Supporting Information

Anchored complexes of rhodium and iridium in the hydrogenation of alkynes and olefins with parahydrogen

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Experimental Section

The synthesis of immobilized catalysts (Ir^P, Rh^P, Ir^N, Rh^N) was carried out by interacting the iridium complex [Ir(COD)Cl]^2 (STREM Chemicals, CAS: 12112-67-3; COD - 1,5-cyclooctadiene) or the rhodium complex [Rh(COD)Cl]$_2$ [1] with 2-diphenylphoshinoethyl-functionalized silica gel (Sigma-Aldrich, 538019) or with 3-aminopropyl-functionalized silica gel (Sigma-Aldrich, 364258) in dried and deoxygenated benzene. The complex [Rh(COD)Cl]$_2$ was prepared according to the procedure described in the literature.[1] All manipulations were carried out in an inert atmosphere of Ar. A mixture of 0.5 g of functionalized silica gel and 0.15 g of [Ir(COD)Cl]$_2$ or 0.13 g of [Rh(COD)Cl]$_2$ was placed in a Schlenk tube and dried under vacuum for 30 minutes. Dried and deoxygenated benzene (5 ml) was added to the dry mixture of the functionalized silica gel and an organometallic complex and kept under stirring for 24 hours. After that, the excess solvent and the unbound complex were removed by decantation. The remaining precipitate was washed three times with benzene and two times with methanol under argon until stable colorless washings. All obtained samples are stable in air for a long time except for Ir^N, which gradually turns green. Therefore, it is preferable to store Ir^N under argon. The resulting precipitate was dried under vacuum for 4-5 h. The metal loading was 3.3 wt.% for Ir^N, 3.8 wt.% for Ir^P, 3.2 wt.% for Rh^N, and 3.4 wt.% for Rh^P. The metal loading of immobilized catalysts was determined by X-ray fluorescence analysis on a VRA-30 instrument with a Cr anode of the X-ray tube. The relative error of determination was 5 %.

The experimental setup is shown in Fig. S1. Hydrogen gas was enriched with parahydrogen up to ~90 % using Bruker parahydrogen generator BPHG 90. A standard 10 mm NMR tube with 20 mg of catalyst (1) was placed inside the sensitive area of the NMR spectrometer (a). The gaseous mixture of reagents (propene/p-H$_2$ or propyne/p-H$_2$ in the 1/4 ratio) was supplied from a cylinder into the NMR tube containing the catalyst through a 1/16" OD PTFE capillary. Hydrogenation was carried out in a 7.1 T magnetic field of a Bruker 300 MHz NMR spectrometer at atmospheric pressure. All catalysts were tested at the gas flow rate of 2.2 ml/s. The reaction temperature varied in the range from 25 to 120 °C. PHIP ^{1}H NMR spectra were recorded using a single $\pi/4$ radiofrequency pulse while the mixture of gases was flowing. Thermal equilibrium NMR spectra were recorded after collecting the reaction mixture from the exhaust 1/4" OD PTFE capillary (Fig. S1) in another NMR tube (2), which was positioned in the Earth's magnetic field and contained no catalyst (b).
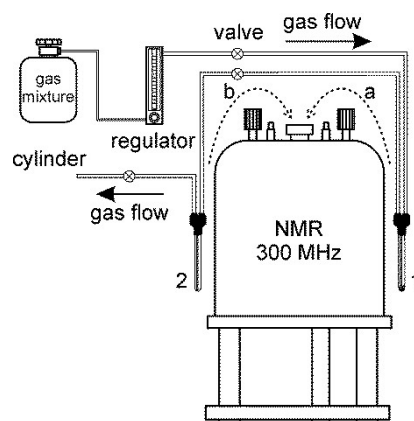
Figure S1. The scheme of the experimental setup used in the gas-phase hydrogenation of propyne or propene with parahydrogen.

A delay of 2-3 min between the gas collection and NMR spectrum acquisition, with the gas flow terminated, ensured the complete relaxation of hyperpolarization. This approach greatly simplifies the procedure for obtaining a thermally equilibrated mixture in the PASADENA experiment, because in the main NMR tube, where the catalyst is in a direct contact with the mixture of gases, the amount of the product is increasing as a result of hydrogenation of the remaining substrate with the excess of H_2 after the gas flow is interrupted. At the same time, the use of the second tube in which the reaction mixture is collected in the absence of any catalyst allows one to avoid the need to perform additional hydrogenation experiments with an equilibrium mixture of ortho- and parahydrogen (25% of p-H_2). Moreover, this procedure minimizes potential errors associated with an unexpected and rapid catalyst degradation. The same reaction mixture is used to detect both the PHIP effect and the NMR signals under thermal equilibrium.

The XPS experiments [2] were performed with a SPECS (Germany) spectrometer equipped with a hemispherical PHOIBOS-150-MCD-9 analyzer. The non-monochromatic MgKα radiation (hv = 1253.6 eV) at 200 W was used as the primary excitation. The spectrometer was calibrated using the Au $4f_{7/2}$ (binding energy (BE) = 84.0 eV) and Cu$2p_{3/2}$ (BE = 932.7 eV) peaks from metallic gold and copper foils.[2] The binding energies of detected peaks were calibrated by the position of the Si 2p peak for SiO_2 (BE = 103.3 eV).[2] Spectral analysis and data processing were carried out with Peak 4.1 XPS. The binding energy values and the areas of XPS peaks were determined after Shirley background subtraction and analysis of line shapes. The curves were fitted with Gaussian–Lorentzian functions for each XPS region. The ratios of surface atomic concentrations of elements were calculated from the integral photoelectron peak intensities corrected by the corresponding relative atomic sensitivity factors based on the atomic sensitivity factors and transmission function of the analyzer. The samples were fixed on the holder with the 3M double-sided adhesive copper conducting tape.

Table S1. Compilation of XPS data for Ir and Rh catalysts

	Ir^N		Ir^P		Rh^N		Rh^P	
	Ir 4f$_{7/2}$ BE, eV	Ir/Si at. ratio	Ir 4f$_{7/2}$ BE, eV	Ir/Si at. ratio	Rh 3d$_{5/2}$ BE, eV	Rh/Si at. ratio	Rh 3d$_{5/2}$ BE, eV	Rh/Si at. ratio
fresh	62.3	0.030	61.9	0.037	309.7	0.031	309.3	0.032
propyne hydrogenation	62.0	0.025	61.7	0.033	n/a	n/a	308.6	0.031
propene hydrogenation	62.2	0.024	61.8	0.034	307.5 309.7	0.005 0.009	308.7	0.023

Characterization of immobilized catalysts by ^{31}P MAS NMR

^{31}P MAS NMR experiments were performed at 161.98 MHz (9.4 T magnetic field) on a Bruker AVANCE 400 spectrometer. The samples were placed in a ZrO$_2$ rotor with an outer diameter of 2.5 mm and rotated at a magic angle at a frequency of 20 kHz. An 85% H$_3$PO$_4$ solution (0 ppm) was used as an external standard. The spectra were recorded using the Hahn echo π/2-τ-π sequence, where the π/2 pulse length was 2.4 µs, and the delay τ between the pulses was synchronized with the rotation of the rotor and amounted to 50 µs.
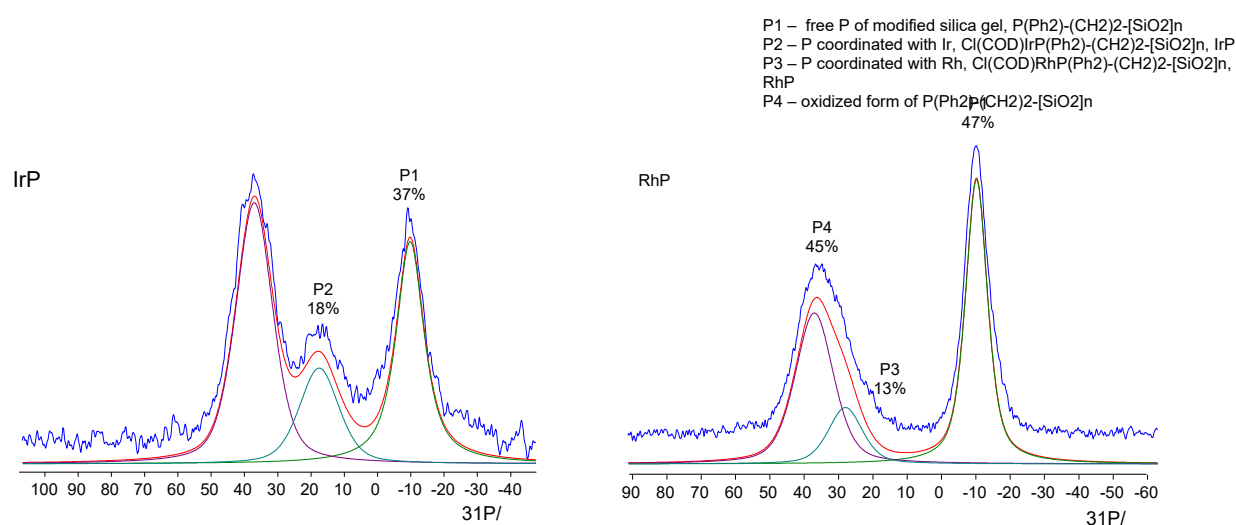
P1 – free P of modified silica gel, P(Ph2)-(CH2)2-[SiO2]n
P2 – P coordinated with Ir, Cl(COD)IrP(Ph2)-(CH2)2-[SiO2]n, IrP
P3 – P coordinated with Rh, Cl(COD)RhP(Ph2)-(CH2)2-[SiO2]n, RhP
P4 – oxidized form of P(Ph2)(CH2)2-[SiO2]n

Figure S2. ^{31}P MAS NMR spectra recorded for immobilized catalysts Ir^P and Rh^P (blue traces) and their decomposition into individual components.

Additional NMR data

^{1}H NMR spectra of the reaction mixtures recorded while testing the immobilized catalysts Ir^N, Ir^P, Rh^N and Rh^P.
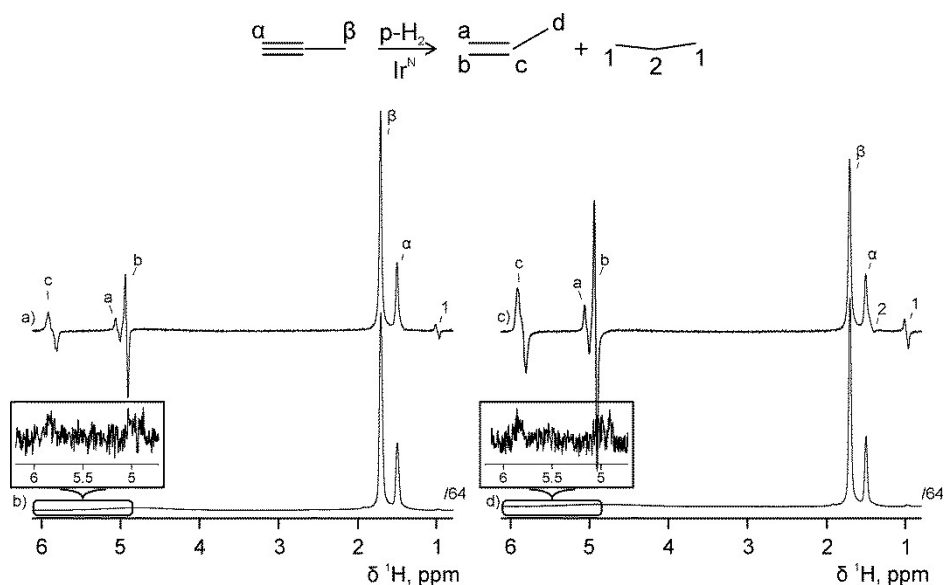
Figure S3. ^{1}H NMR PHIP spectra recorded with propyne/p-H$_2$ mixture flowing (2.2 ml/s) through Ir^N at 100 °C (a) and 120 °C (c). Thermal equilibrium ^{1}H NMR spectra (b, d) were recorded on the corresponding reaction mixture (a, and c, respectively) after relaxation of the hyperpolarized propene. Spectra (a) and (c) were acquired with 16 signal accumulations, (b) and (d) with 1024 signal accumulations; they are scaled accordingly and are presented on the same vertical scale.
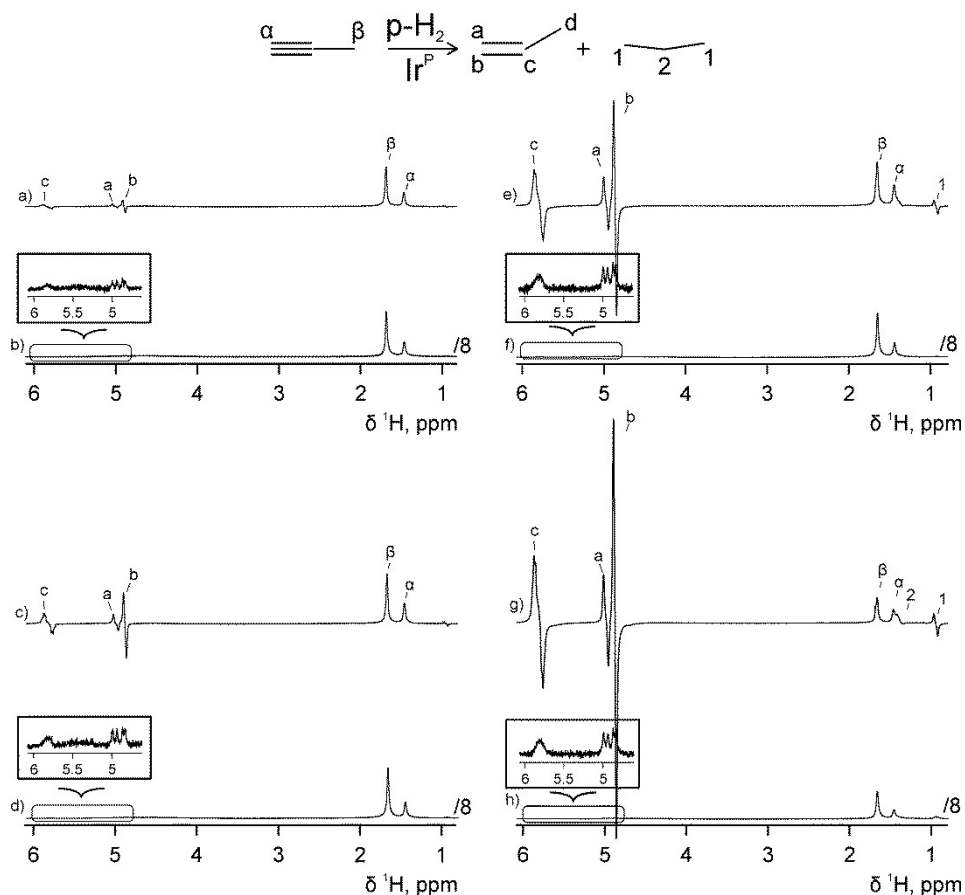

Figure S4. ^{1}H NMR PHIP spectra recorded with propyne/p-H$_2$ mixture flowing (2.2 ml/s) through Ir^P at (a) 60 °C, (c) 80 °C, (e) 100 °C and (g) 120 °C. Thermal equilibrium ^{1}H NMR spectra (b, d, f, h) were recorded on the corresponding

reaction mixture (a, c, e, and g, respectively) after relaxation of the hyperpolarized propene. Spectra (a, c, e, g) were acquired with 16 signal accumulations, (b, d, f, h) with 128 signal accumulations; they are scaled accordingly and are presented on the same vertical scale.
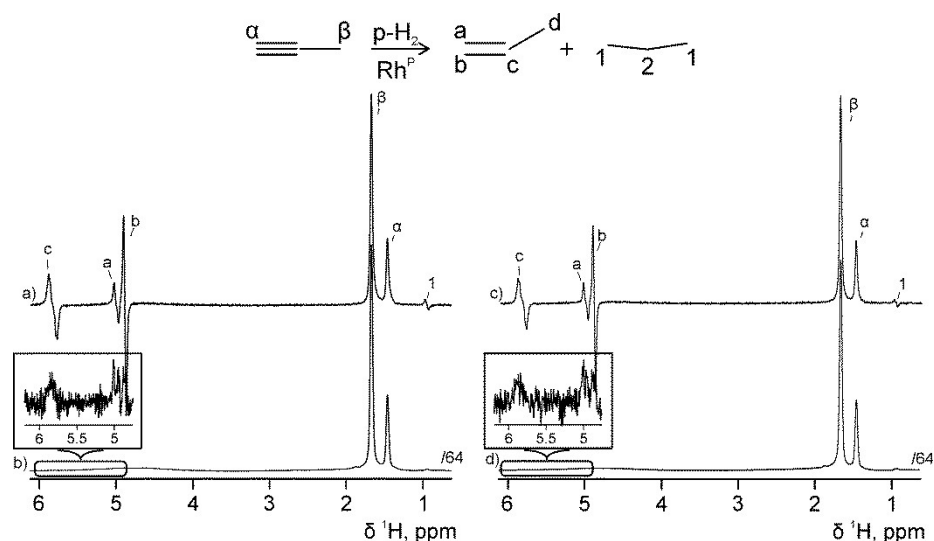

Figure S5. ^{1}H NMR PASADENA spectra recorded with propyne/p-H_2 mixture flowing (2.2 ml/s) thought Rh^P at 100 °C (a) and 120 °C (c). ^{1}H NMR thermal spectra (b, d) were recorded in the corresponding reaction mixture ((a) and (c), respectively) after relaxation of hyperpolarized propene. Spectra (a, c) were acquired with 16 signal accumulations, (b, d) with 1024 signal accumulations and are presented on the same vertical scale.
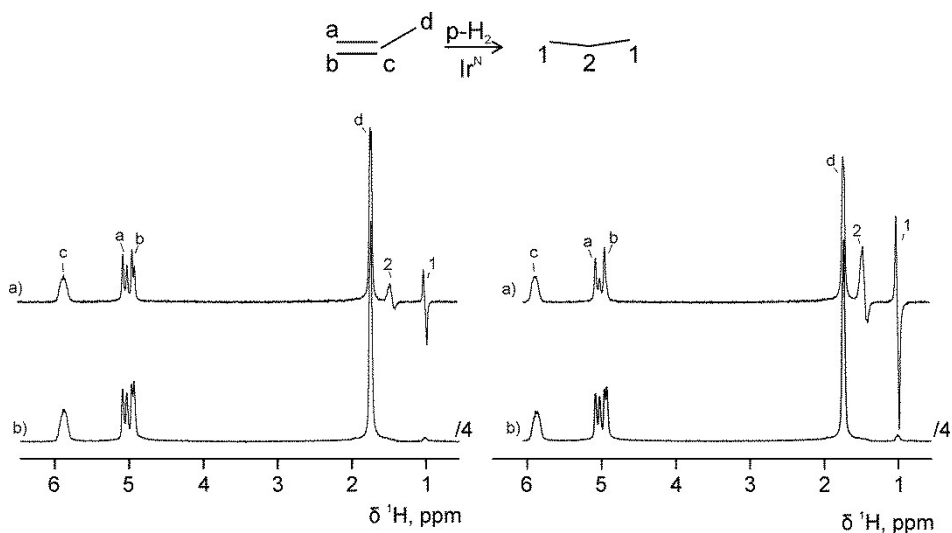

Figure S6. ^{1}H NMR PASADENA spectra recorded with propene/p-H_2 mixture flowing (2.2 ml/s) thought Ir^N at 100 °C (a) and 120 °C (c). ^{1}H NMR thermal spectra (b, d) were recorded on the corresponding reaction mixture (a and c, respectively) after relaxation of hyperpolarized propane. Spectra (a, c) were acquired with 16 signal accumulations, (b, d) with 64 signal accumulations and are presented on the same vertical scale.
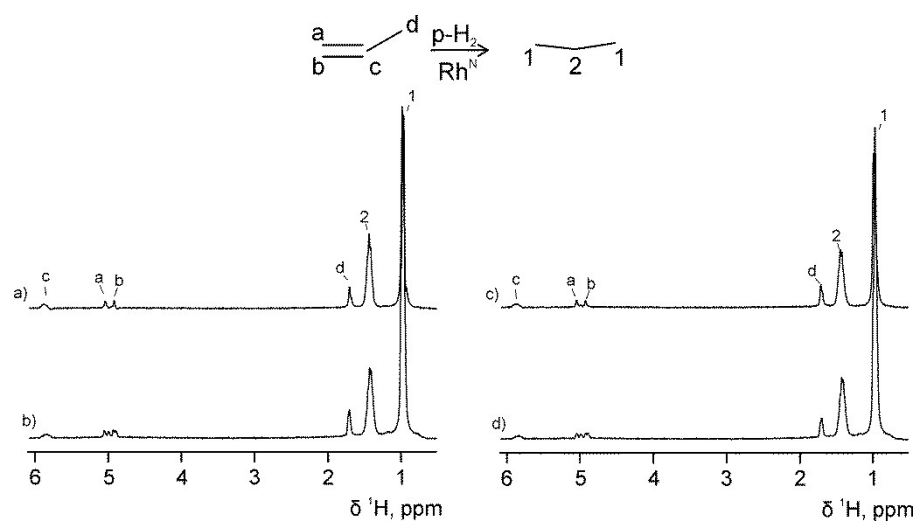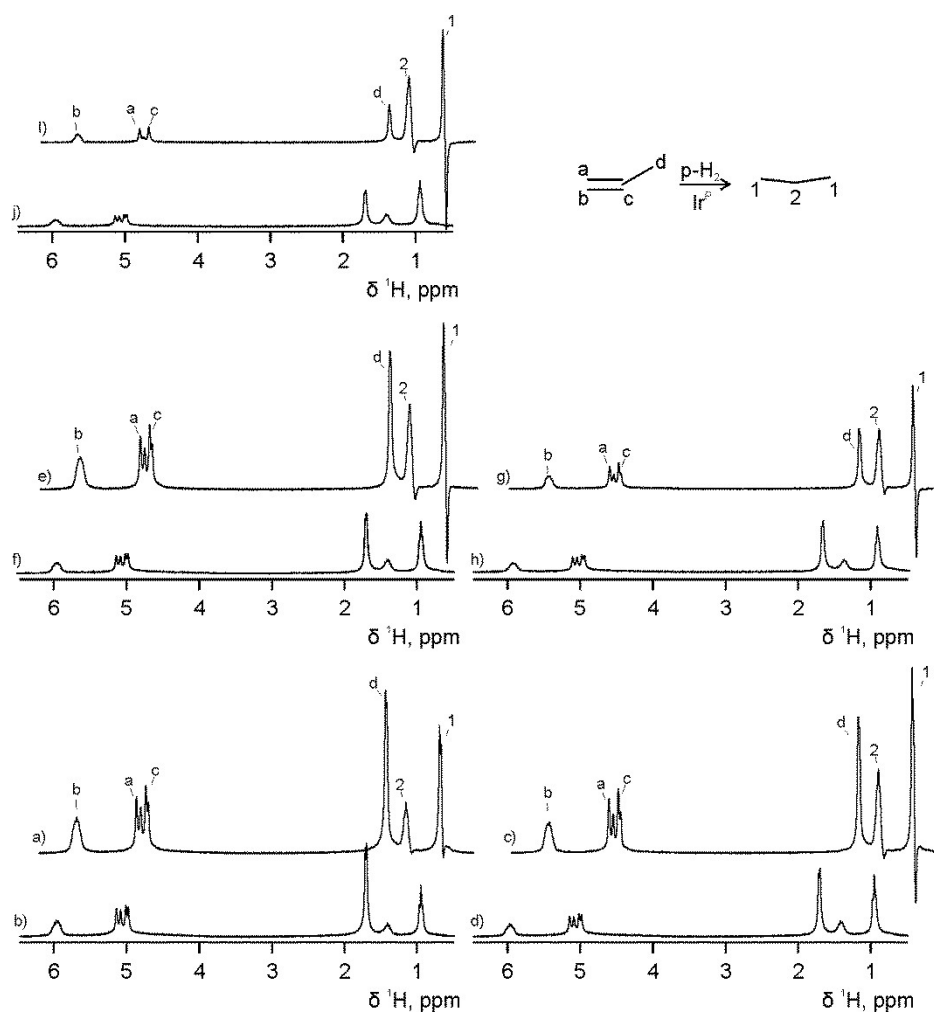
Figure S7. ^{1}H NMR PASADENA spectra recorded with propene/p-H$_2$ mixture flowing (2.2 ml/s) thought Ir^P at 40 ^{o}C (a), 60 ^{o}C (c), 80 ^{o}C (e), 100 ^{o}C (g) and 120 ^{o}C (i). ^{1}H NMR thermal spectra (b, d, f, h, j) recorded on the corresponding reaction mixture (a, c, e, g, and i, respectively) after relaxation of hyperpolarized propene. Spectra (a, c, e, g, i) were acquired with 16 signal accumulations, (b, d, f, h, j) with 64 signal accumulations and are presented on the same vertical scale.

Figure S8. ^{1}H NMR PASADENA spectra recorded with propene/p-H$_2$ mixture flowing (2.2 ml/s) thought Rh^N at 100 °C (a) and 120 °C (c). ^{1}H NMR thermal spectra (b, d) were recorded from the corresponding reaction mixture (a and c, respectively) after relaxation of hyperpolarized propane. All spectra were acquired with 16 signal accumulations.
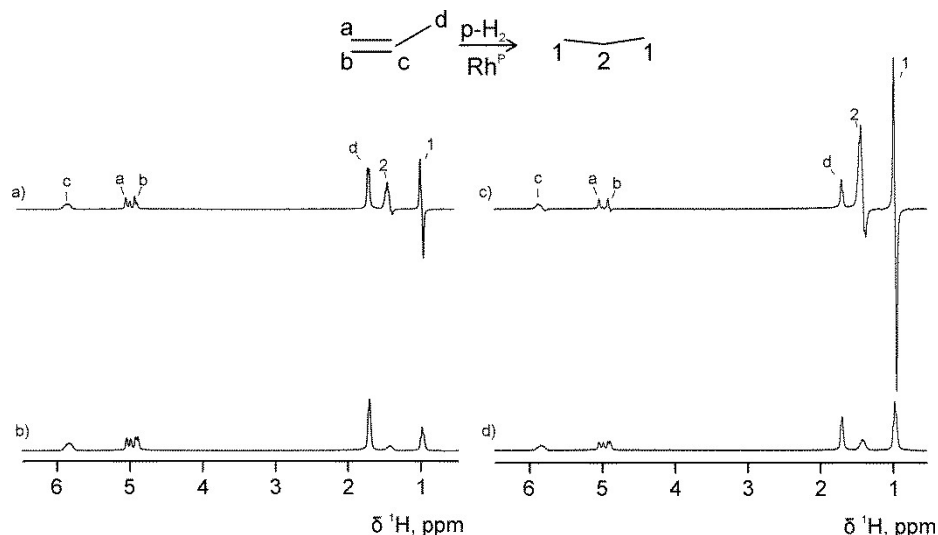

Figure S9. ^{1}H NMR PASADENA spectra recorded with propene/p-H$_2$ mixture flowing (2.2 ml/s) thought Rh^P at 100 °C (a) and 120 °C (c). ^{1}H NMR thermal spectra (b, d) were recorded from the corresponding reaction mixture (a and c, respectively) after relaxation of hyperpolarized propane. All spectra were acquired with 16 signal accumulations.

References.

1   G. Giordano, R. H. Crabtree, R. M. Heintz, D. Forster and D. E. Morris, Inorganic syntheses, D. F. Shriver, Ed., Wiley-Interscience, New York, 1979, vol. XIX, pp. 218–220.

2   J. F. Moulder, W. F. Stckle, P. E. Sobol and K. D. Bomben, *Handbook of X-ray photoelectron spectroscopy*, Physical Electronics Division, Perkin-Elmer Corporation, Eden Prairie, 1992.