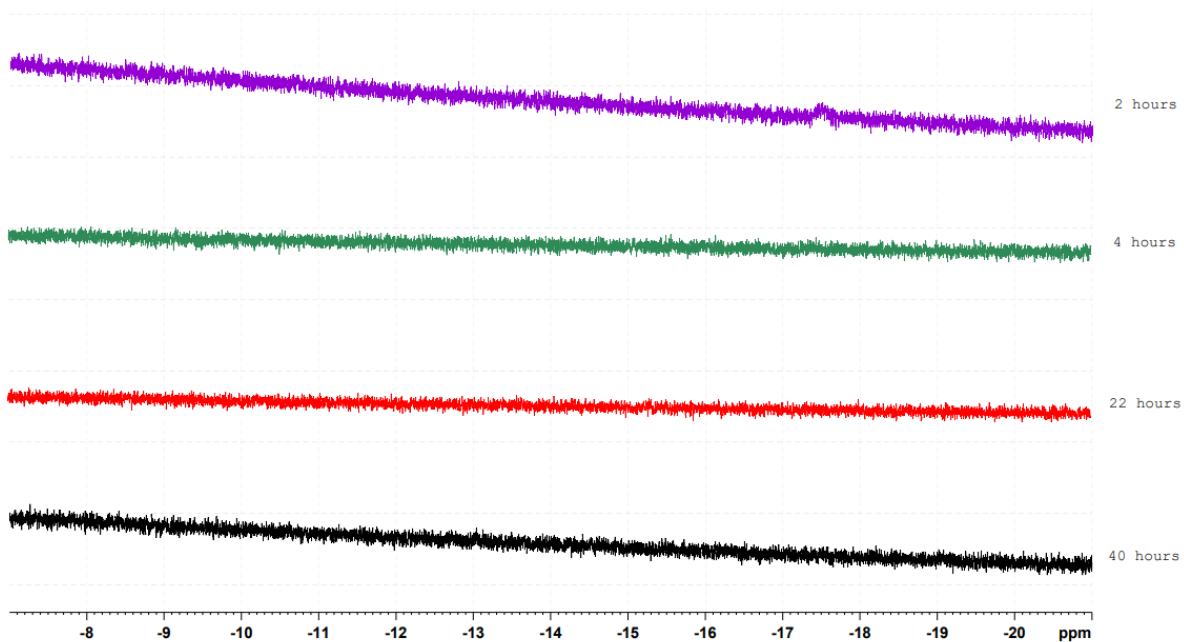


Figure S17: Detail of the hydride region of the ¹H NMR (400.2 MHz in C₆D₆) spectra at select times after Rh(COE)[P₂N₂]Cu was treated with excess D₂ in a Schlenk flask. The labels on the right correspond to time after the first addition of 4 atm D₂. After each spectra was taken, the Schlenk flask was re-charged with 4 atm D₂. Note that no hydride peaks are observed under these conditions.

X-ray Crystallographic Analyses

Crystal structures were obtained from suitable single crystals coated in Fomblin oil and mounted on a glass loop. Diffraction data was collected on a Bruker Apex II area detector diffractometer using graphite-monochromated radiation from either a Cu K α ($\lambda = 1.54178 \text{ \AA}$) or Mo K α ($\lambda = 0.71073 \text{ \AA}$) source. Data was integrated using the Bruker SAINT software package. Crystal structures were solved using the Olex2¹ software package with the ShelXT² program using the Intrinsic Phasing method and refined using the ShelXL³ using a Least Squares minimisation. All non-hydrogen atoms were refined anisotropically. Hydrogens of interest attached to metal centers or to nitrogen atoms in the P₂N₂ ligand backbone were located on the density difference map and refined isotropically. The remaining hydrogens were placed in calculated positions and assigned to an isotropic displacement parameter. Representations of the crystal structure were generated using the Olex2 package. Diffraction experiments were carried out by Dr. Brian O. Patrick at the Department of Chemistry, University of British Columbia.

CCDC Identification

Rh(COE)[P₂N₂]Cu	2087925
([P₂N₂H]RhH(μ-H)₂Cu)₂	2087926

Table S1: Crystal data and structure refinement parameters for Rh(COE)[P₂N₂]Cu

Empirical formula	C ₃₂ H ₅₆ CuN ₂ P ₂ RhSi ₄
Formula weight	809.53
Temperature/K	90.0
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	15.9598(7)
b/Å	13.5924(6)
c/Å	18.3198(8)
α/°	90
β/°	102.314(3)
γ/°	90
Volume/Å ³	3882.7(3)
Z	4
ρ _{calc} /g/cm ³	1.385
μ/mm ⁻¹	6.250
F(000)	1688.0
Crystal size/mm ³	0.2 × 0.13 × 0.08
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	5.668 to 118.736
Index ranges	-16 ≤ h ≤ 17, -15 ≤ k ≤ 15, -20 ≤ l ≤ 20
Reflections collected	43620
Independent reflections	5623 [R _{int} = 0.1088, R _{sigma} = 0.0591]
Data/restraints/parameters	5623/896/460
Goodness-of-fit on F ²	1.027
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0450, wR ₂ = 0.1075
Final R indexes [all data]	R ₁ = 0.0651, wR ₂ = 0.1171
Largest diff. peak/hole / e Å ⁻³	0.96/-0.93

Table S2: Crystal data and structure refinement parameters for $([P_2N_2H]RhH(\mu-H)_2Cu)_2$

Empirical formula	$C_{62}H_{108}Cu_2N_4P_4Rh_2Si_8$
Formula weight	1591.02
Temperature/K	90.0
Crystal system	monoclinic
Space group	C2/c
a/Å	33.949(3)
b/Å	13.5303(10)
c/Å	21.6795(17)
$\alpha/^\circ$	90
$\beta/^\circ$	128.4150(10)
$\gamma/^\circ$	90
Volume/Å ³	7802.5(10)
Z	4
ρ_{calc}/cm^3	1.354
μ/mm^{-1}	1.195
F(000)	3312.0
Crystal size/mm ³	0.16 × 0.13 × 0.08
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	3.062 to 61.136
Index ranges	-41 ≤ h ≤ 48, -19 ≤ k ≤ 19, -31 ≤ l ≤ 30
Reflections collected	57083
Independent reflections	11955 [$R_{int} = 0.0413$, $R_{sigma} = 0.0382$]
Data/restraints/parameters	11955/0/445
Goodness-of-fit on F ²	1.014
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0306$, $wR_2 = 0.0653$
Final R indexes [all data]	$R_1 = 0.0485$, $wR_2 = 0.0723$
Largest diff. peak/hole / e Å ⁻³	0.78/-0.47

Gas Chromatography-Mass Spectrometry Experiments

To determine the degree of H/D exchange between rhodium complexes and cyclooctene observed when Rh(COE)[P₂N₂]Cu was treated with D₂, the organic products generated in the reaction were isolated and analyzed by GC-MS.

In each of three trials completed a sample of Rh(COE)[P₂N₂]Cu was dissolved in ~2.5 mL C₆D₆ and treated with D₂ dried by passing across activated molecular sieves in a 200 mL Schlenk bomb flask with a Teflon stopper. The samples were stirred vigorously for 72 hours. Thereafter, the organics in C₆D₆ solvent were distilled and collected. The samples were analyzed on an Agilent 5977A MSD mass spectrometer equipped with an Agilent 7890B GC chromatograph. In each trial, the column was initially heated to 90°C and held for 2 minutes prior to sample injection. Upon injection of sample, the temperature was increased at a rate of 1°C/min to 100°C and held at 100°C for 2 minutes. Thereafter, the temperature was increased to a final temperature of 200°C at a rate of 40°C/min and held for 1 minute. Ionization for mass spectrometry was affected by electron impact with an electron multiplier voltage of 1989.2 V. The GC-MS method was developed and carried out by Dr. Yun Ling at the Department of Chemistry, University of British Columbia.

NMR-monitoring experiments indicated that when treated with D₂, the cyclooctene from Rh(COE)[P₂N₂]Cu becomes deuterated to cyclooctane-d_n. The specific value of n is variable, as demonstrated by the GC-MS experiments. The cyclooctane-d_n elutes as a broad peak with a maximum around a retention time at 5.25 mins. Since it was observed that the degree of deuteration influences retention time, scans taken within a retention time range of 5.05 to 5.35 minutes were combined to accurately reflect the distribution of isotopomers.

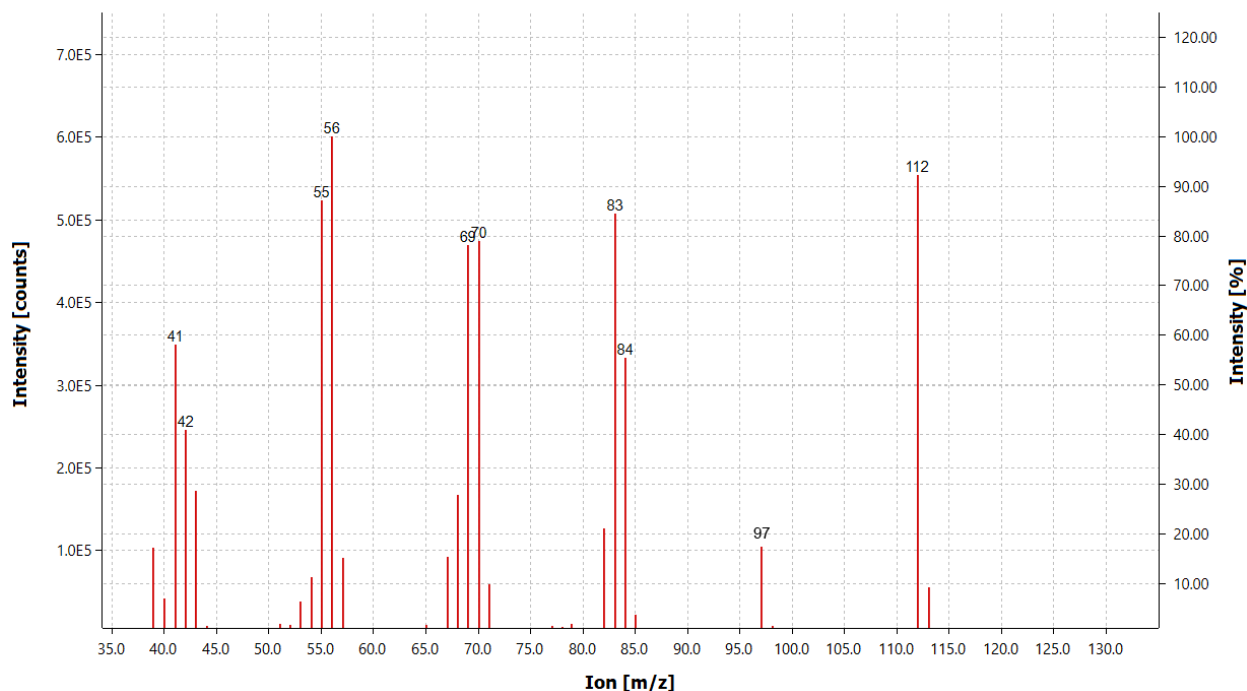


Figure S18: Reference mass spectrum of cyclooctane obtained using the GC-MS method outlined. The above mass spectrum was taken at a retention time of 5.288 minutes.

Table S3: Intensities of major ionic species in the mass spectrum of cyclooctane.

Ion (m/z)	Relative intensity (%)
41	58.06
42	40.86
55	87.11
56	100
69	78.05
70	78.81
83	84.33
84	55.31
97	17.40
112	92.24

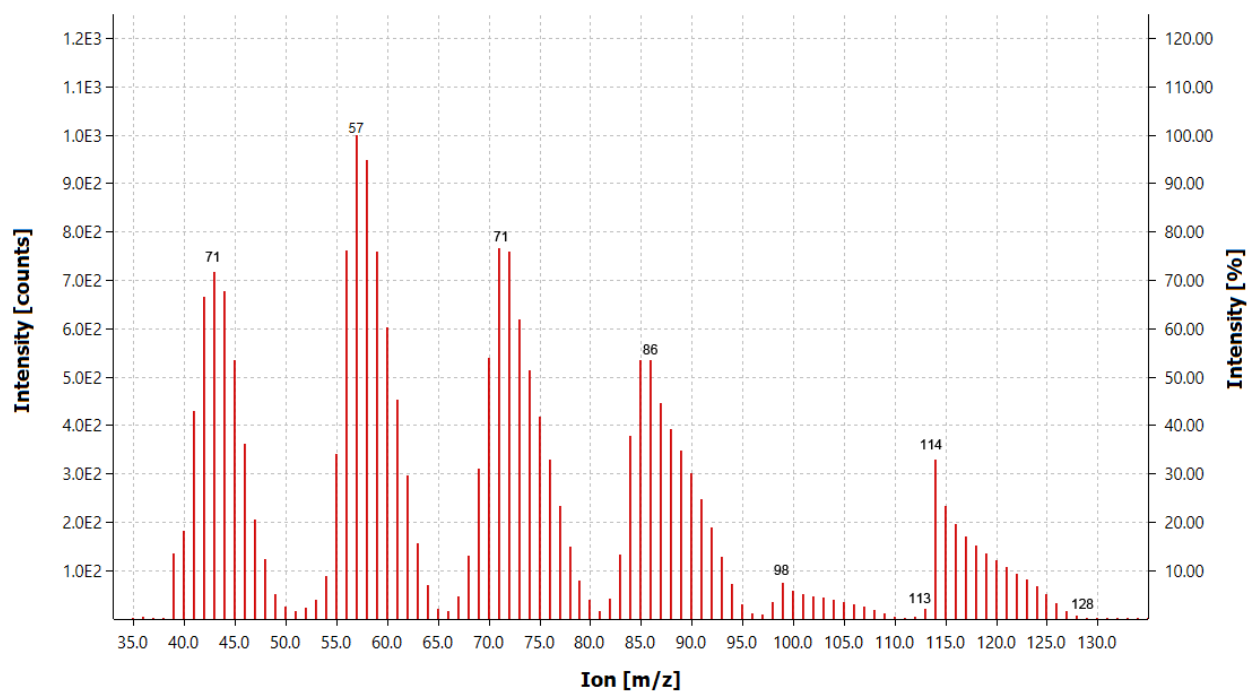


Figure S19: Combined mass spectrum (RT 5.05-5.35 min.) of the collected organic products of the reaction of Rh(COE)[P₂N₂]Cu (0.040 g) with D₂ (1 atm) at ambient temperature (~20°C). Note the peaks at m/z 114 through 128 corresponding to the molecular ions of isotopologues cyclooctane-d₂ through cyclooctane-d₁₆.

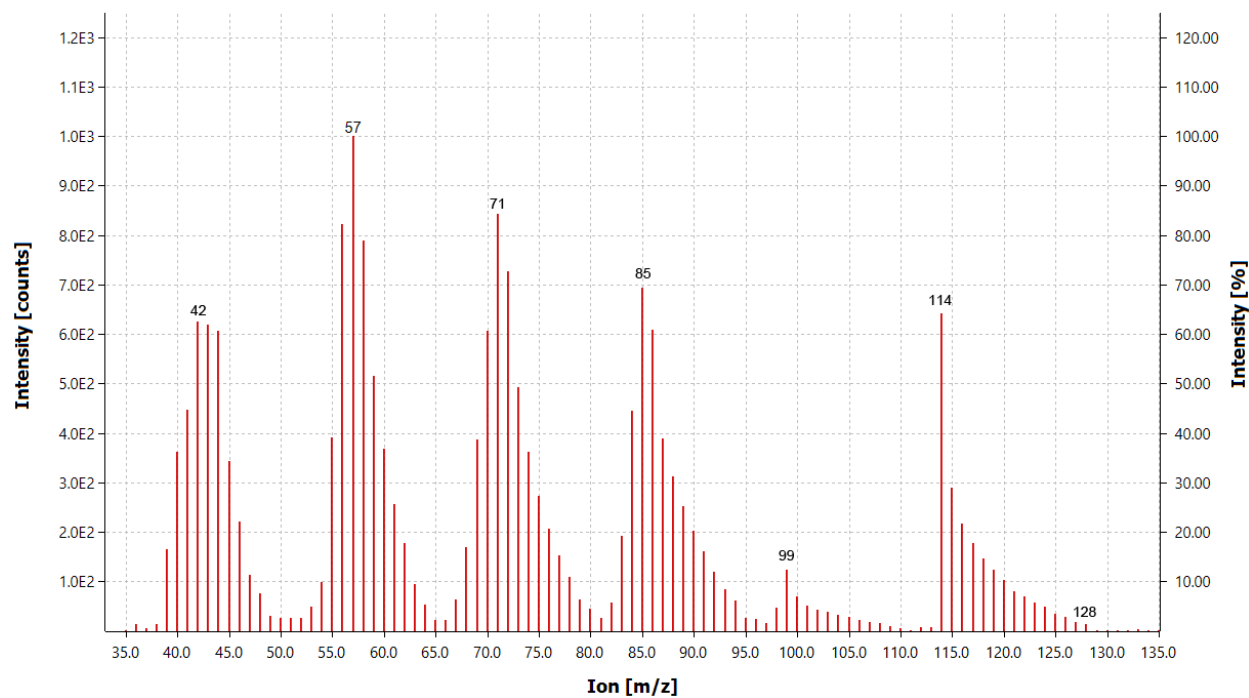


Figure S20: Combined mass spectrum (RT 5.05-5.35 min.) of the collected organic products of the a second trial of the reaction of Rh(COE)[P₂N₂]Cu (0.031 g) with D₂. For this second trial, the D₂ pressure was increased to 4 atm and the reaction was stirred at an elevated ambient temperature of ~30-35°C.

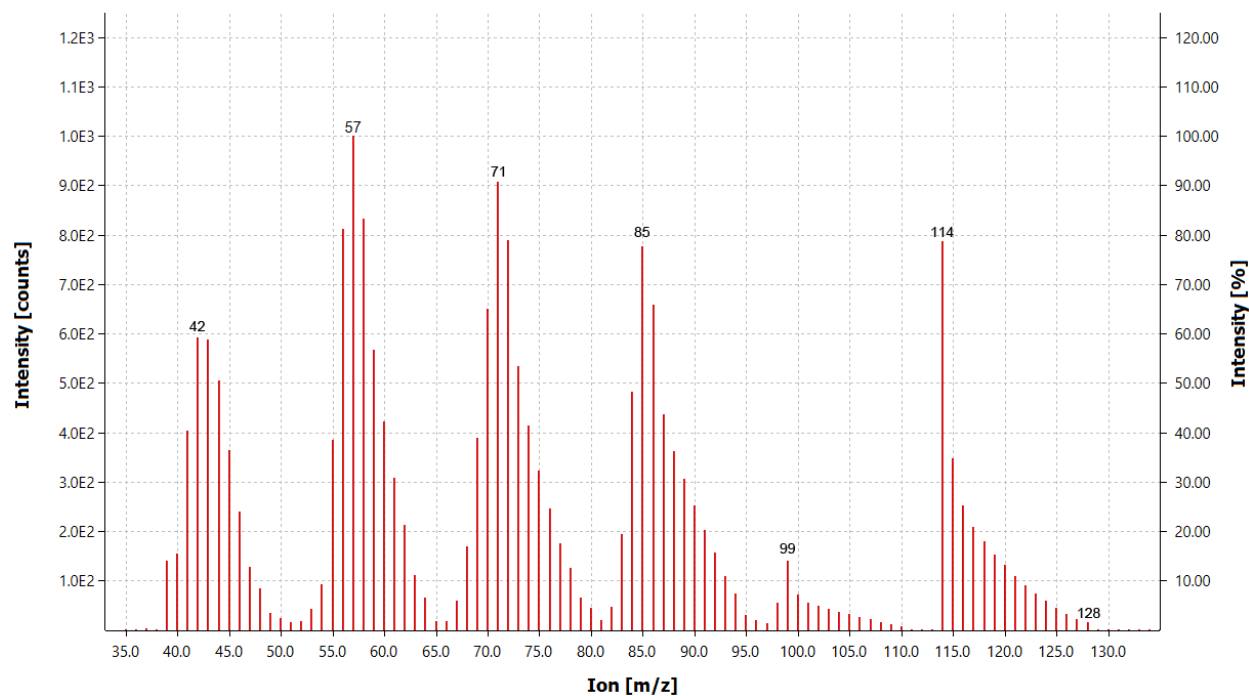


Figure S21: Combined mass spectrum (RT 5.05-5.35 min.) of the collected organic products of the a third trial of the reaction of Rh(COE)[P₂N₂]Cu (0.032 g) with D₂. For the trial, 4 atm of D₂ pressure was used and the temperature was maintained at ~10°C by chilling with ice in a water bath.

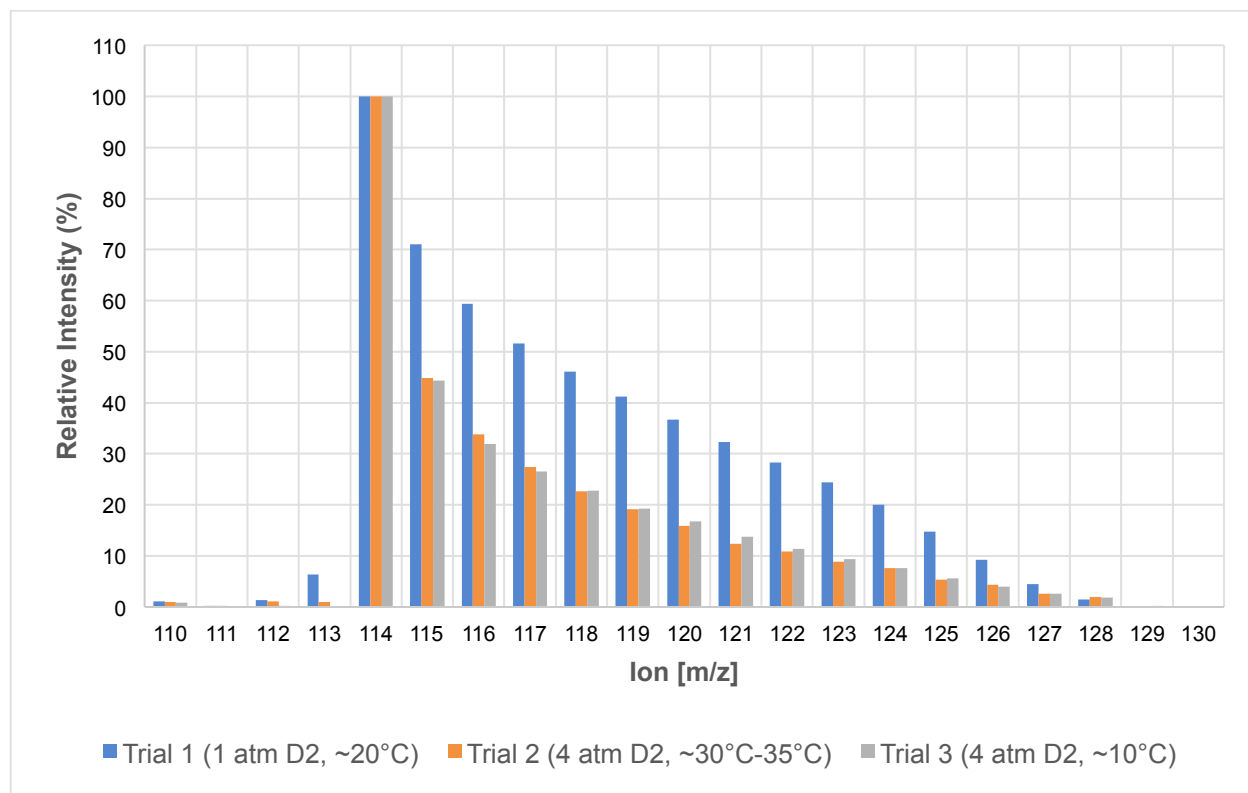


Figure S22: Comparison of the isotopologue distributions of the molecular ion in the three GC-MS experiments where Rh(COE)[P₂N₂]Cu was treated with D₂. Ion intensities are scaled relative to that of cyclooctane-d₂ (m/z 114).

In-Silico Simulation of Deuteration Experiments

In silico modelling was used to determine whether the mechanism composed could be consistent with the isotopologue distribution observed by mass spectrometry. The python program was written and run using the initial conditions corresponding to the deuteration experiments.

```
1  ### INITIAL PARAMETERS ###
2
3  import numpy as np
4  import matplotlib.pyplot as plt
5
6  M=0.032          # Mass of Rh(COE)[P2N2]Cu used in reaction
7  N=M/805.54*(6.022*10**23)/(10**15) # Number of molecules of Rh(COE)[P2N2]Cu in units of 10^15
8  N=int(N)
9  nH=0            # Number of hydrogen atoms as H2 or HD in units of 10^15
10
11 P=1              # Pressure of D2 (in atm) initially introduced
12 T=77             # Temperature (in K) at time of nitrogen introduction
13                 # For ~4 atm D2 at r.t., 'T' should be liquid nitrogen temperature (77)
14
15 nD=P*101325*0.0002/(8.3145*T)*(6.022*10**23)/(10**15)*2
16                 # Number of deuterium atoms as D2 or HD in units of 10^15
17                 # Calculated initially by D2 pressure introduced assuming ideal gas
18
19 pre=0.20         # Probability of reductive elimination, arbitrarily assigned
20
21
22 # Let each COE molecule be represented as an array of length 8, where the value in the nth element represents
23 # the mass of the (n+1)th carbon and attached hydrogen/deuterium atoms. Thus 14 indicates a carbon with two
24 # hydrogen atoms, 15 indicates a carbon with one hydrogen and one deuterium, and 16 indicates a carbon with two
25 # deuterium atoms.
26
27 set=np.ones((N,8))*14          # An array of N cyclooctane molecules (each representing 10^15 molecules)
28
29 enedex=np.empty(N)            # Index of the location of the alkene moiety. An array of length N, corresponding
30 # to the COE molecules in 'set'. Each element, x, in enedex indicates that
31 # the corresponding molecule in 'set' has a double bond between the (x+1)th
32 # and (x+2)th carbon, or is coordinated to the Rh atom, as a cyclooctyl group,
33 # at the (x+1)th carbon.
34
35 done=np.zeros((N,8))         # The array of fully saturated cyclooctane-dn molecules which no longer react
36 d=0                           # Number of fully saturated cyclooctane-dn molecules
37
38
39 #####
40
41 ### SIMULATION OF DEUTERATION ###
42
43 ### - Initial Insertion - ###
44
45 j=0                             # Index for the element (molecule) in 'set' being iterated.
46
47 todel=[]                          # Array of molecules to delete from 'set' and migrate to 'done'. Lists the
48 # molecules that undergo reductive elimination to generate cyclooctane-dn.
49
50
51
52 for i in set:
53     m=np.random.randint(0,7)      # Randomly select a position at which to introduce the alkene moiety
54     i[m]-=1                        # The (m+1)th and (m+2)th carbon are changed from -CH2- to -CH-
55     i[m+1]-=1                      # reflected by a decrease in mass by 1
56     enedex[j]=m
57
```

```

58 # In the mechanism proposed, initially complex (3) reacts with D2 to generate complex (5-d1). Upon dissociation
59 # of the COE ligand to yield (A-d1), D2 adds to complex (A-d1) to give complex (6-d3). Then, the cyclooctene
60 # coordinates to give (B-d3). The COE ligand in (B-d3) undergoes alkene insertion to give (C-d3). Insertion
61 # can occur, with equal probability at either of the two carbons of the alkene moiety.
62
63 if np.random.random()<0.5: # Insert at the (m+1)th carbon, add a deuterium to the (m+2)th carbon
64     if m==7:
65         i[0]+=2 # Nested if/else statement required to account for molecule's cyclic nature
66     else:
67         i[m+1]+=2
68     else: # Insert at the (m+2)th carbon, add a deuterium to the (m+1)th carbon
69         i[m]+=2
70         enedex[j]=m+1
71         m=m+1
72
73 if np.random.random()<pre: # With some pre-defined probability, 'pre', reductively eliminate complex (C-d3)
74     i[m]+=2 # to give complex (A-d1) and cyclooctane-d2
75     done[d,:]=i
76     d+=1 # If reductive elimination happens, migrate molecule to done list
77     todel.append(j) # Also append index of saturated molecules to 'todel' list to delete from 'set'
78
79     j+=1
80
81
82
83 set=np.delete(set,todel,axis=0) # Delete saturated molecules from 'set' list and corresponding 'enedex' element
84 enedex=np.delete(enedex,todel)
85
86 nD=nD-d*2 # Subtract the number of deuterium atoms required to saturate the cyclooctane-d2
87 # from 'nD'
88
89
90
91 ### - Propagation - ###
92
93 # Definition of functions used in propagation:
94
95
96 # Function modelling the beta-hydride elimination of complex (C-dn) to form (B-dn). Takes 'mol', a cyclooctyl from
97 # 'set', as an array of length 8, and 'pos', an integer indicating that the cyclooctyl is coordinated at the (pos+1)th
98 # carbon. Returns 'mol' as a beta-hydride eliminated cyclooctene molecule and 'pos' indicating a double bond between
99 # the (pos)th and (pos+1)th carbon.
100 def elim(mol, pos):
101     if np.random.random()<0.5: # Beta-hydride eliminate with at the (pos+1)th carbon with 50% probability
102         if pos==7:
103             mol[0]=subtract(mol[0]) # Calls 'subtract' function to take either a hydride or
104         else: # deuterium from beta carbon
105             mol[int(pos+1)]=subtract(mol[int(pos+1)])
106
107         return mol,pos
108
109     else: # Beta-hydride eliminate with at the (pos)th carbon with 50% probability
110         if pos==0:
111             mol[7]=subtract(mol[7])
112             pos=7
113         else:
114             mol[int(pos-1)]=subtract(mol[int(pos-1)])
115             pos-=1
116
117         return mol,pos
118
119

```



```

120 # Function that removes a hydride or deuterium from the beta-carbon during beta-hydride elimination. Takes 'x', an
121 # integer representing the mass of the beta-carbon and attached hydrogen/deuterium atoms. Returns an integer
122 # corresponding to the mass of the respective carbon and attached hydrogen/deuterium atoms after beta-hydride
123 # elimination. If 13 returned, indicates -CH-, if 14 returned, indicates -CD-.
124 def subtract(x):
125
126     global nH,nD
127     if x==14:
128         nH+=1
129         return 13
130     if x==16:
131         nD+=1
132         return 14
133     else:
134         if np.random.random()<0.5:
135             nD+=1
136             return 13
137         else:
138             nH+=2
139             return 14
140
141
142
143
144 # Function that simulates the alkene insertion of the COE ligand in complex (B-dn) to generate complex (C-dn) Takes
145 # 'mol', a COE molecule as a 8-element array, and 'pos', an integer indicating that the double bond exists between the
146 # (pos)th and (pos+1)th carbon. Returns 'mol', a cyclooctyl ligand, and 'pos', an integer indicating that the
147 # cyclooctyl ligand is bonded to the rhodium at the (pos+1)th carbon.
148 def insert(mol, pos):
149     if np.random.random()<(nD/(nH+nD)):
150         a=2
151     else:
152         a=1
153
154
155     if np.random.random()<0.5:
156         if pos==7:
157             mol[0]+=a
158         else:
159             mol[int(pos+1)]+=a
160
161     else:
162         if pos==7:
163             mol[int(pos)]+=a
164             pos=0
165         else:
166             mol[int(pos)]+=a
167             pos+=1
168
169     return mol,pos
170
171
172

```

```

173 # Propagation loop:
174
175 while len(set)>0:          # Propagate until 'set' is empty and all COE molecules are fully saturated
176
177     if len(set)==1:      # Randomly cycle through 'set' list (unless it is only one element in 'set')
178         m=0
179     else:
180         m=np.random.randint(0,(len(set)-1))
181
182     # With the population of complex (C-dn) that have not undergone reductive elimination, undergo beta-hydride
183     # elimination to generate complex (B-dn)
184     mol,pos=elim(set[m,:], enedex[m])
185
186     # With each molecule of complex (B-dn), undergo alkene insertion
187     mol,pos=insert(mol, pos)
188
189     # With some pre-defined probability, 'pre', reductively eliminate complex (B-dn) to generate fully-saturated
190     # cyclooctane-dn. When undergoing reductive elimination, couple a deuteride with the cyclooctyl with probability
191     # proportional to the relative abundance of deuterium in the environment. Else, couple a hydride with probability
192     # proportional to the relative abundance of hydrogen in the environment.
193     if np.random.random()<(nD/(nH+nD)):
194         a2=2
195     else:
196         a2=1
197
198     if np.random.random()<pre:
199         mol[int(pos)]+=a2
200         done[d,:]=mol          # Append fully saturated COE molecules to 'done'
201         d+=1
202
203         set=np.delete(set,m,axis=0) # Delete fully saturated COE molecules
204         enedex=np.delete(enedex,m)
205
206     else:
207         set[m]=mol          # Otherwise, if a given molecule of complex (C-dn) does not undergo reductive
208         enedex[m]=pos       # elimination, undergo beta-hydride elimination to complex (B-d3) by iterating
209                             # through loop again
210
211 # Write 'done' array as .txt file
212 np.savetxt('cyclooctane-dn.txt', done)
213
214
215 #####
216
217 ### VISUALIZATION OF ISOTOPOMER DISTRIBUTION ###
218
219 sums=[]                    # Array of size N corresponding to the mass of each saturated cyclooctane-dn
220                             # molecule
221 for i in done:
222     sums.append(sum(i))
223
224 # Generate Histogram:
225
226 hist,bin_edges=np.histogram(sums,17,(112,112+17))
227 plt.hist(hist,bin_edges)
228 plt.show()
229
230 isotopomers=np.stack((hist,bin_edges[0:17]), axis=1)
231 np.savetxt('Isotopomers.txt', isotopomers)
232
233

```

```

234 #=====#
235
236 ### SIMULATION OF MASS SPECTROMETRY FRAGMENTATION ###
237
238 # Carry out the fragmentation of the distribution of isotopomers in 'done' according to mechanisms forming each
239 # fragment
240
241
242
243 ### - Distribution of cyclooctane molecules -
244
245 np.random.shuffle(done)          # Randomly shuffle order of saturated cyclooctane-dn molecules
246
247 # Relative intensities of major ions observed in cyclooctane (C8H16) standard analysed by GC-MS procedure; refer
248 # to Figure S18 and Table S3
249 i_112=92.24
250 i_97=17.40
251 i_84=55.31
252 i_83=84.33
253 i_70=78.81
254 i_69=78.05
255 i_56=100
256 i_55=87.11
257 i_42=40.86
258 i_41=58.06
259
260
261 # Total, summed intensities
262 i_tot=i_112+i_97+i_84+i_83+i_70+i_69+i_56+i_55+i_42+i_41
263
264 # Calculating the total percent abundance of each major ion observed in fragmentation of cyclooctane
265 pa_112=i_112/i_tot
266 pa_97=i_97/i_tot
267 pa_84=i_84/i_tot
268 pa_83=i_83/i_tot
269 pa_70=i_70/i_tot
270 pa_69=i_69/i_tot
271 pa_56=i_56/i_tot
272 pa_55=i_55/i_tot
273 pa_42=i_42/i_tot
274 pa_41=i_41/i_tot
275
276
277 # Distribute the 'N' total cyclooctane-dn molecules into populations into divisions corresponding to the major ions
278 # observed in the mass spectrum of the cyclooctane standard according to their percent abundance.
279 d1=int(pa_41*N)
280 d2=d1+int(pa_42*N)
281 d3=d2+int(pa_55*N)
282 d4=d3+int(pa_56*N)
283 d5=d4+int(pa_69*N)
284 d6=d5+int(pa_70*N)
285 d7=d6+int(pa_83*N)
286 d8=d7+int(pa_84*N)
287 d9=d8+int(pa_97*N)
288
289 f_41=done[0:d1,:]
290 f_42=done[d1:d2,:]
291 f_55=done[d2:d3,:]
292 f_56=done[d3:d4,:]
293 f_69=done[d4:d5,:]
294 f_70=done[d5:d6,:]
295 f_83=done[d6:d7,:]
296 f_84=done[d7:d8,:]
297 f_97=done[d8:d9,:]
298 f_112=done[d9:,:]

```

```

299
300
301
302 ### - Definition of Functions Used in Fragmentation - ###
303
304 # Function which takes an integer, 'x', corresponding to the mass of a particular carbon and its attached hydrogen and
305 # deuterium atoms and removes a proton or a deuteron based on the mass. If 'x' is 14, carbon is -CH2-, therefore
306 # simply remove a proton by subtracting 1. If 'x' is 16, carbon is -CD2-, therefore simply remove a deuteron by
307 # subtracting 2. If 'x' is 15, carbon is -CHD-, therefore remove a proton with 50% probability and remove a deuteron
308 # with 50% probability.
309 def deprot(x):
310
311     if x==14:
312         return 13
313     if x==16:
314         return 14
315     else:
316         if np.random.random()<0.5:
317             return 13
318         else:
319             return 14
320
321
322 ### - Deprotonation according to mechanism - ###
323
324 # Each fragmentation mechanism begins first with the cleavage of a bond and breakage of the cyclic structure to form
325 # a linear molecular ion
326
327
328 # Loss of a methyl radical by deprotonation of terminal carbocation and formation of cycloheptyl carbocation
329 v for i in f_97:
330     i[0]=0
331     i[7]=deprot(i[7])
332
333 # Elimination of ethylene leaving a hexyl radical cation
334 v for i in f_84:
335     i[0:2]=0
336
337 # Loss of an ethyl radical by deprotonation of terminal carbocation and formation of cyclohexyl carbocation
338 v for i in f_83:
339     i[0:2]=0
340     i[7]=deprot(i[7])
341
342 # Elimination of propylene leaving a propyl radical cation
343 v for i in f_70:
344     i[0:3]=0
345
346 # Loss of a propyl radical by deprotonation of terminal carbocation and formation of cyclopentyl carbocation
347 v for i in f_69:
348     i[0:3]=0
349     i[7]=deprot(i[7])
350
351 # Elimination of 1-butene leaving a butyl radical cation
352 v for i in f_56:
353     i[0:4]=0
354
355 # Loss of a butyl radical by deprotonation of terminal carbocation and formation of cyclobutyl carbocation
356 for i in f_55:
357     i[0:4]=0
358     i[7]=deprot(i[7])
359
360 # Elimination of 1-pentene leaving a propyl radical cation
361 for i in f_42:
362     i[0:5]=0
363

```

```

364 # Loss of a pentyl radical by deprotonation of terminal carbocation and formation of cyclopropyl carbocation
365 for i in f_41:
366     i[0:5]=0
367     i[7]=deprot(i[7])
368
369
370 # Gather all fragments in single array
371 fragments=np.concatenate((f_41,f_42,f_55,f_56,f_69,f_70,f_83,f_84,f_97,f_112), axis=0)
372
373 # Obtain masses of fragments by summing the elements in each element of 'fragments'
374 sums2=[]
375 for i in fragments:
376     sums2.append(sum(i))
377
378 # Generate histogram
379 hist2,bin_edges2=np.histogram(sums2,(112+16-36),(36,112+16))
380
381 plt.figure(figsize=(18,10))
382
383 plt.hist(sums2,bin_edges2,rwidth=0.4, color='red')
384 plt.xlabel('Ions [m/z]', fontsize=14)
385
386 labels=[]
387
388 for i in np.arange(32,132):
389     if i%2==0:
390         labels.append(str(i))
391
392     else:
393         labels.append("")
394
395 plt.xticks(ticks=(np.arange(32.5,132.5, step=1)), labels=labels)
396 plt.ylabel('Intensity [counts]', fontsize=14)
397 plt.grid(axis='y')
398 plt.show()

```

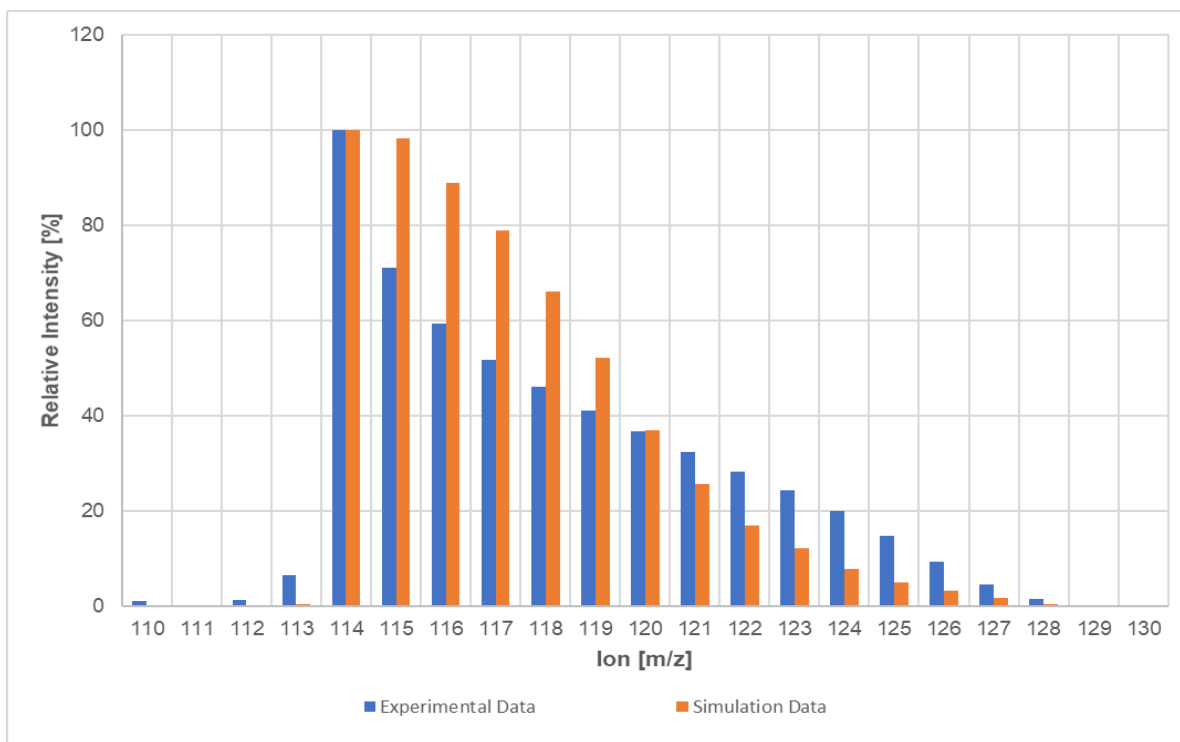


Figure S23: Comparison of simulation and experimental data for isotopologue distribution when Rh(COE)[P₂N₂] (0.041 g) is exposed to 1 atm of D₂. In this case, the probability of reductive elimination was tuned to be 17%. Intensities are scaled relative to that of cyclooctane-d₂ (m/z 114). Note that the simulation shows non-zero abundance for ions with m/z 128 showing that exchange of all hydrogen atoms for deuterium atoms is possible with the mechanism proposed and used to develop the simulation.

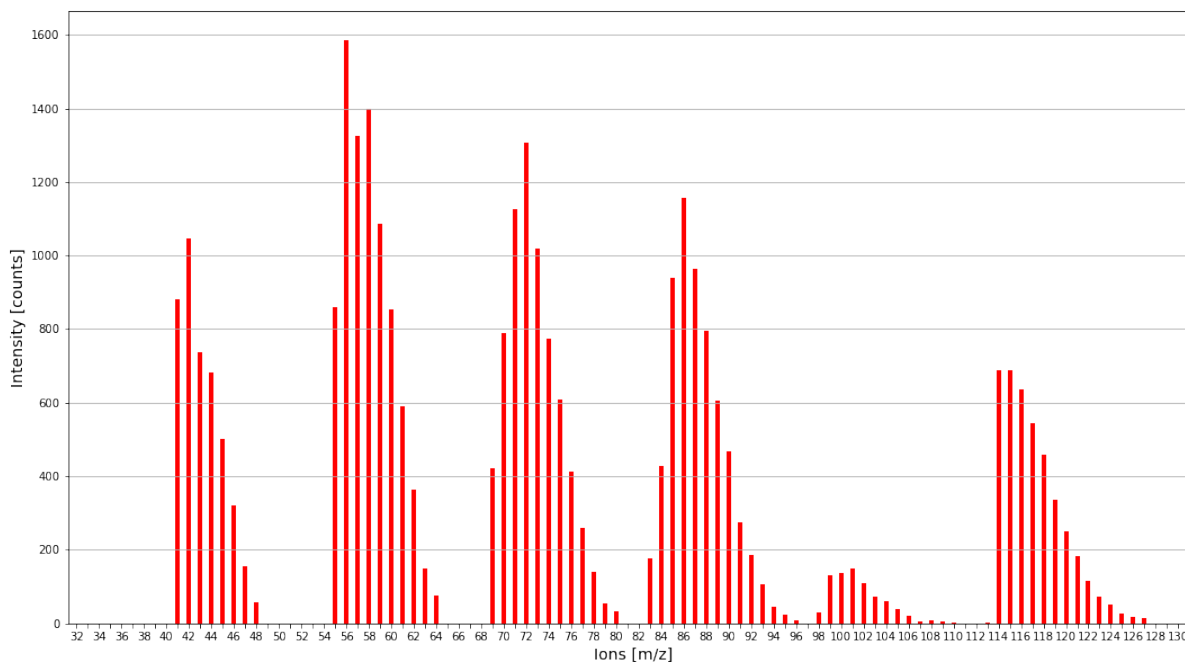


Figure S24: Simulated mass spectrum of the isotopomers of cyclooctane generated when Rh(COE)[P₂N₂] (0.041 g) is exposed to 1 atm of D₂, simulated with a probability of reductive elimination of 13%.

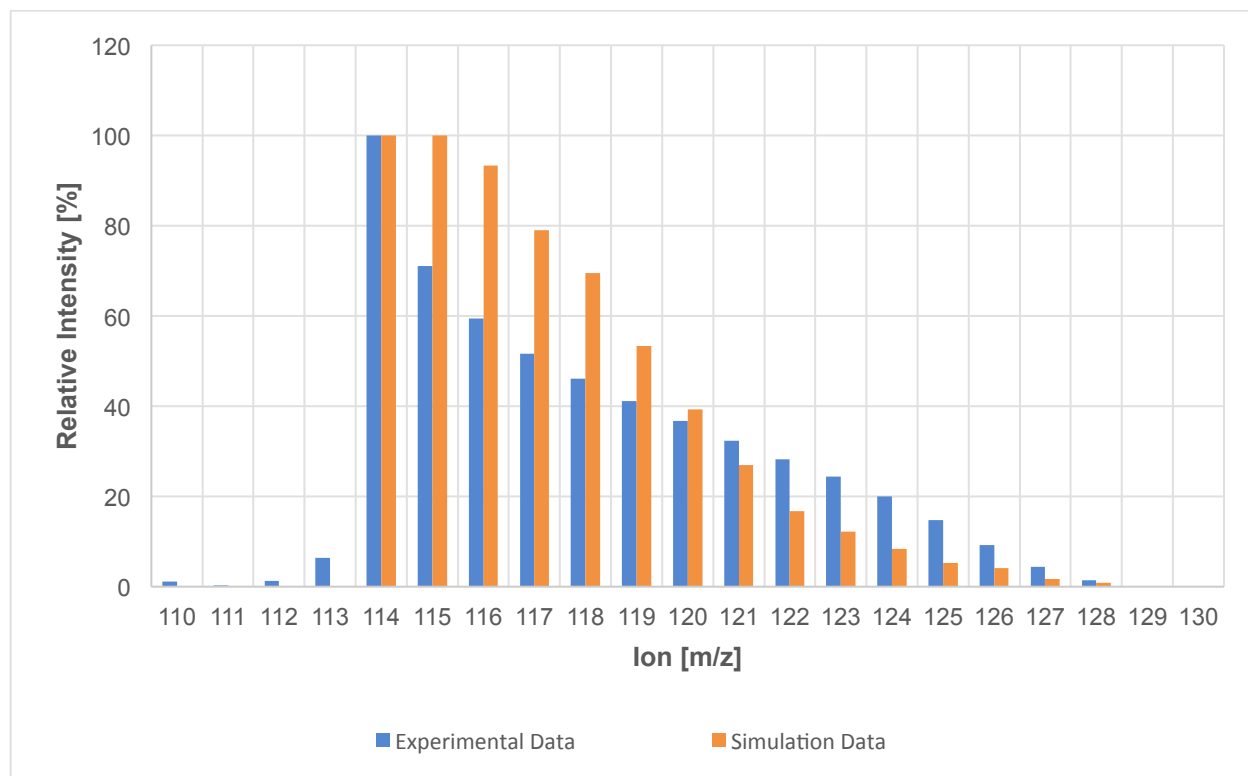


Figure S25: Comparison of simulation and experimental data for isotopomer distribution when Rh(COE)[P₂N₂] (0.032 g) is exposed to 4 atm of D₂. In this case, the probability of reductive elimination was tuned to be 20%. Intensities are scaled relative to that of cyclooctane-d₂ (m/z 114).

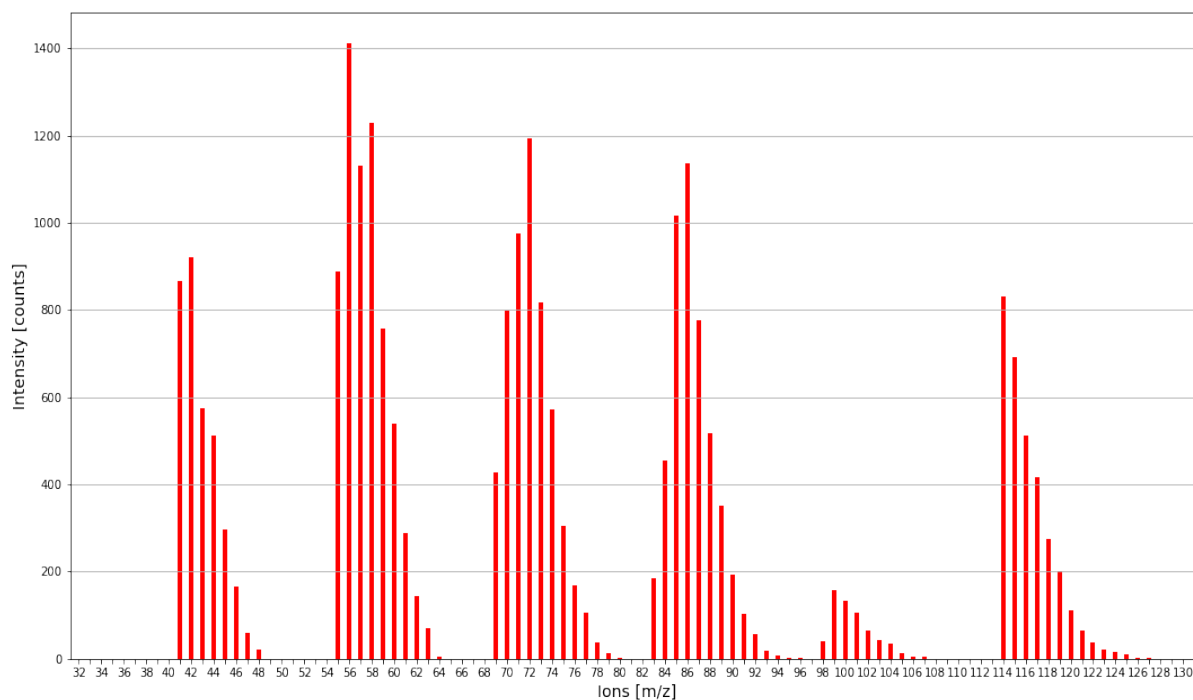


Figure S24: Simulated mass spectrum of the isotopomers of cyclooctane generated when Rh(COE)[P₂N₂] (0.032 g) is exposed to 4 atm of D₂, simulated with a probability of reductive elimination of 20%.

References

1. Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H., *J. Appl. Cryst.* **2009**, *42*, 339-341.
2. Sheldrick, G. M. *Acta Cryst.* **2015**, A71, 3-8.
3. Sheldrick, G. M. *Acta Cryst.* **2015**, C71, 3-8.