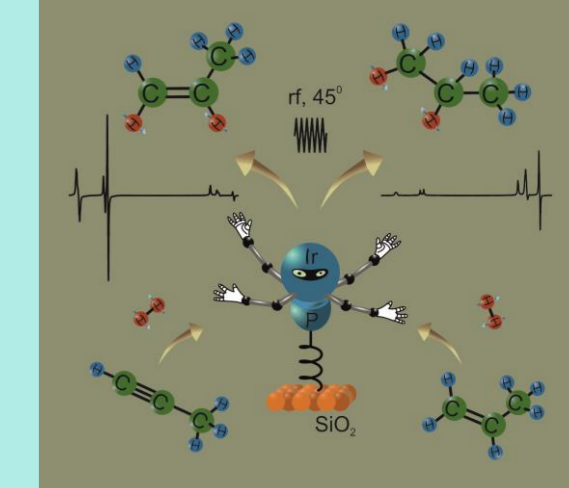


Anchored complexes of rhodium and iridium in the hydrogenation of alkynes and olefins with parahydrogen

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Additionally to the use as an NMR sensitivity boosting technique, parahydrogen-induced polarization (PHIP) is a powerful tool for studying hydrogenation reaction mechanisms, since it provides means for detecting short-lived reaction intermediates and thus can shed light on possible routes of dihydrogen addition. For a long time this technique was applied only for investigations of homogeneous hydrogenation reactions, because heterogeneous catalysts were not expected to account for the necessary condition of PHIP observation – the pairwise addition of both atoms of a dihydrogen molecule. Recently, however, it was shown that PHIP can be observed in hydrogenation reaction over heterogeneous catalysts. Several catalysts synthesized by covalently binding Rh and Ir complexes to NH₂- and PPh₂- functional groups of the linker chains on functionalized silica gel surface were compared in gas-phase hydrogenation of propyne and propene. Their stability, activity and product selectivity were evaluated. Furthermore, the use of parahydrogen in the reaction provided useful mechanistic information by delivering nuclear spin hyperpolarization of the reaction products with the associated enhancement of their NMR signals.

Sensitivity of NMR

NMR sensitivity ~ population difference of nuclear spin levels

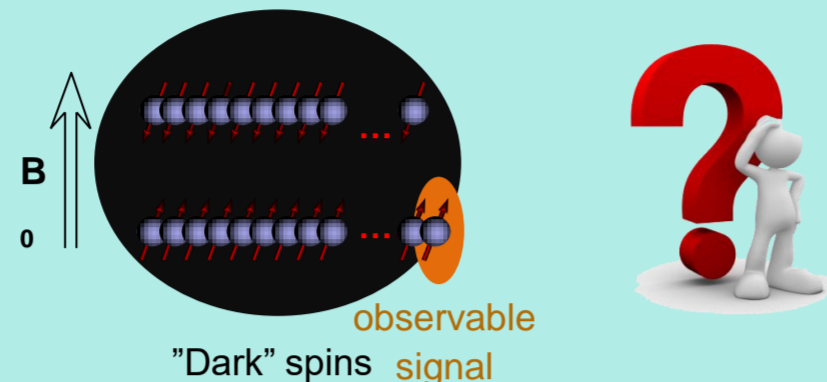
$$I \propto \Delta n$$

$$N_{\alpha}/N_{\beta} = \exp(\Delta E/kT)$$

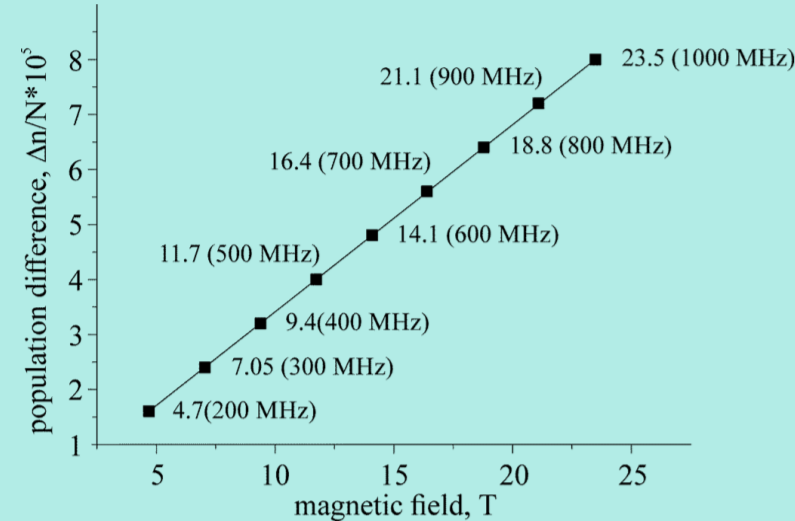
$$\Delta E \ll kT \implies \Delta n \ll 1$$

Boltzmann distribution

extremely low population differences



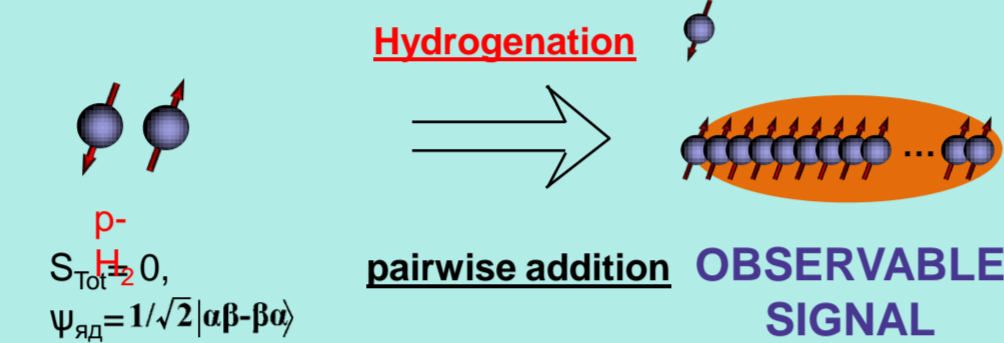
1. Increase in magnetic field of NMR devices



An increase in the magnetic field strength, from 3 T to 20 T gives an increase in the population difference of only about one order of magnitude.

2. Parahydrogen Induced Polarization

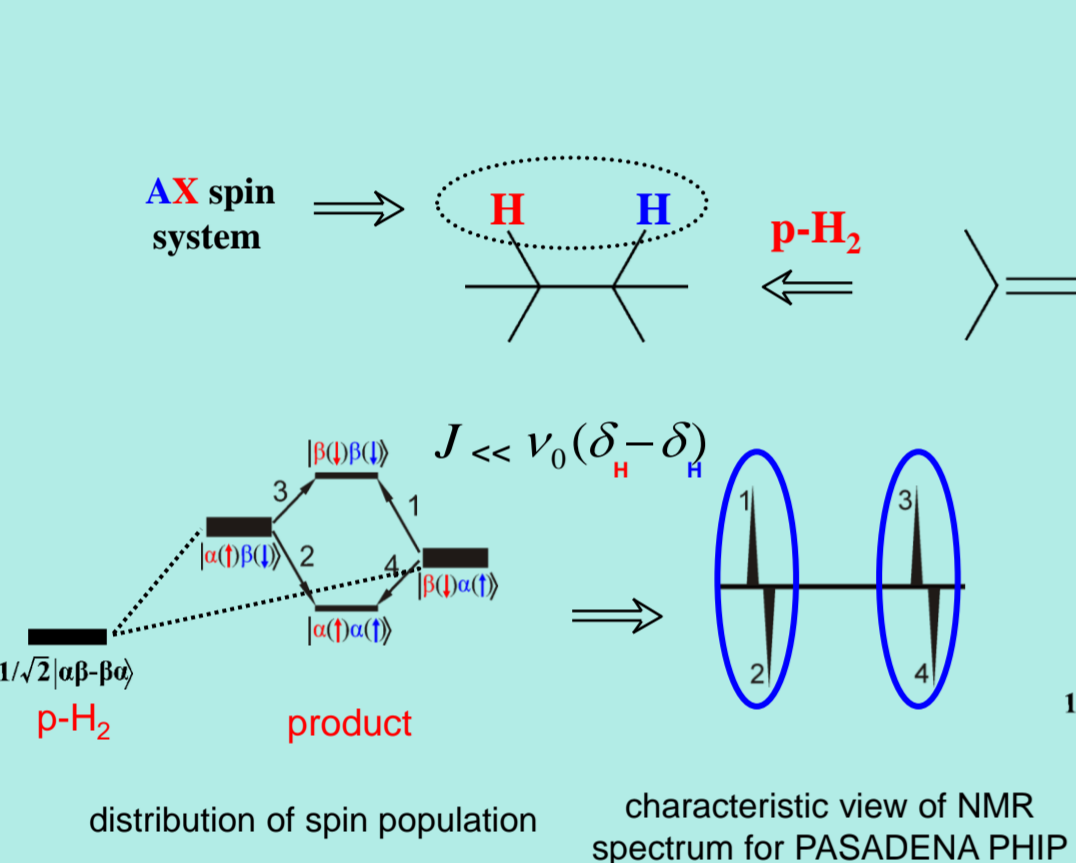
Parahydrogen Induced Polarization or PHIP is one of the methods for creating hyperpolarized spin systems



population differences ≈ 1 in magnetic field 7.1 T enhancement of NMR signal ~ 10⁴ for lower magnetic fields the enhancement of NMR signal is even greater

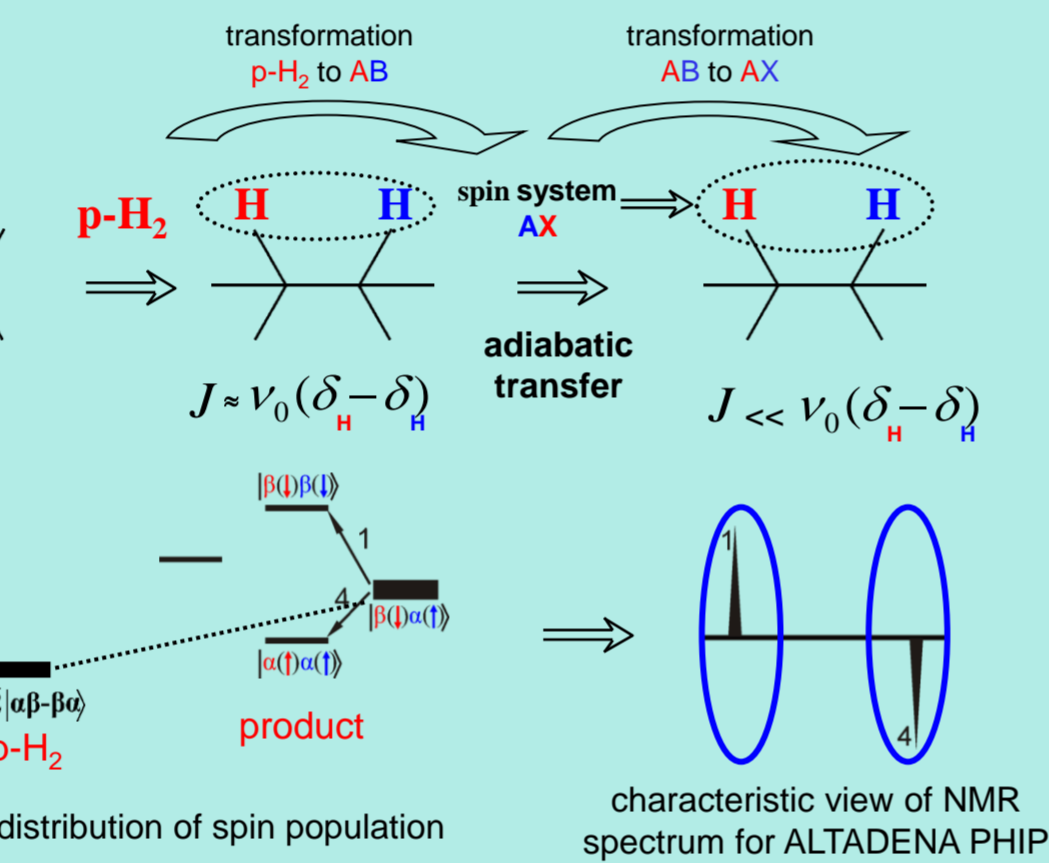
Creation of PHIP

Case 1) interaction with p-H₂ occurs in high magnetic field of NMR spectrometer, PASADENA* PHIP



*Parahydrogen and Synthesis Allows Dramatically Enhanced Nuclear Alignment

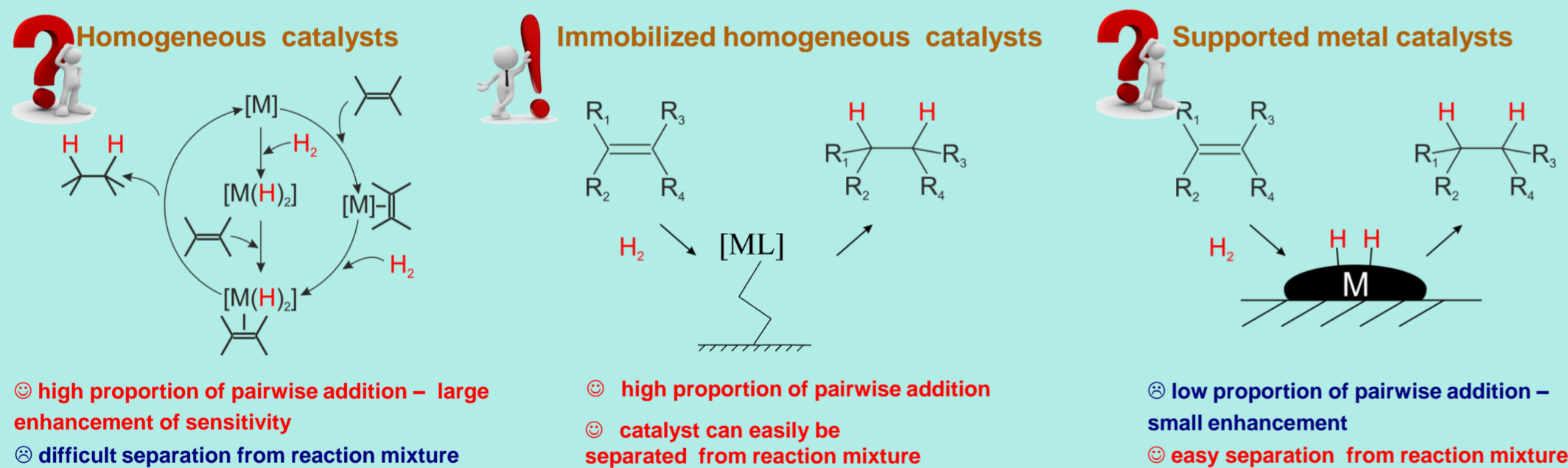
Case 2) interaction with p-H₂ occurs in low magnetic field and then product is adiabatically transferred to high magnetic field of NMR spectrometer, ALTADENA* PHIP



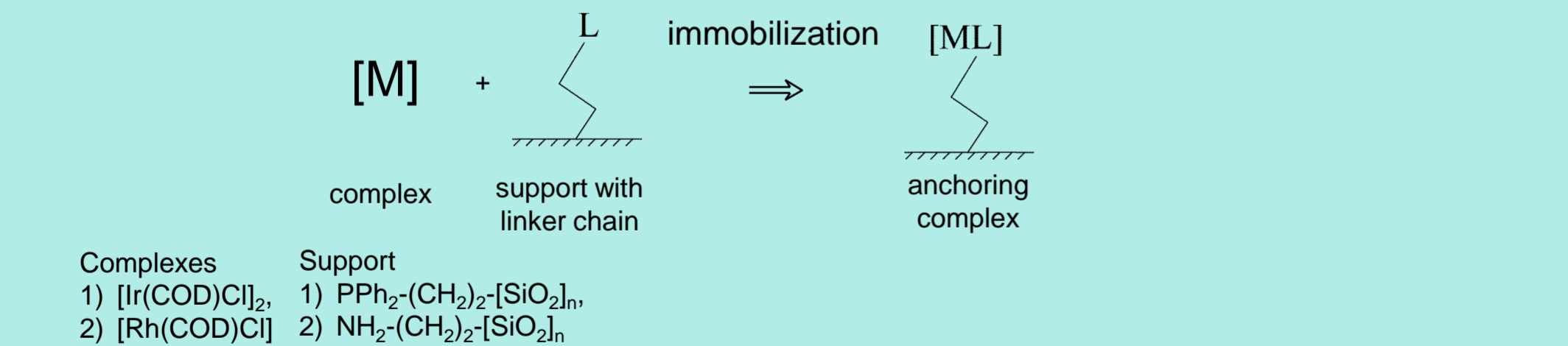
*Adiabatic Longitudinal Transport After Dissociation Engenders Nuclear Alignment

Hydrogenation reaction and PHIP

Necessary condition of PHIP observation is pairwise addition of both atoms of one hydrogen molecule to one substrate molecule

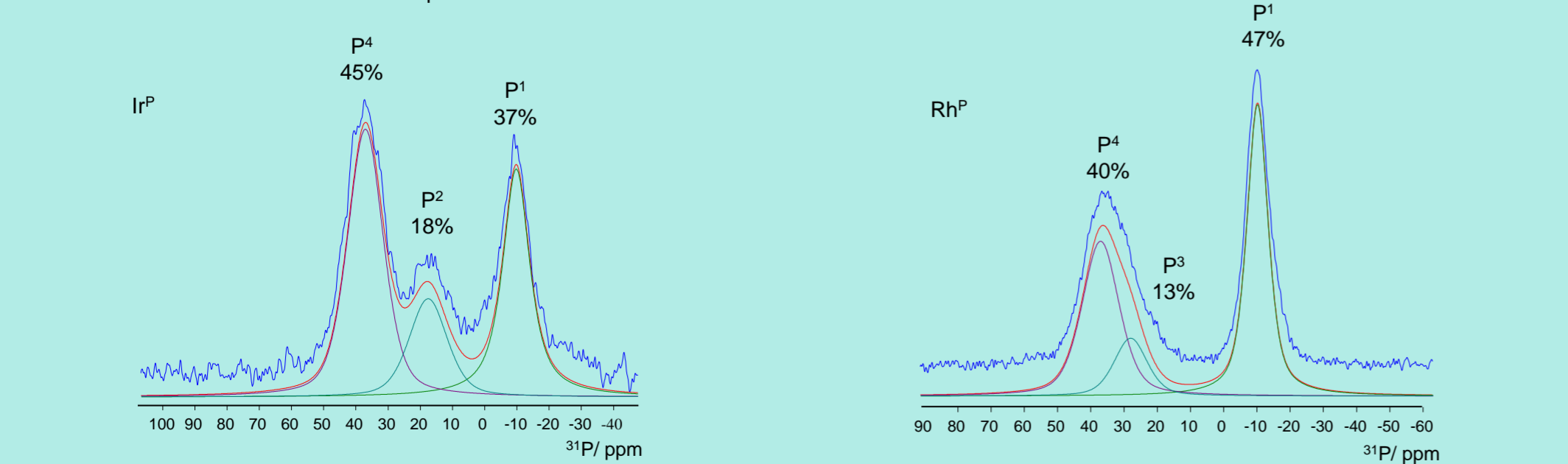


Synthesis of immobilized catalysts Ir and Rh



Characterization of immobilized catalysts by ³¹P MAS NMR

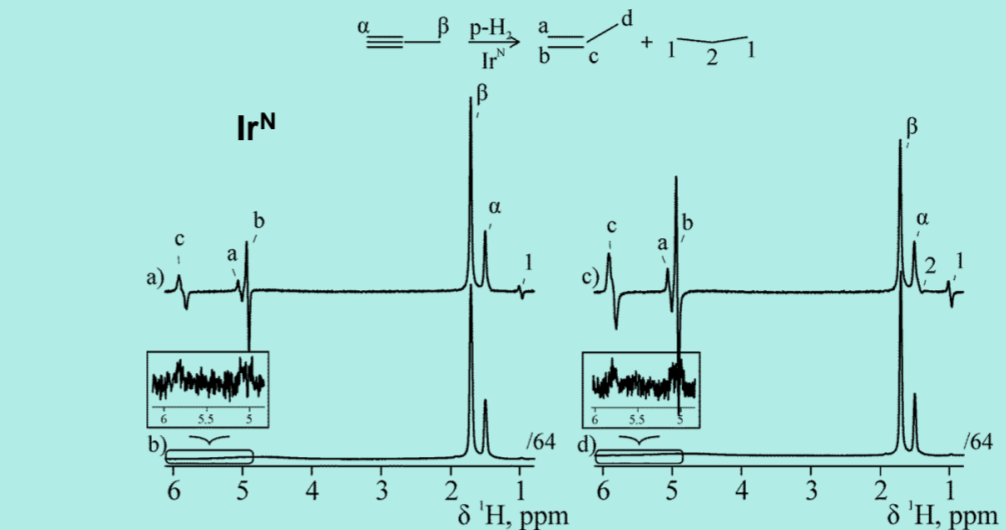
³¹P MAS NMR experiments were performed at 161.98 MHz (9.4 T magnetic field) on a Bruker AVANCE 400 spectrometer. The samples were placed in a ZrO₂ rotor with an outer diameter of 2.5 mm and rotated at a magic angle at a frequency of 20 kHz. An 85% H₃PO₄ solution (0 ppm) was used as an external standard. 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



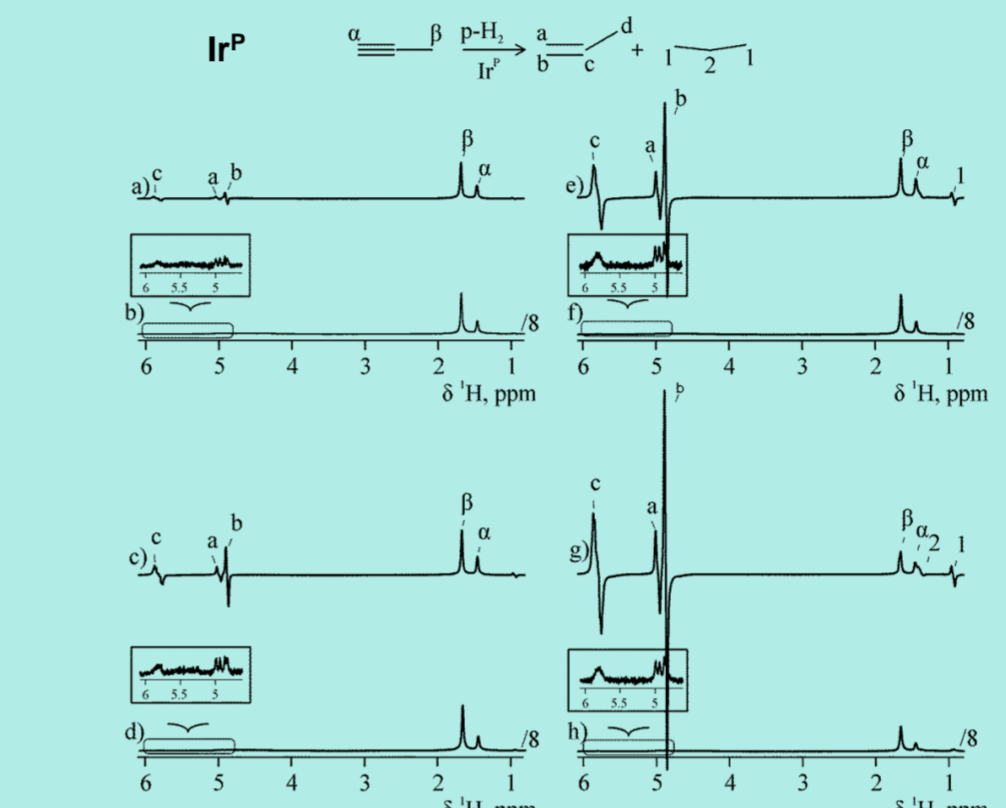
³¹P MAS NMR spectra recorded for immobilized catalysts Ir^P and Rh^P (blue traces) and their decomposition into individual components.

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, Ir^P
 P³ – P coordinated with Rh, Cl(COD)RhP(Ph₂)-(CH₂)₂-[SiO₂]_n, Rh^P
 P⁴ – oxidized form of P(Ph₂)-(CH₂)₂-[SiO₂]_n

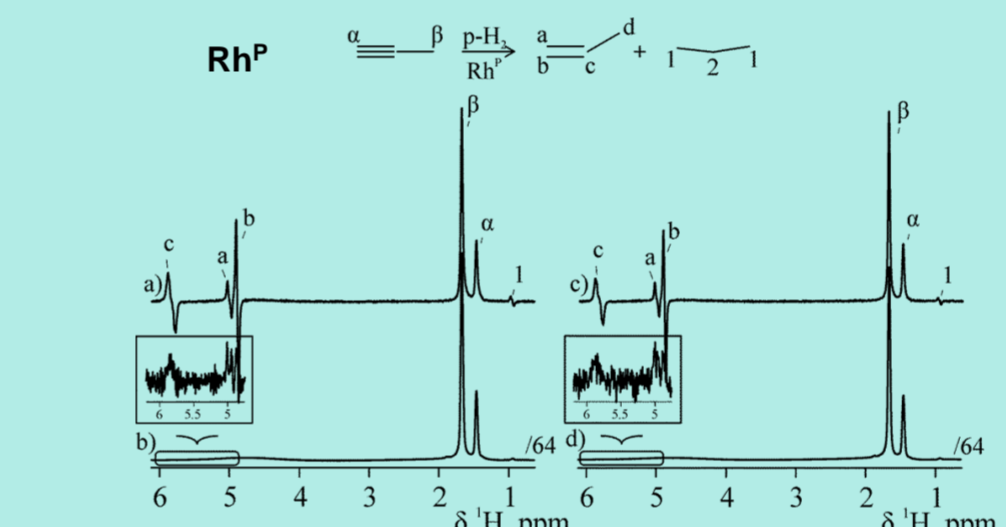
Gas-phase hydrogenation of propyne using p-H₂



¹H NMR PHIP spectra recorded with propyne/p-H₂ mixture flowing (2.2 ml/s) through Ir^N at 100 °C (a) and 120 °C (c). Thermal equilibrium ¹H 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 64 signal accumulations; they are scaled accordingly and are presented on the same vertical scale

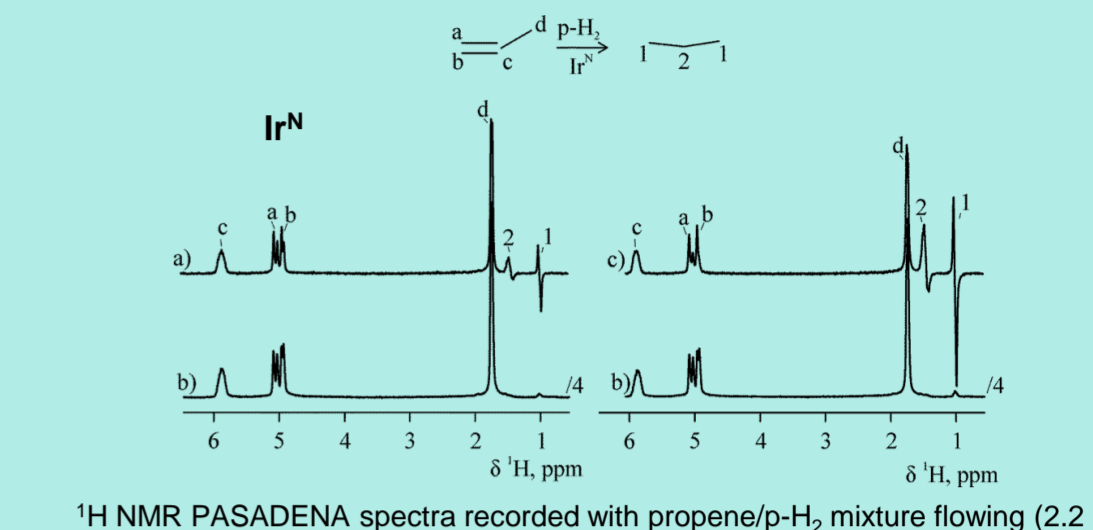


¹H NMR PHIP spectra recorded with propyne/p-H₂ mixture flowing (2.2 ml/s) through Ir^P at (a) 60 °C, (c) 80 °C, (e) 100 °C and (g) 120 °C. Thermal equilibrium ¹H NMR spectra (b, d, f, h) were recorded on the corresponding reaction mixture (a, c, e, and g, respectively) after relaxation of the hyperpolarized 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.

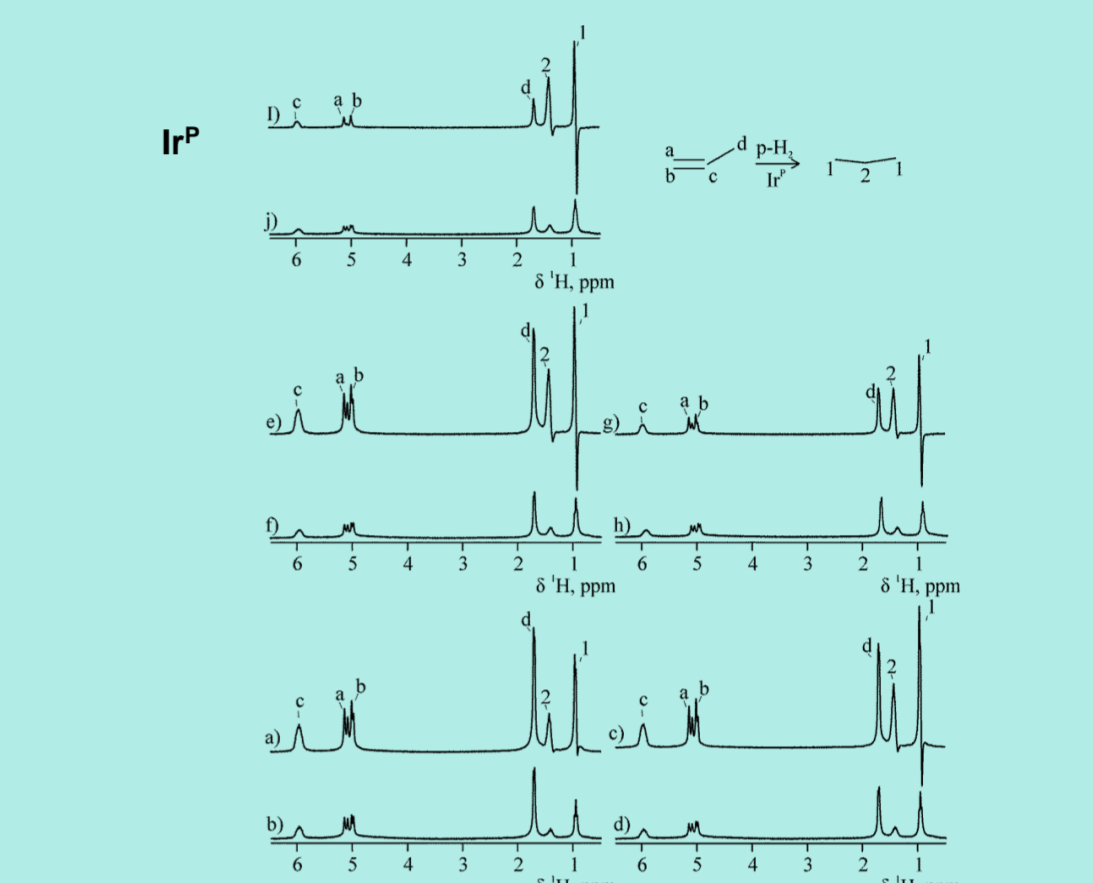


¹H NMR PASADENA spectra recorded with propyne/p-H₂ mixture flowing (2.2 ml/s) through Rh^P at 100 °C (a) and 120 °C (c). ¹H NMR thermal spectra (b, d) were recorded on the corresponding reaction mixture (a and c, respectively) after relaxation of hyperpolarized propene. Spectra (a, c) were acquired with 16 signal accumulations, (b, d) with 1024 signal accumulations and are presented on the same vertical scale

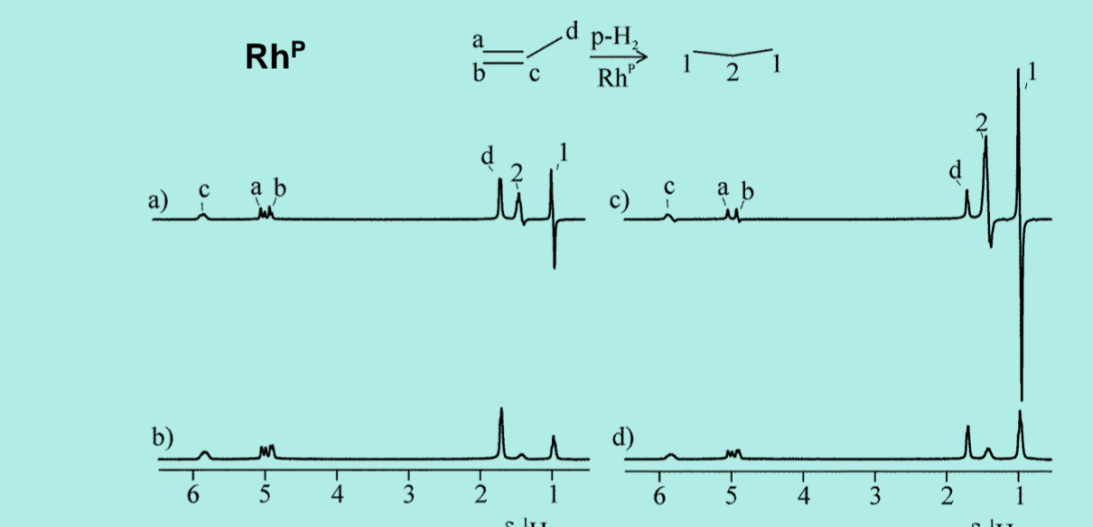
Gas-phase hydrogenation of propene using p-H₂



¹H NMR PASADENA spectra recorded with propene/p-H₂ mixture flowing (2.2 ml/s) through Ir^N at 100 °C (a) and 120 °C (c). ¹H NMR thermal spectra (b, d) were recorded on 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 64 signal accumulations and are presented on the same vertical scale

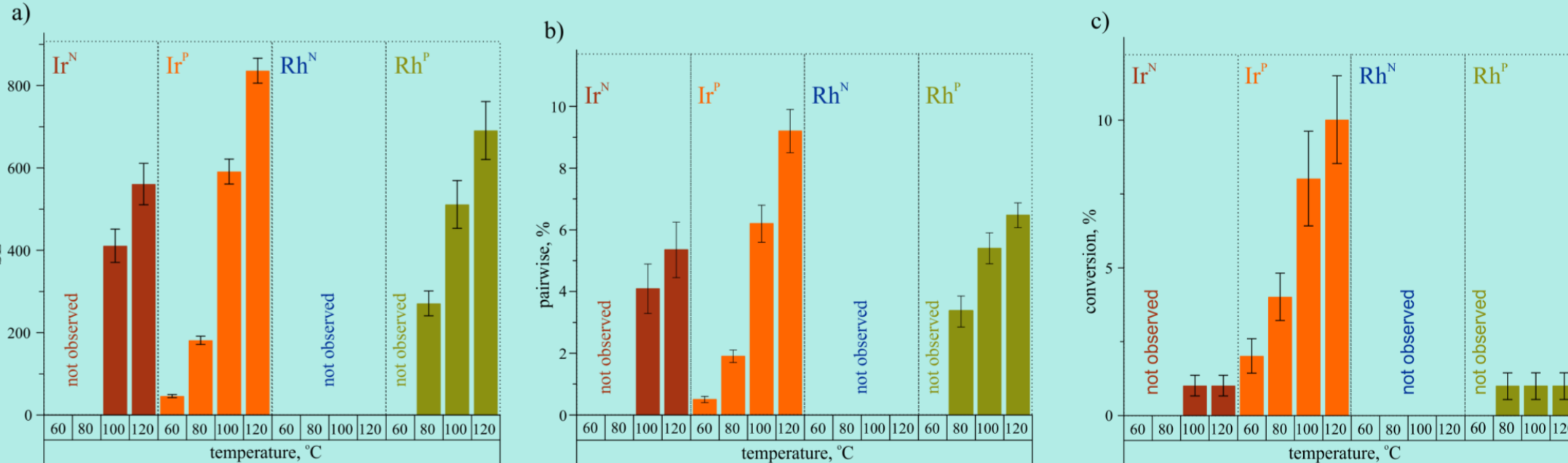


¹H NMR PASADENA spectra recorded with propene/p-H₂ mixture flowing (2.2 ml/s) through Ir^P at 40 °C (a), 60 °C (c), 80 °C (e), 100 °C (g) and 120 °C (i). ¹H NMR thermal spectra (b, d, f, h, j) recorded on the corresponding reaction mixture (a, c, e, g, and i, respectively) after relaxation of hyperpolarized 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.



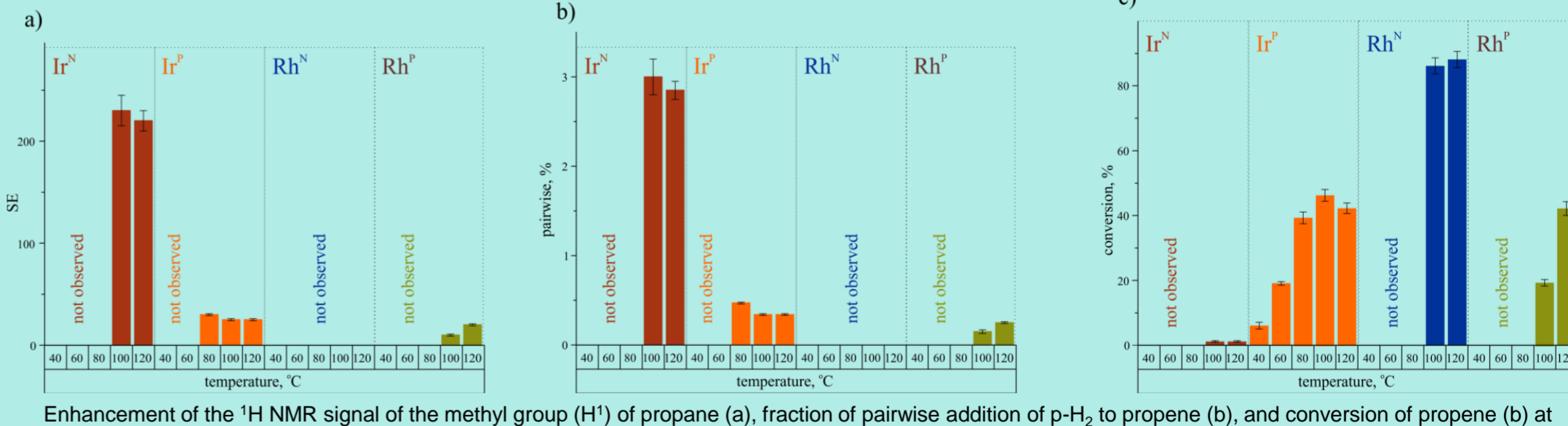
¹H NMR PASADENA spectra recorded with propene/p-H₂ mixture flowing (2.2 ml/s) through Rh^P at 100 °C (a) and 120 °C (c). ¹H NMR thermal spectra (b, d) were recorded on the corresponding reaction mixture (a and c, respectively) after relaxation of hyperpolarized propene. All spectra were acquired with 16 signal accumulations

Gas-phase hydrogenation of propyne using p-H₂

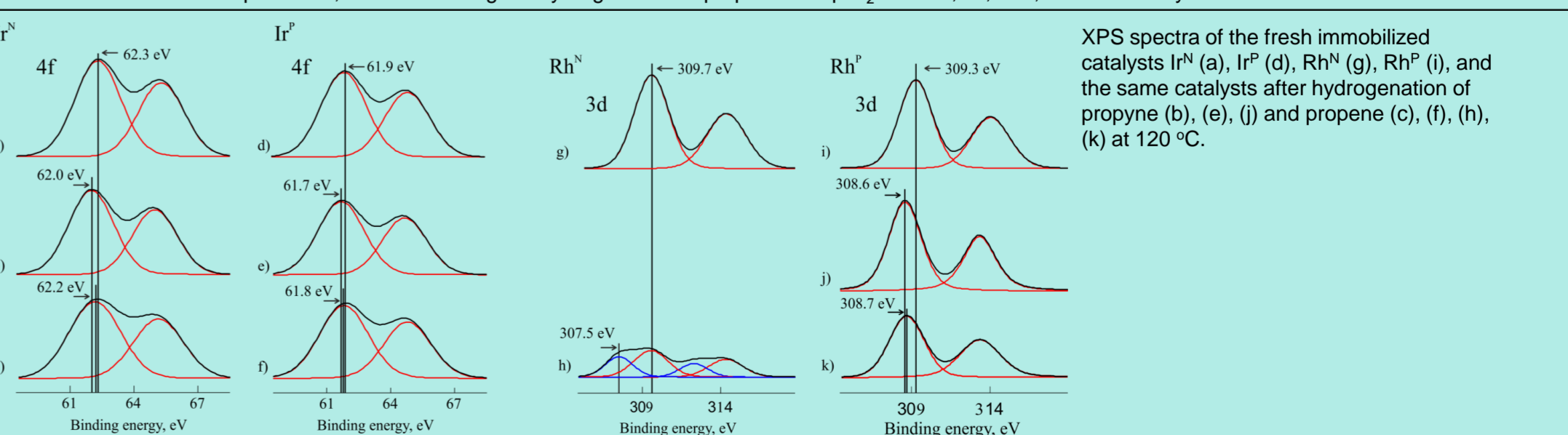


Enhancement of the ¹H NMR signal of the H atom in the methylene group (H^b) of propene which is trans to the CH₃ group (a), pairwise selectivity of p-H₂ addition to propyne (b), and conversion of propyne (c) at different reaction temperatures, observed during the hydrogenation of propyne with p-H₂ over Ir^N, Ir^P, Rh^N, and Rh^P catalysts.

Gas-phase hydrogenation of propene using p-H₂



Enhancement of the ¹H NMR signal of the methyl group (H¹) of propene (a), fraction of pairwise addition of p-H₂ to propene (b), and conversion of propene (b) at different reaction temperatures, observed during the hydrogenation of propene with p-H₂ over Ir^N, Ir^P, Rh^N, and Rh^P catalysts.



Conclusions. In contrast to Rh-based catalysts which showed a pronounced tendency to reduction, for Ir-based catalysts an XPS analysis did not reveal any indication of the formation of metal phase under the reducing conditions upon hydrogenation of propyne or propene at 120 °C. Catalysts with a π-acceptor ligand PPh₂ demonstrated greater activity in the gas-phase hydrogenation of propyne/propene in comparison with σ-donor ligand NH₂. Furthermore, NMR signal enhancements of up to ca. 700- (Rh) and 800-fold (Ir) were achieved. Remarkably, the Ir metal complex bound via the phosphine moiety demonstrated high stability in gas-phase hydrogenation of propyne along with high catalytic activity and pairwise H₂ addition selectivity, yielding substantial quantities of strongly hyperpolarized propene.