A stable 16-electron iridium(III) hydride complex grafted on SBA-15: A single-site catalyst for alkene hydrogenation

Martino Rimoldi, Daniel Fodor, Jeroen A. van Bokhoven* and Antonio Mezzetti*

Department of Chemistry and Applied Biosciences
ETH Zürich
CH-8093 Zürich (Switzerland)
E-mail: mezzetti@inorg.chem.ethz.ch, jeroen.vanbokhoven@chem.ethz.ch

Supporting Information
# Table of Contents

1. General

2. Synthesis of [IrH(O-SBA-15)(POCOP)] (2)

3. Proof of H₂-evolution during the synthesis of 2

4. Nitrogen physisorption

5. Synthesis of [IrH(OSiMe₃)(POCOP)] (4) as model for 2

6. Catalytic hydrogenation of alkenes

7. Monitoring of the hydrogenation reaction by ¹H NMR spectroscopy
1. General

**Materials.** Solvents were dried and degassed by standard methods. All the manipulations were carried out under inert atmosphere by means of standard Schlenk techniques under argon or in a glove box in purified nitrogen, unless otherwise stated. Hydrogen (5.0), ethene (3.5), propene (2.5), propane (3.5), and ethane (3.5) were purchased by Pangas or Messer and used without further purification. Sodium hydride, di-tert-butylchlorophosphine, 1,5-cyclooctadiene (stored under argon and protected from light), potassium trimethylsilanolate were purchased from Aldrich, and resorcinol and tetraethoxysilane from Fluka, iridium trichloride hydrated was obtained by JM, Pluronic P123 from BASF. All the reagents were used as received. Deuterated solvents were purchased by Armar Chemicals, dried and stored over activated molecular sieves and degassed by several freeze-pump-thaw cycles. [IrH₂(POCOP)] (1), [IrHCl(POCOP)] (3), and SBA-15³ were prepared according to published procedures.

**NMR measurements.** Chemical shifts (δ) are given in ppm and coupling constants are given in Hz. 

1H NMR gas-phase spectra were recorded on a Bruker AVANCE DPX 500 spectrometer and the shifts were referenced to liquid CHCl₃ (δ 7.27) as external standard. Chemical shifts are uncorrected for bulk magnetic susceptibility. Unless otherwise stated, the spectra were recorded collecting 16 scans and with an acquisition time of 2.74 s. The d₁ delay time was set at five times the T₁ relaxation time at least. Authentic samples of the alkenes and of the corresponding alkanes in the gas phase were measured as a reference: ethene: δ 8.00 (s); ethane: δ 3.57 (s); propene: δ 8.48 (CH₂CH₃, m, 1H), 7.65 (trans-CH₂CH₃, d, J = 17 Hz), 7.53 (cis-CH₂CH₃, d, J = 10 Hz, 1H), 4.35 (CH₃, d, J = 6.5 Hz, 3H); propane: δ 4.07 (CH₃, septet, J = 7.3 Hz, 2H), 3.62 (CH₃, t, J = 7.3 Hz, 6H). Solution NMR spectra were recorded on Bruker DPX 200, DPX 250, AVANCE III 300, AVANCE III 400, or AVANCE DPX 500 spectrometers. ¹H and ¹³C chemical shifts were measured relative to the residual resonance of the deuterated solvent. The signal of the residual protio methyl group of p-xylene-d₁₀ was set at δ 2.296 in the ¹H NMR and at δ 20.90 in the ¹³C NMR spectrum. ³¹P NMR spectra were referenced to external 85 % H₃PO₄. Solid-state ¹H MAS, ¹³C CP MAS and ³¹P MAS NMR spectra were recorded on a Bruker AVANCE I 400 with a conventional double resonance 2.5 mm probe head or a conventional triple resonance 4 mm probe head in double resonance mode. The samples were filled in a glove box into a zirconia rotor and tightly closed.
spinning frequency was set at 20.00 kHz (2.5 mm rotor) or 10.00 kHz (4 mm rotor). Chemical shifts are referenced to adamantane for $^{13}$C and to (NH$_4$)H$_2$PO$_4$ for $^{31}$P. $^1$H MAS NMR spectra measured with the 2.5 mm rotor were obtained subtracting the background spectrum measured with an empty rotor and the baseline was corrected. All other $^1$H and $^{31}$P spectra were baseline-corrected.

FT IR measurements. FT IR spectra were recorded on a Nicolet 6700, equipped with CsI optics, collecting 16 scans at a resolution of 4 cm$^{-1}$. The spectra were acquired in absorbance, baseline corrected, and no other corrections were applied. 7 mm-Pellets (self-supported) were pressed in a glove box and introduced in a 10 cm gas-tight cell with KBr windows. Spectra were measured between 4000 cm$^{-1}$ and 1400 cm$^{-1}$.

Nitrogen physisorption measurements. Nitrogen adsorption-desorption was carried out with a Micromeritics Tristar 3000 instrument at liquid nitrogen temperature. The BET surface area was determined from the data points collected in the range between 0.01-0.2 relative pressures. The external surface area and micropore volume were derived from the t-plot. The total pore volume was determined from a single point at 0.945 relative pressure. Pore size analysis was carried out on the desorption branch of the nitrogen adsorption/desorption isotherm applying BJH analysis.

Elemental analyses. C, H, and P analyses were performed at the Micro-Laboratory of the Laboratory of Organic Chemistry, ETH Zurich. Phosphorus elemental analyses were quantified by photometrical methods. Iridium elemental analyses were performed at the Laboratory of Inorganic Chemistry, ETH Zurich. Method used: ICPOES after MW-extraction at 250°C.

2. Synthesis of [IrH(O-SBA-15)(POCOP)] (2)

Scheme S1. Synthesis of 2

In a typical synthesis of the grafted complex 2, SBA-15 (1.700 g) (pretreated at 400°C in vacuum for 12 h) was introduced in a 50 mL Young Schlenk tube in a glove box under N$_2$. The Schlenk tube was evacuated and filled with Ar. A solution of [IrH$_2$(POCOP)] (1) (130 mg,
0.22 mmol) in pentane (20 mL) was introduced in the Schlenk tube, and the resulting mixture was stirred at room temperature for 1 h, during which the solution became colorless. The orange solid was recovered by filtration on a glass filter, washed with pentane (10 mL), and dried in vacuum for 12 h. Yield: 1.71 g. The elemental analysis gave C, 2.78 %; P, 0.66 %; Ir, 1.84(±0.03) % (calcld P:C:Ir mole ratio 1:11:0.5; found: 1:10.86:0.45), which corresponds to a loading of 1 of 6.1 % w/w (based on [IrH₂(POCOP)] (1) and calculated as an average of the values for the three elements determined). Characteristic NMR data: ³¹P NMR: δ 170, ¹H NMR: δ −38 (Ir–H).

The catalyst loading was tuned by varying the amount of 1 in the synthesis. The maximum achievable loading was determined by performing the synthesis of 2 with increasing amounts of 1. When 830 mg of SBA-15 were treated with 300 mg (0.51 mmol) of 1, the reaction solution did not turn colorless, which indicated that not all of 1 present in solution had reacted with SBA-15. The elemental analysis of this sample gave C, 9.55 %; P, 2.19 % (calcld P:C mole ratio 1:11; found: 1:11.24), which corresponds to a loading of 1 of 21.2 % (w/w). The ¹H and ³¹P MAS NMR spectra of 2 are shown in Figures S1 and S2, respectively. Signals marked "*" are spinning side bands. Figure S3 highlights the low-intensity ¹H MAS NMR signals of 2.

![Figure S1. ¹H MAS NMR spectrum of 2 (400 MHz, 20 kHz, 2.5 mm rotor).](image)

Both the ³¹P and ¹H chemical shifts are significantly shifted upfield with respect to the starting material [IrH₂(POCOP)] (1), which feature a singlet at δ 204.9 in the ³¹P NMR
spectrum and a $^1$H NMR triplet for the hydride ligand at $\delta$ –17.0 (C$_6$D$_6$ solution).$^1$ The $^1$H and $^{31}$P NMR chemical shifts of 2 are very close to those reported for [IrHCl(POCOP)] (3) ($^{31}$P NMR: $\delta$ 175.8; $^1$H NMR: $\delta$ –41.39, CD$_2$Cl$_2$)$^2$ and for the square-pyramidal anilido complexes 6a and 6b: $^{31}$P NMR: $\delta$ 171–174, 6a.$^5$ $^1$H NMR: $\delta$ –33 to –43 (6a and 6b) (Scheme S2).$^5, 6$

Thus, the $^{31}$P NMR spectrum of 2 strongly supports the formation of an iridium(III) complex bearing an intact POCOP ligand in a five-coordinate environment.

Scheme S2. Five-coordinate, square pyramidal complexes reported in the literature.

---

Figure S2. $^{31}$P MAS NMR spectrum of 2 (162 MHz, 20 kHz, 2.5 mm rotor)
Figure S3. Vertical expansion of the $^1$H MAS NMR spectrum of 2 shown in Figure S1.

The IR spectra of 2 at 13 and 21.2 % loading (Figures S4 and S5, respectively) provide information about the fate of the isolated silanols in SBA-15. Before grafting, SBA-15 shows the sharp peak of the O–H-stretching band of isolated silanols at 3743 cm$^{-1}$ along with the broad band in the range 3700–3300 cm$^{-1}$ related to the presence of hydrogen-bonded silanols.

Upon grafting dihydride 1 onto SBA-15 at 13 % loading (Figure S4), the intensity of the band at 3743 strongly decreases, which indicates the consumption of isolated silanols. The Ir–H stretching of 2 appears at 2120 cm$^{-1}$. The other signals that appear in the IR spectrum of 2, in addition to those of SBA-15, are the aromatic and aliphatic C–H bands of the pincer ligand. Compared to the IR spectrum of 2 at 13 % loading (Figure S4), the spectrum of 2 at the maximum achievable loading of 21.2 % (based on 1) shows an analogous decrease of the band of the isolated silanols (Figure S5).
Figure S4. The FT IR spectrum of unreacted SBA-15 (blue line) is compared with the spectrum of 2 at a loading of 13 % (red line). The intensity was normalized using the band at 1970 cm\(^{-1}\).

Figure S5. The FT IR spectrum of unreacted SBA-15 (blue line) is compared with the spectrum of 2 at a loading of 21.2 % (red line). The intensity was normalized using the band at 1970 cm\(^{-1}\).
3. Proof of H₂ evolution during the synthesis of 2

SBA-15 (32 mg) and 1 (18 mg, 0.03 mmol, in excess of the maximum loading of 21.2 %) were introduced in a Young NMR tube under argon, and toluene-\(d_8\) was added (ca. 2 mL) to minimize the headspace. The tube was immediately closed with a Teflon Young cap and shaken to mix the reagents. Most of the solid deposited on the bottom upon centrifugation and the mixture analyzed by \(^{31}\)P and \(^1\)H NMR. The \(^1\)H and \(^{31}\)P NMR spectra (Figures S6 and S7, respectively) of the supernatant reaction solution showed the signals of unreacted dihydride complex 1 along with those of a new species (\(^{31}\)P NMR: \(\delta 182.8\), \(^1\)H NMR: \(\delta -8.35\)), which we assign to the tetrahydride complex \([\text{IrH}_4(\text{POCOP})]\) (5) on the basis of the chemical shift of the hydride signal as reported in the literature (\(\delta -8.60\), THF-\(d_8\))\(^7\) and by comparison with an authentic sample prepared by treating complex 1 with H₂ gas in \(p\)-xylene-\(d_{10}\) (\(^{31}\)P NMR: \(\delta 182.6\), Figure S8; \(^1\)H NMR: \(\delta -8.25\), Figure S9) according to a literature procedure.\(^1\)

![Scheme S3. Synthesis of 2 in NMR tube and observation of the tetrahydride complex 5.](image)

![Figure S6. \(^{31}\)P NMR spectrum of the reaction solution after addition of an excess of 1 to SBA-15 (see Scheme S3) (161 MHz, 25 °C, toluene-\(d_8\)).](image)
Figure S7. Hydride region of the $^1$H NMR spectrum of the reaction solution after addition of an excess of 1 to SBA-15 (see Scheme S3) (400 MHz, 25 °C, toluene-$d_8$)

Figure S8. $^{31}$P NMR spectrum of 5 (101 MHz, 25 °C, p-xylene-$d_{10}$).

Figure S9. Hydride region of the $^1$H NMR spectrum of 5 (250 MHz, 25 °C, p-xylene-$d_{10}$)

4. Nitrogen physisorption

Prior to measurement, the parent SBA-15 and the samples of 2 were degassed for at least 4 h at 300 °C and 130 °C, respectively. The nitrogen adsorption-desorption isotherms of SBA-15 and 2 are shown in Figure S10, and the results are summarized in Table S1.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Total surface area (m²/g)</th>
<th>External surface area (m²/g)</th>
<th>Micropore surface area (m²/g)</th>
<th>Total pore volume (cm³/g)</th>
<th>Micropore volume (cm³/g)</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SBA-15</td>
<td>666</td>
<td>517</td>
<td>150</td>
<td>0.80</td>
<td>0.063</td>
<td>5.2</td>
</tr>
<tr>
<td>2 (6.1 % w/w)</td>
<td>487</td>
<td>409</td>
<td>79</td>
<td>0.61</td>
<td>0.032</td>
<td>4.8</td>
</tr>
<tr>
<td>2 (21.2 % w/w)</td>
<td>395</td>
<td>379</td>
<td>15</td>
<td>0.44</td>
<td>0.002</td>
<td>3.9</td>
</tr>
</tbody>
</table>

**Table S1.** Derived parameters of nitrogen physisorption measured at the temperature of liquid nitrogen.

**Figure S10.** Nitrogen adsorption-desorption isotherms of (a) SBA-15 as prepared, (b) 2 @ 6.1 % w/w, and (c) 2 @ 21.2 % w/w (loadings are based on 1) measured at the temperature of liquid nitrogen. Filled and open symbols represent adsorption and desorption branches, respectively. The inset shows the corresponding BJH pore size distributions derived from the desorption branches. V: pore volume, D: pore diameter.
Upon grafting complex 1 (21.2 % w/w loading) onto the surface of SBA-15, the BET surface area of the latter decreases from 666 m$^2$/g to 395 m$^2$/g, and the total pore volume from 0.80 cm$^3$/g to 0.44 cm$^3$/g. Lower loadings of the iridium complex gave intermediate values (see Table S1 and Figure S10). The pore diameter, which is 5.2 nm before grafting, decreases to 3.9 nm at the maximum loading of 21.2 % (w/w) (Figure 5).

Estimations based on the crystallographic data of the dihydride pincer complex 1 suggest that the grafted Ir-pincer forms an approximately 6.8 Å thick layer inside the channels of SBA-15. This estimation takes into account that the distance between the iridium atom and the outer rim of the pincer ligand is 4.8 Å$^8$ and assumes an Ir–O bond length in the Ir–O–Si bridge of about 2 Å.$^9$ Thus, at total or close to total coverage, the pore diameter is expected to decrease from 5.2 to 3.8 nm, which is in excellent agreement with the experimentally determined value of 3.9 nm (Figures 1 and 5). The free pore volume is large enough for the efficient diffusion of molecules such as carbon monoxide, ethene, and propene, which is the prerequisite for the catalytic activity in alkene hydrogenation shown by 2 as discussed below.

5. Synthesis of [IrH(OSiMe$_3$)(POCOP)] (4) as model for 2

![Scheme S4. Synthesis of the siloxo complex 4](attachment:SchemeS4.png)

In a typical procedure, KOSiMe$_3$ (28 mg, 0.218 mmol) and [IrHCl(POCOP)] (3) (62 mg, 0.099 mmol) were placed in a 20 mL-Schlenk tube, and $p$-xylene was added while stirring vigorously. The reaction, which was monitored by $^{31}$P NMR spectroscopy, reached completion after 1 h. The filtered solution was evaporated in vacuum to give a reddish brown solid, which contained an impurity (approximately 1 %), as indicated by integration of the signal at $\delta$ 182.1 in the $^{31}$P NMR spectrum (barely visible in Figures S11 and S15). Complex 4 slowly decomposes in solution to give the unknown impurity featuring the signal at $\delta$ 182.1.
Figure S11. \(^1\text{H}\)\(^{31}\text{P}\) NMR spectrum of 4 (81 MHz, \(p\)-xylene-\(d_{10}\), RT).

Figure S12. \(^1\text{H}\) NMR spectrum of 4 (400 MHz, \(p\)-xylene-\(d_{10}\), RT).

Spectroscopic and analytical data of 4: \(^1\text{H}\) NMR (400 MHz, \(p\)-xylene-\(d_{10}\), RT): \(\delta\) 6.87 (t, \(J = 7.8\), 1H), 6.72 (d, \(J = 7.9\), 2H), 1.42 (t, \(J = 7.1\), 18H, 'Bu), 1.46 (t, \(J = 7.3\), 18H, 'Bu), 0.48 (s, 9H, Si(CH$_3$)$_3$), –36.93 (t, \(J = 12.9\), 1H, Ir–H); \(^{31}\text{P}\) NMR (81 MHz, \(p\)-xylene-\(d_{10}\), RT): \(\delta\) 169.5 (s); \(^{13}\text{C}\) NMR NMR (100 MHz, \(p\)-xylene-\(d_{10}\), RT): \(\delta\) 168.2 (C$_q$, \(J = 5.5\), 2C, C–O), 125.2 (s, C arom), 111.7 (br m, C arom), 105.8 (t, \(J = 5.1\), C arom), 43.1 (t, \(J = 10.9\), 2C, C$_q$, C(CH$_3$)$_3$), 40.0 (t, \(J = 12.3\), 2C, C$_q$, C(CH$_3$)$_3$), 29.1 (t, \(J = 3.5\), 6C, CH$_3$), 28.8 (t, \(J = 3.3\), 6C,
CH₃), 6.4 (s, 3C, OSi(CH₃)₃). FT IR (CsI pellet): 2110 cm⁻¹. Elemental analysis: Calcd: C = 44.16 %, H = 7.26 %; Found: C = 44.09 %, H = 7.12 %.

**Figure S13.** Aromatic and aliphatic region of the ¹H NMR spectrum of 4 (400 MHz, p-xylene-d₁₀, RT).

**Figure S14.** Hydride region of the ¹H NMR spectrum of 4 (400 MHz, p-xylene-d₁₀, RT).
Figure S15. $^{31}$P, $^1$H correlation NMR spectrum of 4.

Figure S16. $^{13}$C NMR spectrum of 4 (100 MHz, RT, $p$-xylene-$d_{10}$).
Figure S17. Aliphatic region of the $^{13}$C NMR spectrum of 4 (100 MHz, RT, p-xylene-$d_{10}$).

Figure S18. Aromatic region of the $^{13}$C NMR spectrum of 4 (100 MHz, RT, p-xylene-$d_{10}$).
6. Catalytic hydrogenation of alkenes

In a glove box, catalyst 2 (20 mg, 6.1 % loading based on 1) was introduced in a 55 mL-Young Schlenk flask equipped with a Teflon coated stirring bar. The Schlenk was then evacuated and filled at atmospheric pressure with ethene or propene. The Schlenk tube was then charged with hydrogen to a total pressure of 2 bar (absolute). All the manipulations were done at room temperature. The mixture was then vigorously stirred at 23 °C or 70 °C. The reactions at 70 °C were performed preparing the gaseous mixture at room temperature and immersing half of the volume of the Schlenk tube in a preheated oil bath. After the desired amount of time, the reaction was stopped, and a sample of the gaseous mixture was transferred into an NMR tube fitted with a Young valve. The composition was determined by integration of the signals of the gas-phase $^1$H NMR spectra. To reuse the catalyst, the Schlenk was evacuated for 10 min, after which new gaseous reagents were charged. The above procedure was repeated three times (Table S2, entries 2-4). The moles of reagents were calculated with the ideal gas law, and TON and TOF were determined on the basis of the catalyst loading of 6.1 % (w/w) as determined by C, P, and Ir elemental analysis (see synthesis of 2).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>T [°C]</th>
<th>Cycle</th>
<th>Time [h]</th>
<th>Conv. [%]</th>
<th>TON</th>
<th>TOF [min$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethene</td>
<td>23</td>
<td>I</td>
<td>0.5</td>
<td>20</td>
<td>218</td>
<td>7.3</td>
</tr>
<tr>
<td>2</td>
<td>Ethene</td>
<td>23</td>
<td>II</td>
<td>0.5</td>
<td>20</td>
<td>218</td>
<td>7.3</td>
</tr>
<tr>
<td>3</td>
<td>Ethene</td>
<td>23</td>
<td>III</td>
<td>0.5</td>
<td>16</td>
<td>174</td>
<td>5.8</td>
</tr>
<tr>
<td>4</td>
<td>Ethene</td>
<td>23</td>
<td>IV</td>
<td>0.5</td>
<td>16</td>
<td>174</td>
<td>5.8</td>
</tr>
<tr>
<td>5</td>
<td>70</td>
<td>0.5</td>
<td></td>
<td>79</td>
<td>861</td>
<td></td>
<td>28.7</td>
</tr>
<tr>
<td>6</td>
<td>23</td>
<td>2</td>
<td></td>
<td>64</td>
<td>698</td>
<td></td>
<td>5.8</td>
</tr>
<tr>
<td>7</td>
<td>23</td>
<td>4</td>
<td></td>
<td>93</td>
<td>1014</td>
<td></td>
<td>4.2</td>
</tr>
<tr>
<td>8</td>
<td>23</td>
<td>9</td>
<td></td>
<td>99</td>
<td>1080</td>
<td></td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Propene</td>
<td>23</td>
<td></td>
<td>0.5</td>
<td>14</td>
<td>153</td>
<td>5.1</td>
</tr>
<tr>
<td>10</td>
<td>Propene</td>
<td>70</td>
<td></td>
<td>0.5</td>
<td>68</td>
<td>742</td>
<td>24.7</td>
</tr>
<tr>
<td>11</td>
<td>Propene</td>
<td>23</td>
<td></td>
<td>2</td>
<td>51</td>
<td>556</td>
<td>4.6</td>
</tr>
<tr>
<td>12</td>
<td>Propene</td>
<td>23</td>
<td></td>
<td>4</td>
<td>68</td>
<td>742</td>
<td>3.1</td>
</tr>
<tr>
<td>13</td>
<td>Propene</td>
<td>23</td>
<td></td>
<td>15</td>
<td>99</td>
<td>1080</td>
<td></td>
</tr>
</tbody>
</table>

*Table S2.* Conversion, TON, and TOF (min$^{-1}$) of the hydrogenation of ethene and propene with catalyst 2 (alkene:hydrogen ratio 1:1, initial total pressure: 2 bar absolute.)
After the catalytic run reported in entry 11, the Schlenk tube was evacuated for 10 min, and the $^{31}$P MAS NMR spectrum of the recovered material was then measured. The spectrum is shown in Figure S19 B and compared with the spectrum the spectrum of the same material recorded before the catalytic reaction (Figure S19 A).

**Figure S19.** $^{31}$P MAS NMR spectrum of 2 (6.1 % w/w) before (A) and after (B) catalysis (entry 11) (162 MHz, 2.5 mm rotor, 20 kHz)
Figure S20. $^1$H NMR spectrum of the gas phase after the catalytic hydrogenation of ethene (23 °C, 0.5 h reaction time) (Table S2, entry 1) (500 MHz, RT)

Figure S21. Gas-phase $^1$H NMR spectrum after the 1st catalyst recycling (Table S2, entry 2) (500 MHz, RT)
**Figure S22.** Gas-phase $^1$H NMR spectrum after the 2\textsuperscript{nd} catalyst recycling (Table S2, entry 3) (500 MHz, RT).

**Figure S23.** Gas-phase $^1$H NMR spectrum after the 3\textsuperscript{rd} catalyst recycling (Table S2, entry 4) (500 MHz, RT).
**Figure S24.** $^1$H NMR spectrum of the gas phase after the catalytic hydrogenation of ethene at 70 °C (Table S2, entry 5) (500 MHz, RT).

**Figure S25.** $^1$H NMR spectrum of the gas phase after the catalytic hydrogenation of ethene (23 °C, 2 h reaction time) (Table S2, entry 6) (500 MHz, RT).
Figure S26. $^1$H NMR spectrum of the gas phase after the catalytic hydrogenation of ethene (23 °C, 4 h reaction time) (Table S2, entry 7) (500 MHz, RT).

Figure S27. $^1$H NMR spectrum of the gas phase after the catalytic hydrogenation of ethene (23 °C, 9 h reaction time) (Table S2, entry 8) (500 MHz, RT).
Figure S28. $^1$H NMR spectrum of the gas phase after the catalytic hydrogenation of propene (23 °C, 0.5 h reaction time) (Table S2, entry 9) (500 MHz, RT).

Figure S29. $^1$H NMR spectrum of the gas phase after the catalytic hydrogenation of propene at 70 °C (Table S2, entry 10) (500 MHz, RT).
Figure S30. $^1$H NMR spectrum of the gas phase after the catalytic hydrogenation of propene (23 °C, 2 h reaction time) (Table S2, entry 11) (500 MHz, RT).

Figure S31. $^1$H NMR spectrum of the gas phase after the catalytic hydrogenation of propene (23 °C, 4 h reaction time) (Table S2, entry 12) (500 MHz, RT).
Figure S32. $^1$H NMR spectrum of the gas phase after the catalytic hydrogenation of propene (23 °C, 15 h reaction time) (Table S2, entry 13) (500 MHz, RT).

7. Monitoring of the hydrogenation reaction by $^1$H NMR spectroscopy

A mixture of ethene and dihydrogen (1:1) was prepared in a 50 mL-Young Schlenk and transferred into an evacuated NMR tube (with a volume of approximately 2.5 ml) fitted with a Young valve containing catalyst 2 (4 mg) at the bottom. The final pressure in the NMR tube is estimated to approximately 2 bar (absolute).

The sample was immediately introduced into the spectrometer, and the $^1$H NMR spectra of the gas phase were recorded. The first point was acquired 27 s after the addition of the gaseous reagents in the NMR tube. Each point was determined acquiring a single scan (acquisition time 2.74 s) at intervals of approximately 12 s (300 points), 39 s (50 points) and 130 s (100 points). The progress of the reaction was evaluated by integrating the signal related to ethene and ethane. The resulting values were first normalized to the number of protons, and then the sum of the integrals of ethene and ethane was normalized to one. The obtained values represent the mole fraction of ethene and ethane.
**Figure S33.** Mole fractions of ethene and ethane as function of time (h) as determined by $^1$H NMR spectroscopy.
References


