Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Rhodathiaborane reaction cycles driven by C_2H_4 and H_2: synthesis and characterization of $[(H)_2(PPh_3)RhSB_8H_7(PPh_3)]$ and $[(\eta^2\text{-}C_2H_4)\ (PPh_3)RhSB_8H_7(PPh_3)]$

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General Procedures

Reactions were carried out under argon atmosphere using standard Schlenk-line techniques. Solvents were obtained dried from a Solvent Purification System from Innivative Technology Inc. The thiaborane *arachno*-4-SB_8H_{12} (K. Baše et al. *Polyhedron* 1989, **8**, 2089-2090), the salt [PSH][*arachno*-4-SB_8H_{11}] (S. Luaces et al. *Dalton Trans*. 2012, **41**, 11627-11634) and the Wilkinson's Catalyst $[RhCl(PPh_3)_3]$ (J.A. Osborn and G. Wilkinson, *Inorg. Synth.* 1967, **10**, 67-71) were prepared according to the literature methods.

Infrared spectra were recorded on a Perkin-Elmer Specrtum 100 spectrometer, using a Universal ATR Sampling Accessory. NMR spectra were recorded on Brüker Avance 300-MHz and AV 400-MHz spectrometers, using ^{31}P-{^{1}H}, ^{11}B, ^{11}B-{^{1}H}, ^{1}H, ^{1}H-{^{11}B} and ^{1}H-{^{11}B(selective)} techniques. Residual solvent protons were used as reference (δ, ppm, dichloromethane, +5.32). ^{11}B chemical shifts are quoted relative to $[BF_3(OEt)_2]$ and ^{31}P chemical shifts are quoted relative to H_3PO_4. Mass spectra were obtained with a Micro Tof-Q Bruker Daltonics spectrometer. Elemental analyses C/H/N were carried out in a Perkin-Elmer 2400 CHNS/O analyzer.

Synthesis of [6,6-$(PPh_3)_2$-9-(PPh_3)-*arachno*-6,5-$RhSB_8H_9$] (1).

0.2 g of $[PSH][SB_8H_{11}]$ (0.6 mmol) was placed under argon in a Schlenk tube and dissolved in 18 ml of dry dichloromethane. Then, 0.56 g of $[RhCl(PPh_3)_3]$ (0.6 mmol) was added at -35 ºC and the solution was stirred for 15 minutes at low temperature. After this time, the reaction mixture was filtered through silica gel and the solvent was evaporated to reach a volume of 10 ml. The remaining solvent was degassed and then 0.46 g of PPh_3 (1.18 mmol) was added. The mixture was stirred for 5 hours. After solvent evaporation and addition of hexane, a yellow precipitate was formed. The solid was washed with hexane (6 x 10 ml), filtered with a cannula and dried in vacuum. Yield 0.4 g (67 %).

Reaction of 1 with ethylene: synthesis of [2-(PPh_3)-2-(η^2-C_2H_4)-6-(PPh_3)-*closo*-2,1-$RhSB_8H_7$] (2)

A: 9 mg of **1** (0.009 mmol) was dissolved in CD_2Cl_2, under argon, in a Young NMR tube. The tube was immersed in liquid nitrogen and the system was evacuated under vacuum. Then, the system was espoused to an ethylene atmosphere of 1 bar. The reaction was monitored by ^{1}H, ^{11}B and ^{31}P-{^{1}H} NMR periodically for 7 days. Compound **1** evolved to a new cluster that was characterized as **2**. In the reaction, there was formation of ethane (Figure S1 and S2).

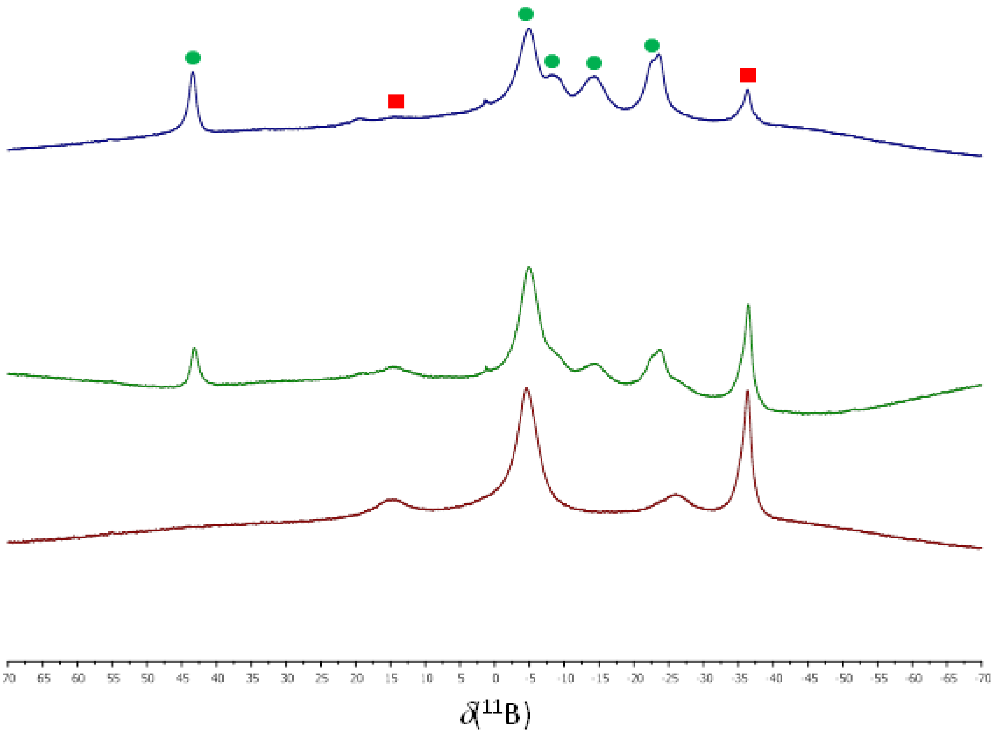


Figure S1: ^{11}B-{^{1}H} NMR spectra illustrating the evolution of the reaction between **1** (red squares in the top trace) and ethylene to give compound **2** (green ellipsoids): (i) Spectrum of **1** before exposure to the olefin (bottom trace), (ii) spectrum after two days of exposure to C_2H_4, (iii) spectrum after seven days.

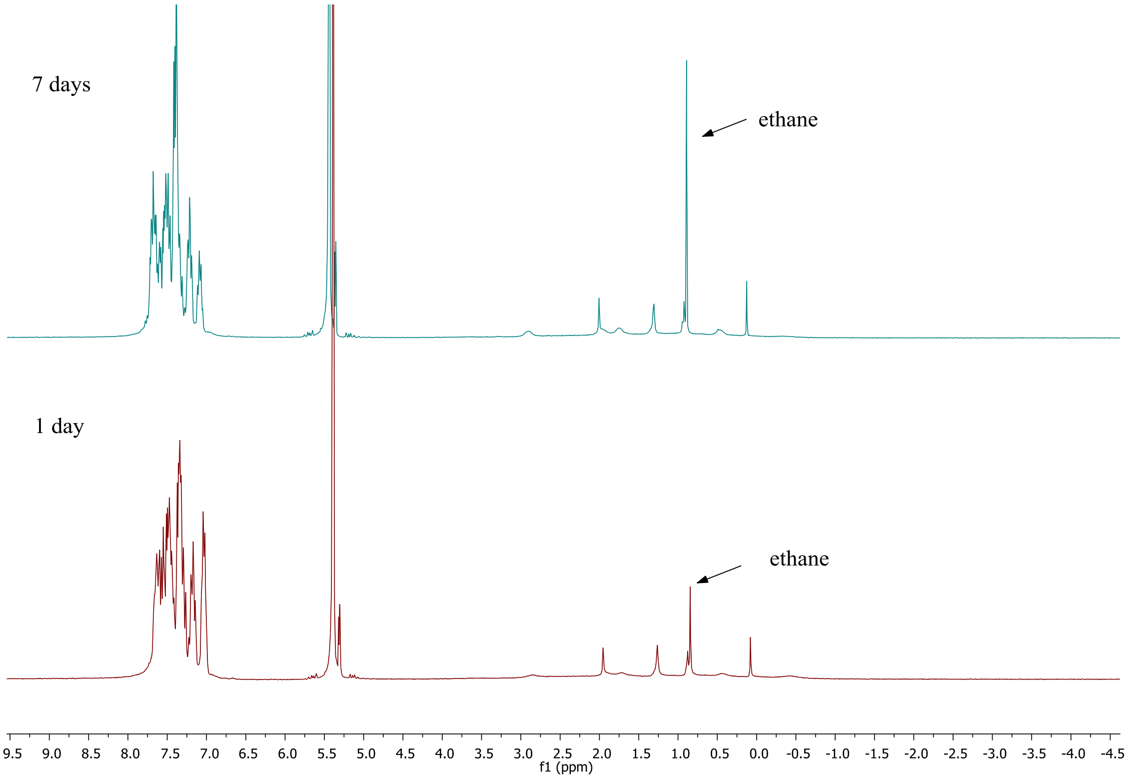
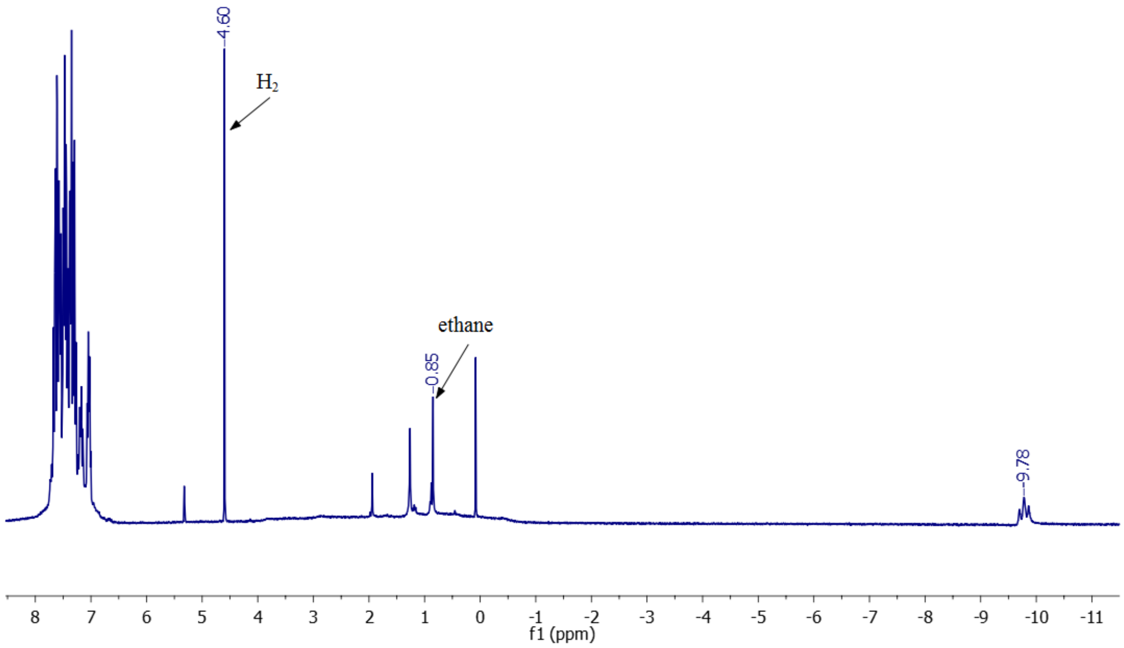


Figure S2: ^{1}H NMR spectra for the reaction of **1** with ethylene to give compound **2**.

B: A Fischer-Porter reactor was charged with 0.15 g of **1** (0.15 mmol) under argon, and 10 ml of dry dichloromethane was injected. After degassing the solvent, the reactor was immersed in liquid nitrogen and the system was evacuated. Then, the solution was espoused to an atmosphere of 1 bar of ethylene. Once the system pressure was stabilized, the solution was stirred at 45 ºC. After 24 hours of reaction, the reactor was cooled to room temperature and then the reaction mixture was transferred to a Schlenk tube with a cannula. The solvent was reduced in volume, and the addition of hexane gave a red precipitate that was washed with hexane (5 x 10 ml) and filtered. After drying under vacuum, 0.1 g of red solid was obtained (Yield 85 %). The product was characterized as: [2-(PPh_3)-2-(η^2-C_2H_4)-6-(PPh_3)-*closo*-2,1-$RhSB_8H_7$] (**2**) IR(ATR): ν_{max} /cm^{-1} 2543-2518 s (BH), 453 m (Rh-C_2H_4), 419 m (Rh-C_2H_4); ^{11}B-{^1H} NMR (96 MHz; CD_2Cl_2, 298 K): δ 43.5 (1B, s, BH), -4.7 (2B, br, BH), -8.6 (1B, br, B-PPh_3), -14.4 (2B, br, BH), -22.2 (1B, s, BH), -23.4 (1B, s, BH). ^1H-{^{11}B} NMR (300 MHz, CD_2Cl_2, 298 K): *δ* 7.66 to 7.14 (30H, m, 2 PPh_3), 6.89 (1H, s, BH), 2.14 (1H, s, BH), 1.58 (1H, s, BH), 1.28 (1H, s, BH), 1.22 (1H, s, BH), 0.63 (1H, s, BH), 0.46 (1H, s, BH); ^1H NMR (300 MHz; C_6D_6; 250K): *δ* 7.66-7.14 (m 30H; 2PPh_3); 2.87 (m, 1H, C_2H_4), 1.92 (m, 1H, C_2H_4), 1.71 (m, 1H, C_2H_4), 0.44 (m, 1H, C_2H_4); ^{13}C{^1H} NMR (75 MHz, CD_2Cl_2, 250 K) *δ* 50.2 (d, 1C, $^1J_{Rh,C}$= 16 Hz, C_2H_4), 39.8(d, 1C, $^1J_{Rh,C}$= 16 Hz, C_2H_4); ^{31}P-{^1H} NMR (121 MHz; CD_2Cl_2, 298 K): δ 30.8 (1P, d, $^1J_{P,Rh}$ = 140 Hz); 11.2 (1P, br, B-PPh_3). HRMS (μ-TOF): *m/z* calcd. maximum for $[M-C_2H_4]^+$ $B_8C_{36}H_{37}P_2RhS$, 753.1943; 753.1972 obsd. The mass envelope for the measured masses for **2** matches that calculated from the isotopic abundances of the constituent elements. Anal. Calcd. for $B_8C_{38}H_{41}P_2RhS$: C, 58.43; H, 5.29; S, 4.1. Found: C, 57.95; H, 5.81; S, 3.92.

Reaction of 2 with H_2 (g): synthesis of [2,2,2-$(H)_2$(PPh_3)-6-(PPh_3)-*closo*-2,1-$RhSB_8H_7$] (3)

A: A quick pressure valve NMR tube was charged with 6 mg of **2** and 0.3 ml of CD_2Cl_2 under argon. The system was immersed in liquid nitrogen and evacuated under vacuum. Then, an atmosphere of 10 bar of H_2 (g) was introduced. The reaction was monitored by ^{11}B, ^1H and ^{31}P-{^1H} NMR, demonstrating the formation of **3** (Figure S3).



Reaction of **2** with H_2

Figure S3: ^{1}H NMR for the reaction of **2** with H_2 (g) to give **3**.

B: A Fischer-Porter reactor was charged with 0.08 g of **2** (0.1 mmol) under argon and 5 ml of dry dichloromethane was injected. After degassing the solution, the system was immersed in liquid nitrogen and evacuated. Then, an atmosphere of 2 bar of H_2 was introduced. After 8 hours of vigorous stirring, the solution was transferred to a Schlenk tube and filtered through silica gel. The solvent was reduced in volume and, upon addition of hexane a yellow-brown precipitated was formed. The product was filtered, dried in vacuum and characterized as **3** (61 mg, 80 % yield): IR (ATR): ν_{max} /cm^{-1} 2545-2460 m (BH), 1991 w (Rh-H); ^{11}B-{^{1}H} NMR (96 MHz; CD_2Cl_2, 298 K): δ 55.1 (1B, s, BH), -2.5 (2B, br, BH), -5.2 (1B, br, B-PPh_3), -6.7 (1B, s, BH), -7.7 (2B, br, BH), -23.6 (1B, s, BH), -26.4 (1B, s, BH). ^{1}H-{^{11}B} NMR (300 MHz, CD_2Cl_2, 298 K): *δ* 7.65 to 7.28 (30H, m, 2 PPh_3), 7.51 (1H, s, BH), 3.17 (1H, s, BH), 2.59 (1H, s, BH), 1.35 (1H, s, BH), 0.50 (1H, s, BH), 0.46 (1H, s, BH), 0.21 (1H, s, BH), -9.77 (2H, t, $^1J_{H,Rh}$ = 21.9 Hz); ^{1}H NMR (300 MHz, CD_2Cl_2, 203 K): *δ* 7.65 to 7.28 (30H, m, 2 PPh_3), -8.42 (t, 1H, $^1J_{H,Rh}$ = 29.5 Hz, $^2J_{H,P}$ = 26 Hz), -11.13 (t, 1H, $^1J_{H,Rh}$ = 14.8 Hz, $^2J_{H,P}$ = 16.0 Hz) ^{31}P-{^{1}H} NMR (121 MHz; CD_2Cl_2, 298 K): δ 50.6 (1P, d, $^1J_{P,Rh}$ = 124 Hz); 9.3 (1P, br,B-PPh_3). HRMS (μ-TOF): *m/z* calcd. maximum for $[M-2H]^+$ $P_2C_{36}RhSB_8H_{37}$, 753.1943; 753.1993 obsd. The mass envelope for the measured masses for **2** matches that calculated from the isotopic abundances of the constituent elements. Anal. Calcd. for $P_2C_{36}RhSB_8H_{39}$: C, 58.43; H, 5.29; S, 4.1. Found: C, 57.95; H, 5.81; S, 3.92.

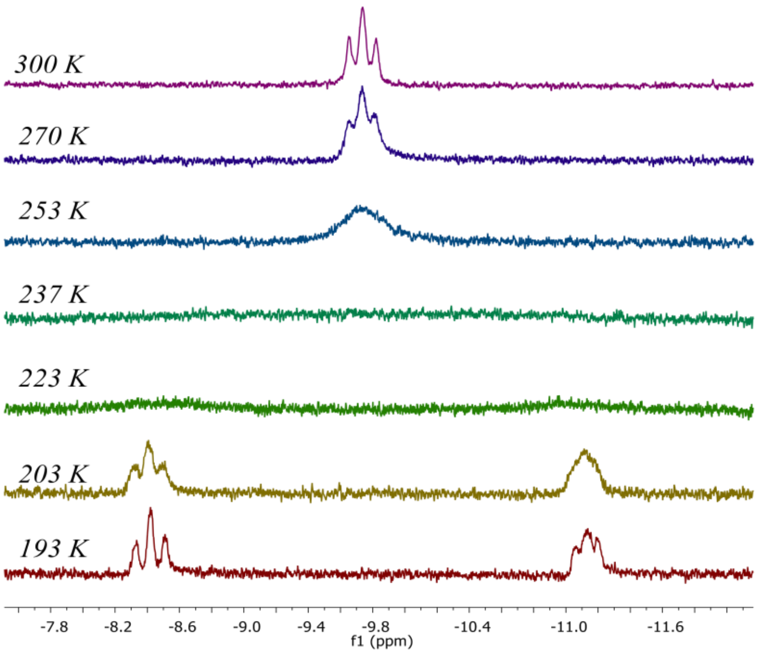


Figure S4: VT ^1H NMR spectra for compound **3** in the hydride region. Hydrides are exchanging at room temperature; thus, one triplet is observed for both of them. Decreasing temperature the exchanging movement slows down and two apparent triplets are observed. The measured $\Delta G^{\ddagger}$ at the coalescence temperature of 237 K is 10.3 kcal/mol.

X-ray analysis of compounds 2 and 3

Crystals of **2** and **3** were grown by slow diffusion of hexane into CH_2Cl_2 solutions of the compounds. The X-ray data were collected at 100(2) K with a Bruker APEX DUO diffractometer equipped with an area detector and graphite monochromated MoKα radiation (0.71073 Å) using narrow ω rotation (0.3º). Data reduction was done with the APEX2 software.

The structure of **2** was solved by direct methods and refined by full-matrix least-squares methods based on F^2 using SHELXS-97 and SHELXL-97 programs. Hydrogen atoms have been observed in Fourier difference maps. In order to improve the data over parameter ratio, hydrogen atoms of the phenyl groups and the solvent have been included in the model in calculated positions and refined within a riding model. The hydrogen atoms of the thiaborane group and the ethylene ligand were observed in the Fourier different map, and freely refined.

The structure of **3** was solved by Patterson methods and anisotropic refinement of all non hydrogen atoms was applied. The asymmetric unit contains a rhodathiaborane molecule. Hydrogen atoms have been observed in Fourier difference maps and freely refined except the hydrogen H18 which has been refined with displacement riding parameters.

Reaction of 3 with ethylene to give 2

6 mg of **3** (0.008 mmol) was dissolved under argon in a Young NMR tube. The tube was immersed in liquid nitrogen and, after evacuation, the solution was espoused to an atmosphere of 1 bar of ethylene. The reaction was monitored by ^{1}H, ^{11}B and ^{31}P-{^{1}H} NMR. (Figures S5 and S6).

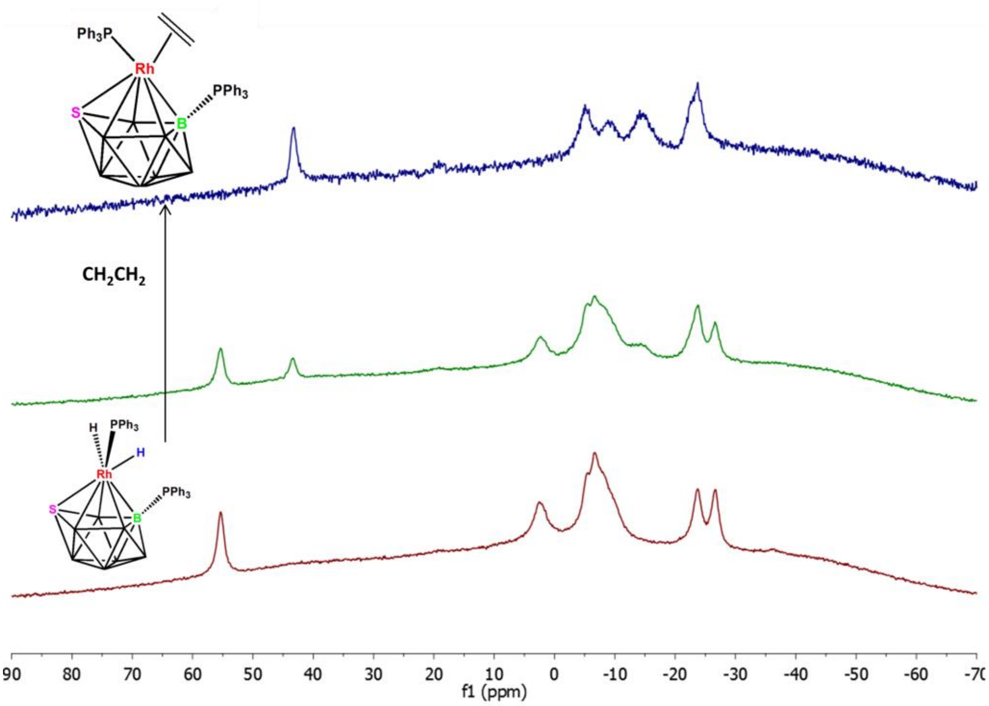


Figure S5: ^{11}B{^{1}H} of the reaction between **3** and ethylene to regenerate **2**.

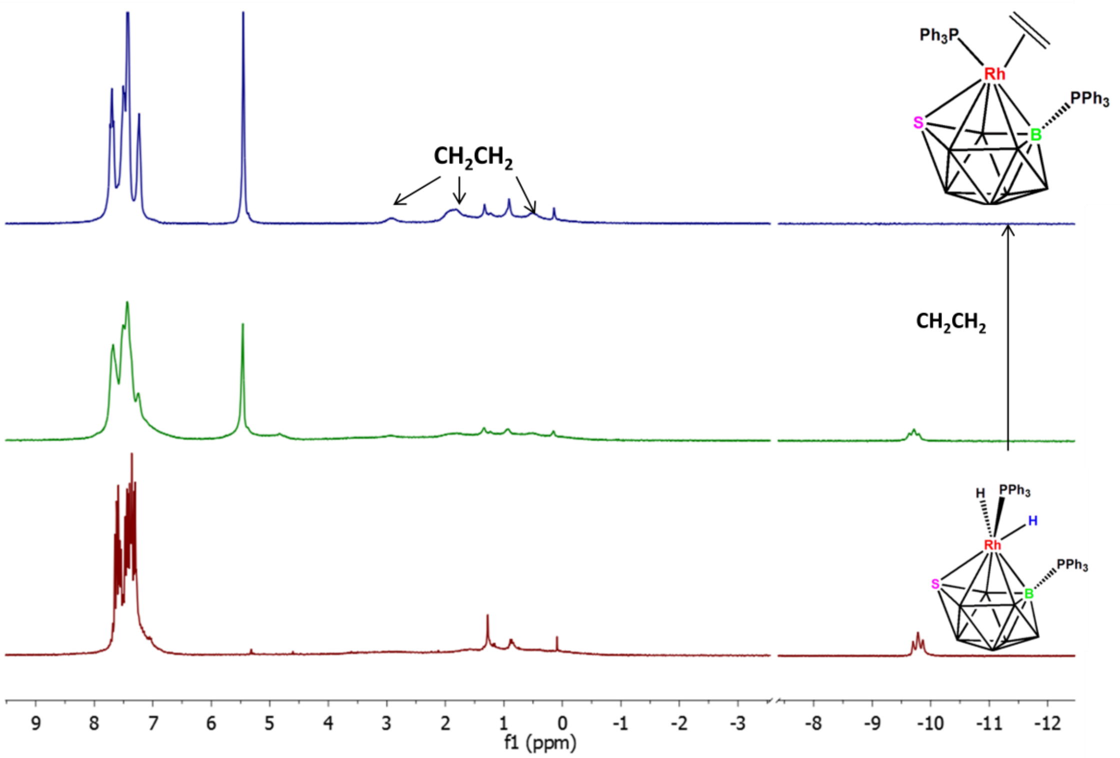


Figure S6: ^{1}H NMR spectra of the reaction between **3** and ethylene to regenerate **2**..

Reaction of 3 with PPh_3 to give 1

6 mg of **3** (0.008 mmol) was dissolved in CD_2Cl_2 in a NMR tube under argon, and an equimolar quantity of PPh_3 was added. The product obtained was identified by ^{1}H, ^{11}B and ^{31}P–{^{1}H} NMR as **1** (Figures S7-S8).

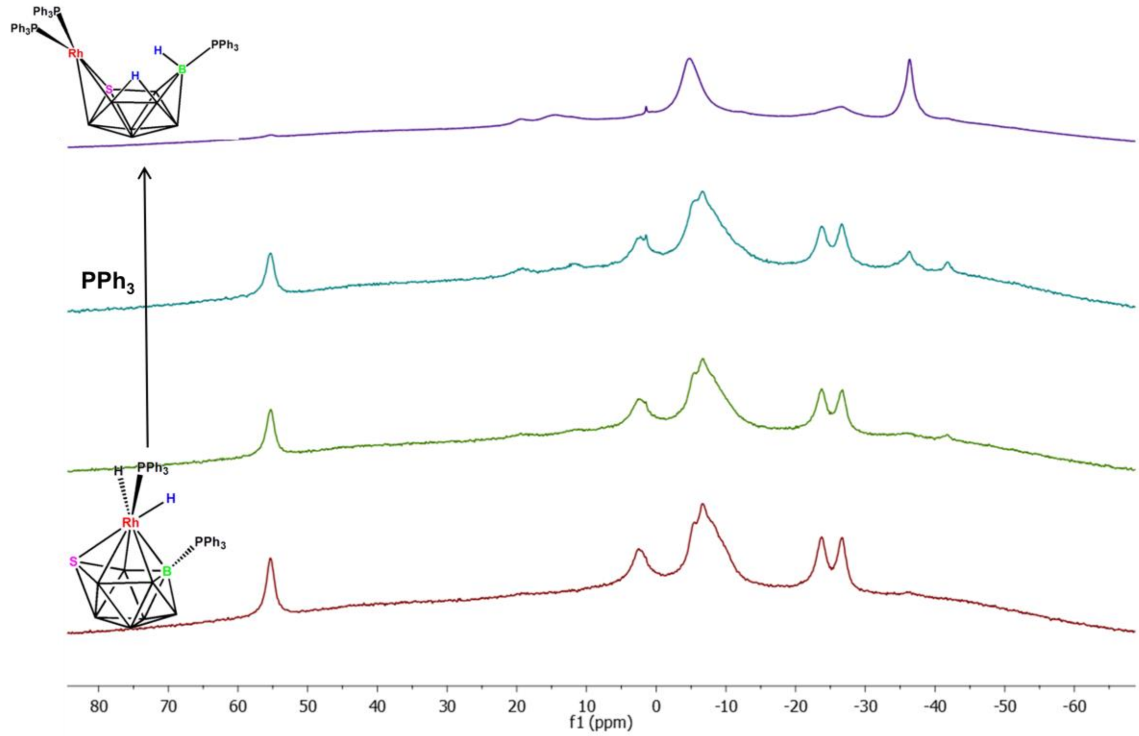


Figure S6: $^{11}B\{^1H\}$ spectra of the reaction between **3** and PPh_3.

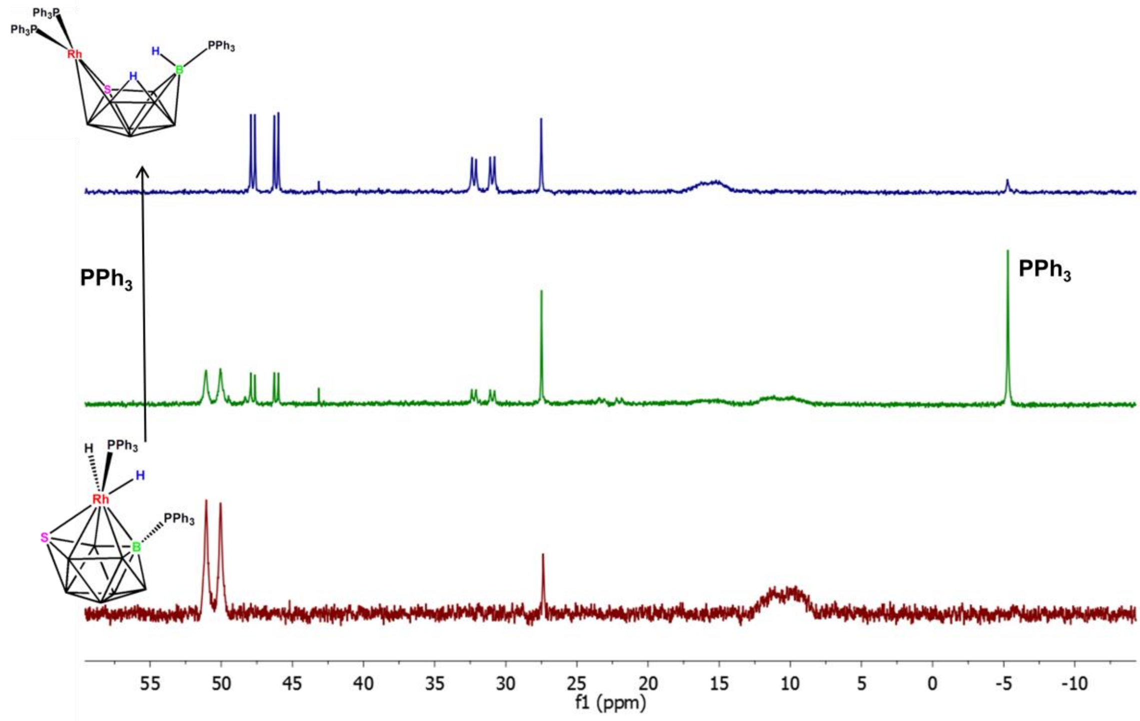


Figure S7: $^{31}P\{^1H\}$ NMR spectra of the reaction between **3** and PPh_3.

Reaction of 2 with PPh_3 and H_2 to give 1

8 mg of **2** (0.01 mmol) were placed in a Young NMR tube with an equimolar amount of PPh_3 (3 mg) and dissolved in CD_2Cl_2 under argon. The tube was evacuated and an atmosphere of 1 bar H_2(g) was introduced. The reaction was monitored by ^1H, ^{11}B and $^{31}P\{^1H\}$ NMR (Figures S8-S9).

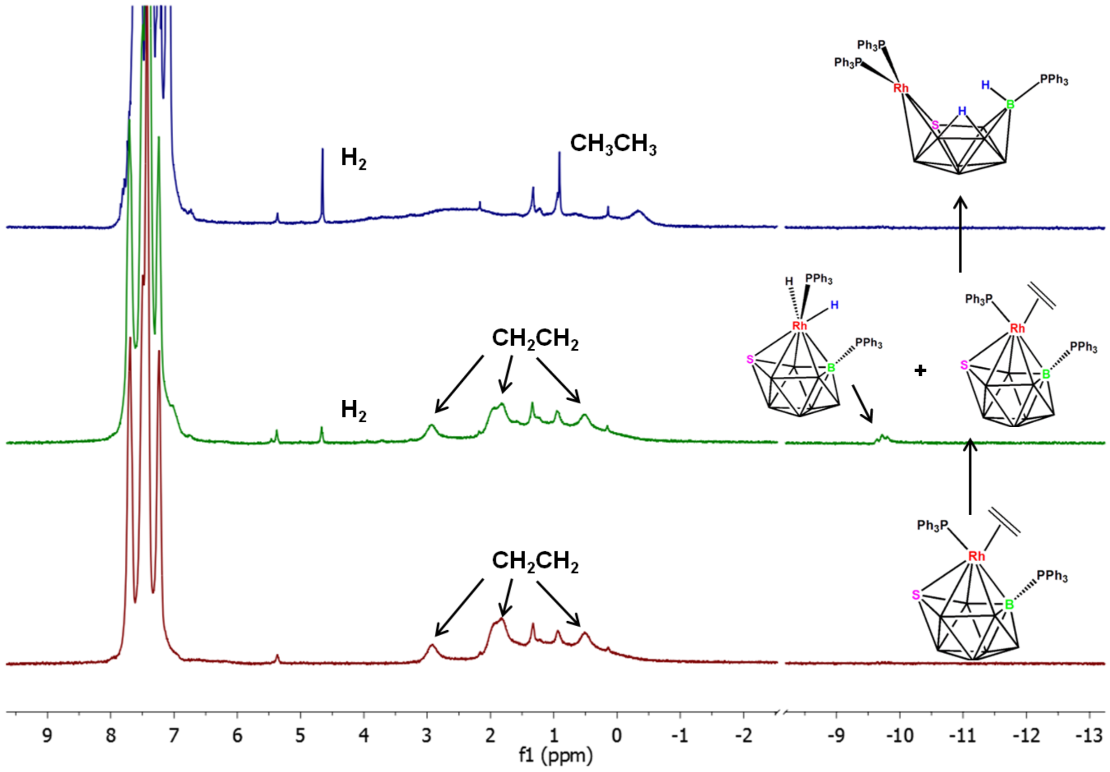


Figure S8: ^1H of the reaction between **2** and H_2 in the presence of PPh_3.

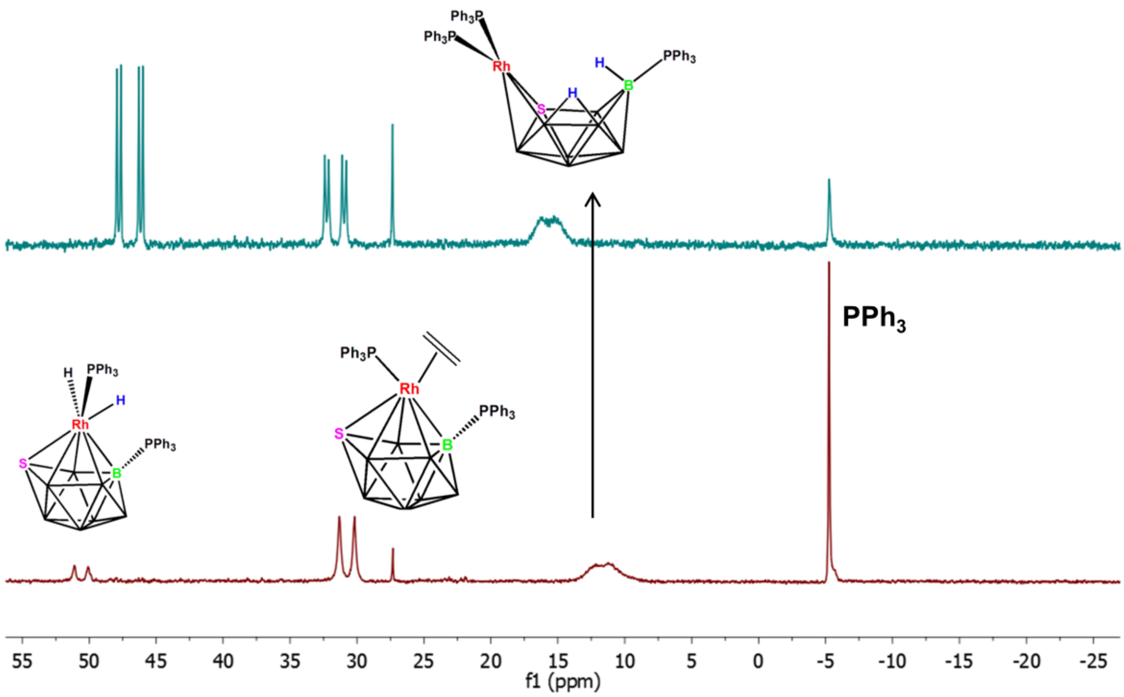


Figure S7: ^{31}P-{^{1}H} NMR spectra between **2** and H_2 in the presence of PPh_3.