



Supporting Information

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# Reactions of olefins with novel ruthenium hydride nanoparticles: NMR characterization, hydride titration and room temperature C-C activation

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## Contents

### General and materials

### Characterization

### Synthesis of ruthenium nanoparticles

### General procedure for the preparation of reaction mixtures for the quantification of hydrogen atoms adsorbed onto the surface of Ru nanoparticles by CPG analyses

### Gas phase NMR experiments

### Solid state NMR experiments

### Desorption experiments

### Supplementary Figures

## General and materials

All operations were carried out using standard Schlenk tube or Fischer-Porter bottle techniques or in a glove-box under argon. Solvents were purified just before use by distillation under a nitrogen atmosphere: toluene and THF over sodium benzophenone, pentane over calcium hydride. Bis(diphenylphosphino)butane (dppb), cyclooctadiene (COD), hexadecylamine (HDA) and polyvinylpyrrolidone (PVP) were purchased from Aldrich,  $\text{RuCl}_3 \cdot 3 \text{H}_2\text{O}$  from Johnson Matthey, CO,  $\text{H}_2$  and  $\text{D}_2$  from Air Liquid,  $\text{C}_2\text{D}_4$  from Eurisotop and  $^{13}\text{CH}_2$   $^{13}\text{CH}_2$  from Cambridge Isotope Laboratoires, respectively; all were used without purification.  $[\text{Ru}(\text{COD})(\text{COT})]^{\text{i}}$  and Bis(diphenylphosphino)decane (dppd)<sup>ii</sup> were prepared according to literature procedures.

## Characterization

Specimen for TEM analysis were prepared in a glove box, by slow evaporation of a drop of each crude colloidal solution deposited onto a holey carbon covered copper grid. The TEM experiments were performed at the “Service Commun de Microscopie Electronique de l’Université Paul Sabatier” on a JEOL 200 CX-T electron microscope operating at 200kV with a point resolution of 4.5 Å. The approximation of the particles mean size was made through a manual analysis of enlarged micrographs by measuring a number of particles on a given grid.

Wide-angle X-ray scattering (WAXS) was performed at the CEMES-CNRS. All samples were sealed in 1 mm -diameter Lindemann glass capillaries. The measurements of the X-ray intensity scattered by the samples irradiated with graphite-monochromatized molybdenum  $\text{K}_\alpha$  (0.071069 nm) radiation were performed using a dedicated two-axis diffractometer. Radial distribution functions (RDF) were obtained after Fourier Transformation of the reduced intensity functions.

Gas phase  $^1\text{H}$  NMR and solid state  $^2\text{H}$  NMR experiments of Ru/dppb nanoparticles were carried out in Berlin. Liquid NMR of the Ru/dppb nanoparticles, solid state  $^{31}\text{P}$  NMR of Ru/dppb and Ru/dppd nanoparticles, solid state  $^{13}\text{C}$  NMR of Ru/dppd and Ru/PVP nanoparticles and gas phase NMR of the desorption experiments were carried out in Toulouse.

Liquid NMR: Liquid NMR spectra were recorded in  $d^8$ -THF on a Bruker DPX 300 and a Bruker AMX 400 operating at 300 MHz and 400 MHz, respectively in  $^1\text{H}$  and 100.71 MHz in  $^{13}\text{C}$ . Solid state NMR: The solid state NMR experiments were performed on two different Pulse-Fourier-NMR spectrometers: (a) a Varian Infinity Plus operating at a field of 14.09 T (599.97 MHz for  $^1\text{H}$ ) and (b) a Bruker MSL at a field of 7.05 T (300.13 MHz for  $^1\text{H}$ ). Both spectrometers use Oxford wide bore (89 mm) superconducting magnets. On both spectrometers, Chemagnetics probes are used: a 6 mm o.d. pencil double resonance probe with the 7 T spectrometer, and 4 mm o.d. and 5 mm o.d. HXY probes of T3 type with the 14 T spectrometer. The powdered samples were spun along the magic angle with spinning frequencies between 4 and 8 kHz. In the  $^{13}\text{C}$  and  $^{31}\text{P}$  1 pulse experiments the typical  $90^\circ$  pulse length is 3.0  $\mu\text{sec}$  and 6.0  $\mu\text{s}$ , respectively. For  $^1\text{H}$  decoupling on spectrometer a the maximum power is used for excitation as well as for decoupling. For achieving the optimum decoupling efficiency, the TPPM sequence is employed with a typical flip angle of  $15^\circ (\pm 7.5^\circ)$  and a pulse length of typically 7  $\mu\text{sec}$ . This in conjunction with MAS is sufficient to remove  $^1\text{H}$ -X dipolar line broadening. Gas Phase NMR: The gas state NMR spectra were recorded on a Bruker AMX 500 NMR spectrometer at a magnetic field of 11.7 T, the corresponding resonance frequencies are 500.0 MHz for  $^1\text{H}$ , 125.7 MHz for  $^{13}\text{C}$ . The chemical shift calibration of the NMR spectra was done, using TMS as external standard.

Gas chromatograms were obtained in a HP 5890 Series II Gas Chromatograph with a SGE BP1 non polar 100% dimethyl polysiloxane capillary column of 50m $\times$ 0.32mm $\times$ 0.25 $\mu\text{m}$ . The method used for 1-octene/octane experiments consists on 10 minutes at  $70^\circ\text{C}$  and a ramp of  $8^\circ\text{C}/\text{minute}$  until  $250^\circ\text{C}$ . The method used for 2-norbornene/norbornane experiments consists on 15 minutes at  $40^\circ\text{C}$  and a ramp of  $8^\circ\text{C}/\text{minute}$  until  $250^\circ\text{C}$ .

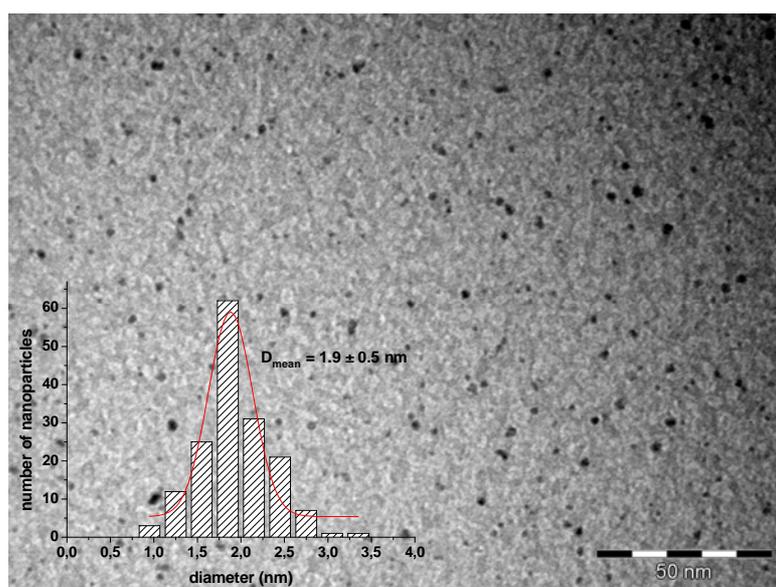
Mass chromatograms were obtained in a HP 6890 Series GC system with a HP5MS Agilent nonpolar 95% dimethyl polysiloxane capillary column of 30m $\times$ 0.25mm $\times$ 0.25 $\mu\text{m}$  and a 70 eV electronic impact detector.

### **Synthesis of ruthenium nanoparticles**

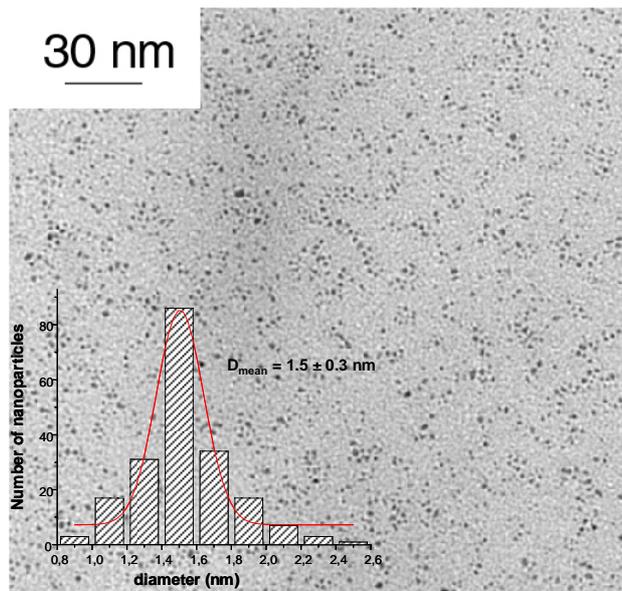
Ru/PVP and Ru/HDA nanoparticles have been synthesized following the method previously described by the group.<sup>iii</sup>

Ru/dppd and Ru/dppb were synthesized as following:

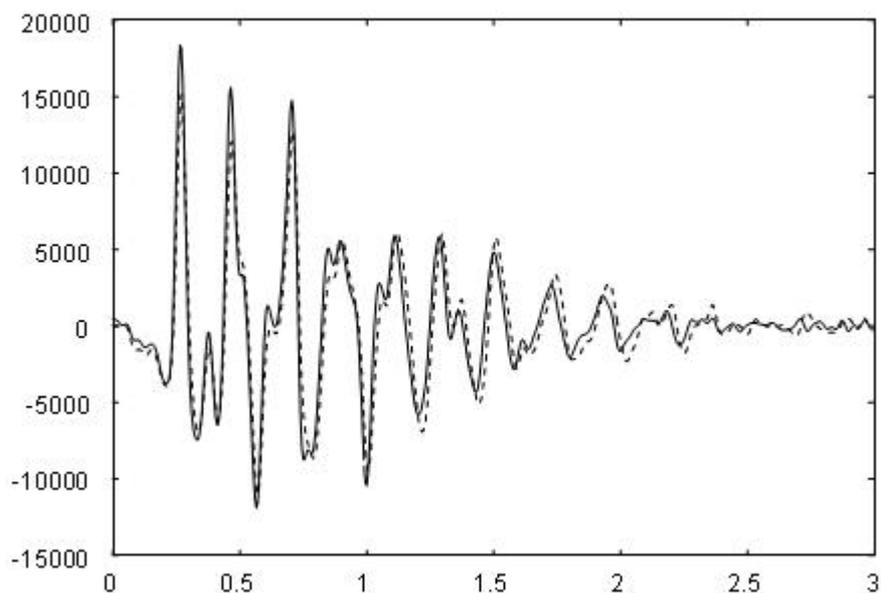
100 mg of [Ru(COD)(COT)] (0.317 mmol) were introduced in a Fisher-Porter bottle and left in vacuum during 30 minutes. 50 ml of THF degassed by three freeze-pump cycles were then added. The resulting yellow solution was cooled to 193K and a solution of 50 ml of THF containing 16.18 mg of dppd (0.032 mmol, 0.1 equivalents) or 13.6 mg of dppb (0.032 mmol, 0.1 equiv.) was introduced into the flask. The Fisher Porter bottle was pressurized with 3 bars of dihydrogen and the solution was left to warm slowly to room temperature under vigorous stirring. After 24 hours, a homogenous brown solution is obtained. The volume of the solution was then reduced to approximately 10 mL and added to 60 mL of deoxygenated and cold pentane (193 K). A brown precipitated formed after several hours, which was filtered, washed with pentane (2 X 60 mL of deoxygenated pentane) and dried in vacuum, giving then rise to the particles as dark brown powders. In all the cases, ruthenium colloids were found to be stable with time and did not show any sign of decomposition under argon atmosphere.



Transmission electron micrograph of ruthenium nanoparticles stabilized by dppd. Size histogram.



Transmission electron micrograph of ruthenium nanoparticles stabilized by dppb. Size histogram.



Experimental RDF of Ru/dppd nanoparticles (solid line).

Comparison with a model of hcp ruthenium structure (broken line).

### **General procedure for the preparation of reaction mixtures for the quantification of hydrogen atoms adsorbed onto the surface of Ru nanoparticles by CPG analyses**

Each colloidal solution (Ru/PVP, Ru/HDA, Ru/dppb and Ru/dppd) has been prepared in THF as previously described. On each fresh colloidal solution, five cycles of 1 minute vacuum/1

minute bubbling of argon were performed in order to eliminate the dihydrogen solved into the solvent. Then, 1 or 5 equivalents of the chosen olefin (1-octene or 2-norbornene), previously filtered through alumina, were added. Samples were regularly taken from the solutions (after 2, 18 and 24 hours) for CPG analyses and estimation of the olefins conversion into alkanes. To get nanoparticles-free solutions, filtration of the samples was realized through an Al<sub>2</sub>O<sub>3</sub> pad.

The reactions were carried out using freshly prepared colloidal solutions degassed from any remaining hydrogen by 5 cycles of 1 minute vacuum/1 minute bubbling of argon to completely eliminate solved hydrogen. Each purified olefin has been added to each colloidal solution, and the reaction mixture has been left at room temperature under vigorous stirring. Samples of the solutions were taken after 2, 18 and 24 hours, analyzed by GC and compared to authentic samples of possible reaction products (alkanes, dienes, isomerized octenes). Remarkably, we found that for a given nanoparticle system and within experimental errors the same conversion was reached for 1 or 5 eq. of either 1-octene or norbornene. This suggests the presence of a definite and reproducible number of hydrides at the surface of the nanoparticles. The kinetic of the reaction follows the tendency Ru/PVP > Ru/HDA > Ru/dppd. In the case of Ru/dppd, the reaction is notably slower and may not be finished after 24 hours. These results are in agreement with the steric hindrance present at the surface of the particles. In the case of 1-octene we find that extensive isomerisation has taken place but, neither in this case, nor in the case of norbornene do we find any trace of formation of dienes. The nanoparticles Ru/PVP and Ru/dppd are spherical and display a very narrow size distribution. If we assume that the particles are monodisperse and perfectly spherical, given their mean size of respectively 1.5 and 1.9 nm and their structure (hcp), the calculated percentage of ruthenium atoms at their surface is respectively 76 and 52%. In the case of Ru/HDA, the particles are slightly elongated, but in a first approximation they can be considered as spheres of 1.9 nm mean diameter and therefore to contain also 52% of ruthenium atoms at their surface. Knowing the total amount of ruthenium introduced and the conversion of the olefins, it is then easy to calculate the number of hydrides which have been consumed for the hydrogenation process. This corresponds respectively to ca. 1.3, 1.3 and 1.1 hydrides per surface ruthenium for the Ru/PVP, Ru/HDA and Ru/dppd nanoparticles.

### Experimental data

	1-octene		2-norbornene	
	1 eq.	5 eq.	1 eq.	5 eq.
<b>Ru/HDA</b>	8 / 50.2 / 25.0	8.0 / 49.7 / 123.6	8.1 / 50.0 / 15.0	8.1 / 50.0 / 74.7
<b>Ru/dppb</b>	6.9 / 50.0 / 24.8	6.9 / 50.2 / 124.8	6.9 / 50.2 / 16.0	7.2 / 50.7 / 75.8
<b>Ru/dppd</b>	9.0 / 49.6 / 24.8	8.8 / 49.7 / 123.6	8.8 / 50.1 / 15.5	8.7 / 49.6 / 74.1
<b>Ru/PVP</b>	502.0 / 80.0 / 39.8	497.4 / 80.2 / 199.4	499.8 / 80.0 / 23.9	500.0 / 80.2 / 119.5

<sup>a</sup> mg ligand / mg [Ru(COD)(COT)] /  $\mu$ L 1-octene or mg 2-norbornene. Solvent: 50 mL THF (HDA and dppd); 30 mL THF (PVP)

#### Gas phase NMR experiments.

Ru/dppb nanoparticles were introduced in a NMR sample tube closed with a Teflon needle valve, in the absence of any solvent. Then, the tube was filled with 1 bar of gaseous ethylene ( $\text{CH}_2\text{CH}_2$  or  $\text{CD}_2\text{CD}_2$ ). Gas phase  $^1\text{H}$  NMR was then recorded.

The gas phase NMR of the desorption experiments were carried out in a similar way. Ru/PVP nanoparticles were introduced in a NMR sample tube closed with a Teflon needle valve, in the absence of any solvent, and the tube was filled with 1 bar of di- $^{13}\text{C}$  ethylene at room temperature. After one night under  $^{13}\text{CH}_2$   $^{13}\text{CH}_2$  the gas was evacuated. Then, the tube was heated at  $180^\circ\text{C}$  in vacuo overnight and the gas phase NMR was recorded.

#### Solid state NMR experiments.

Ru/PVP or Ru/dppb nanoparticles were introduced in a Fisher-Porter bottle and were pressurized with 1 bar of di- $^{13}\text{C}$  ethylene. The nanoparticles were left overnight under  $^{13}\text{CH}_2$   $^{13}\text{CH}_2$ . Then, the gas was evacuated and the  $^{13}\text{C}$  NMR in the solid state was recorded.

#### Desorption experiments

Ru/PVP nanoparticles were introduced in a Fisher-Porter bottle in absence of any solvent. Then, the Fisher-Porter bottle was filled with 1 bar of di- $^{13}\text{C}$  ethylene at room temperature. After one night under  $^{13}\text{CH}_2$   $^{13}\text{CH}_2$  the gas was evacuated. The Fisher-Porter was heated at  $180^\circ\text{C}$  in vacuo overnight and the mass spectrum was recorded.

## Supplementary Figures

Suppl Figure 1 : Solution ( $d^8$ -THF)  $^{31}\text{P}$  NMR spectrum of Ru/dppb nanoparticles: (a) spectrum of the nanoparticles in solution in the absence of air; (b) same spectrum after addition of a drop of  $\text{H}_2\text{O}_2$  (oxidation of the phosphines and release of partially or fully oxidized phosphine in the solution).

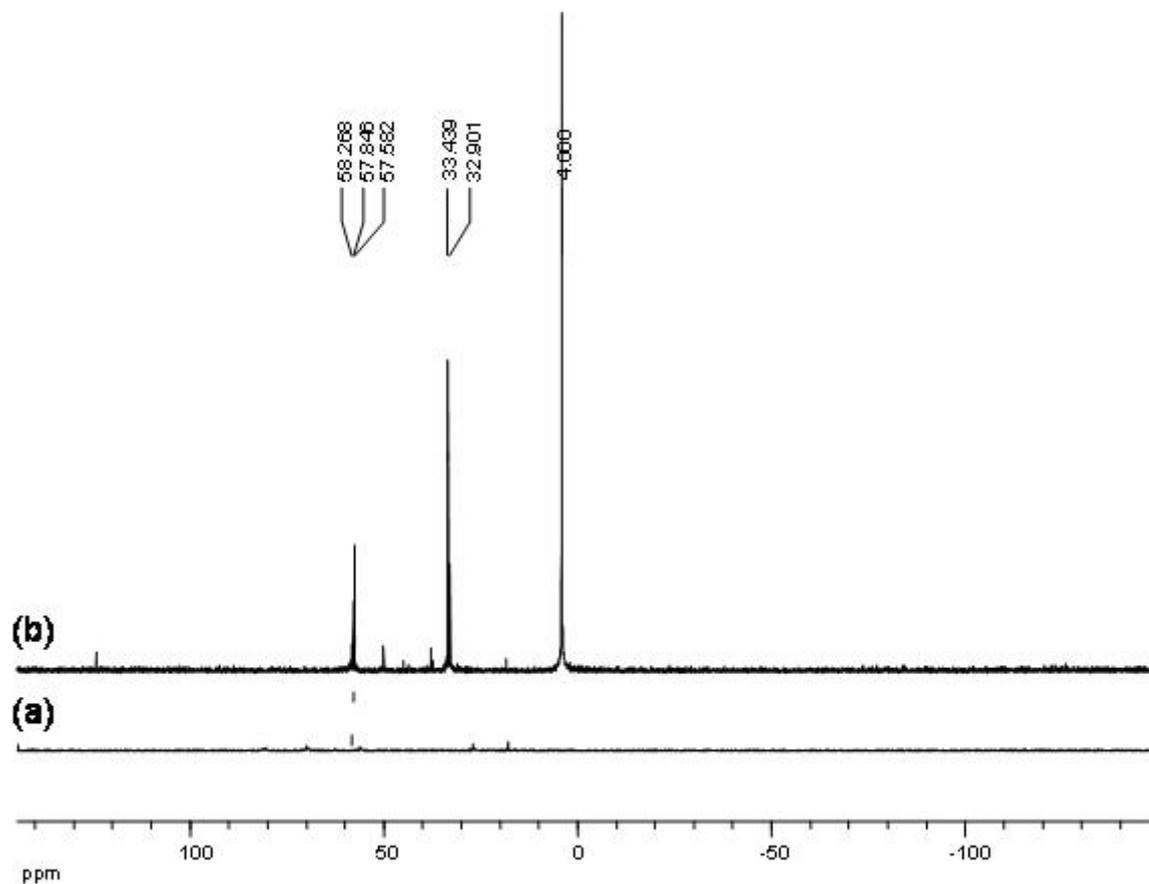
Suppl Figure 2:  $^{31}\text{P}$  MAS NMR spectrum of Ru/dppd nanoparticles.

Suppl Figure 3 : CP  $^{13}\text{C}$  MAS and  $\{^1\text{H}\}^{13}\text{C}$  NMR spectra of the reaction of  $^{13}\text{C}$  ethylene with Ru/dppd nanoparticles.

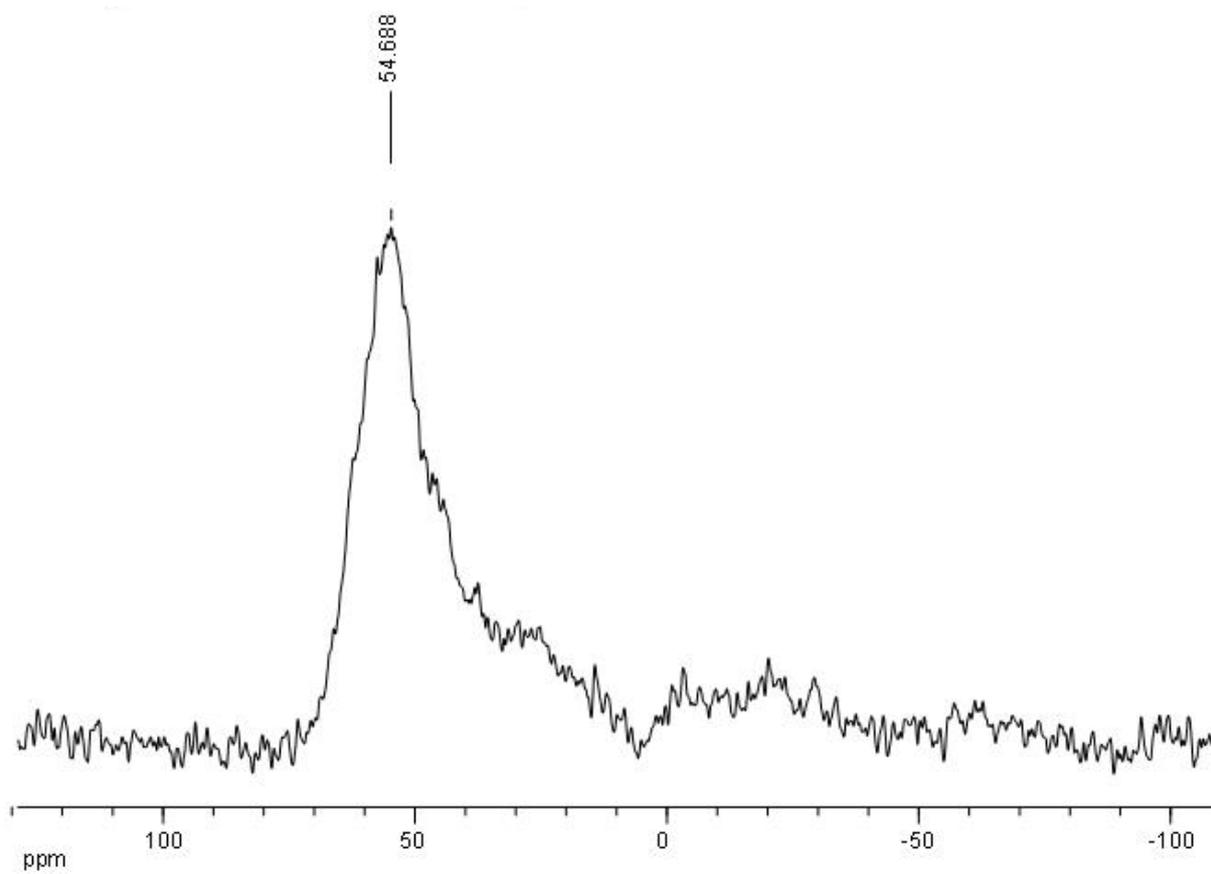
Suppl Figure 4: Gas phase  $^1\text{H}$  and  $^{13}\text{C}$  NMR after the reaction of Ru/PVP with  $^{13}\text{C}$ -ethylene and desorption at  $180^\circ\text{C}$  in vacuo.

Suppl Figure 5: Mass spectra after the desorption experiments a) blank experiment; heating in vacuo of Ru/PVP at  $180^\circ\text{C}$ ; b) reaction of Ru/PVP with ethylene and desorption at  $180^\circ\text{C}$  in vacuo; c) reaction of Ru/PVP with  $^{13}\text{C}$ -ethylene and desorption at  $180^\circ\text{C}$  in vacuo.

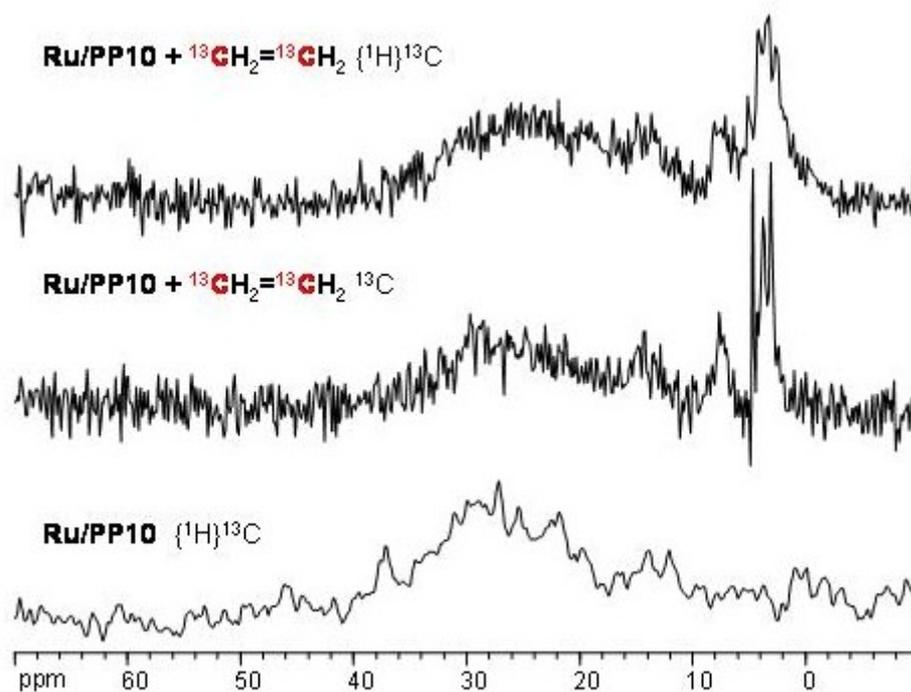
**Suppl Figure 1:** Solution ( $d^8$ -THF)  $^{31}\text{P}$  NMR spectrum of Ru/dppb nanoparticles: (a) spectrum of the nanoparticles in solution in the absence of air; (b) same spectrum after addition of a drop of  $\text{H}_2\text{O}_2$  (oxidation of the phosphines and release of partially or fully oxidized phosphine in the solution).



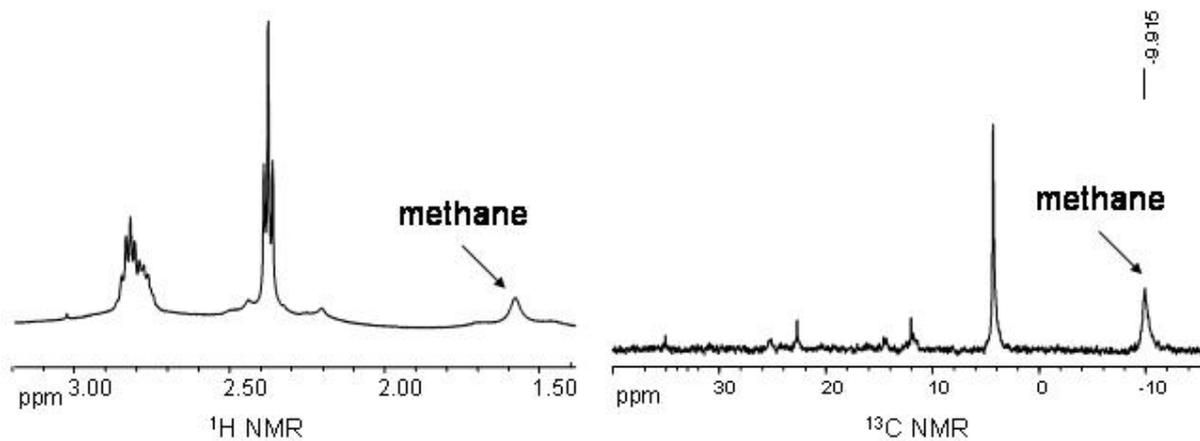
**Suppl Figure 2 :** MAS NMR spectrum of Ru/dppd nanoparticles.



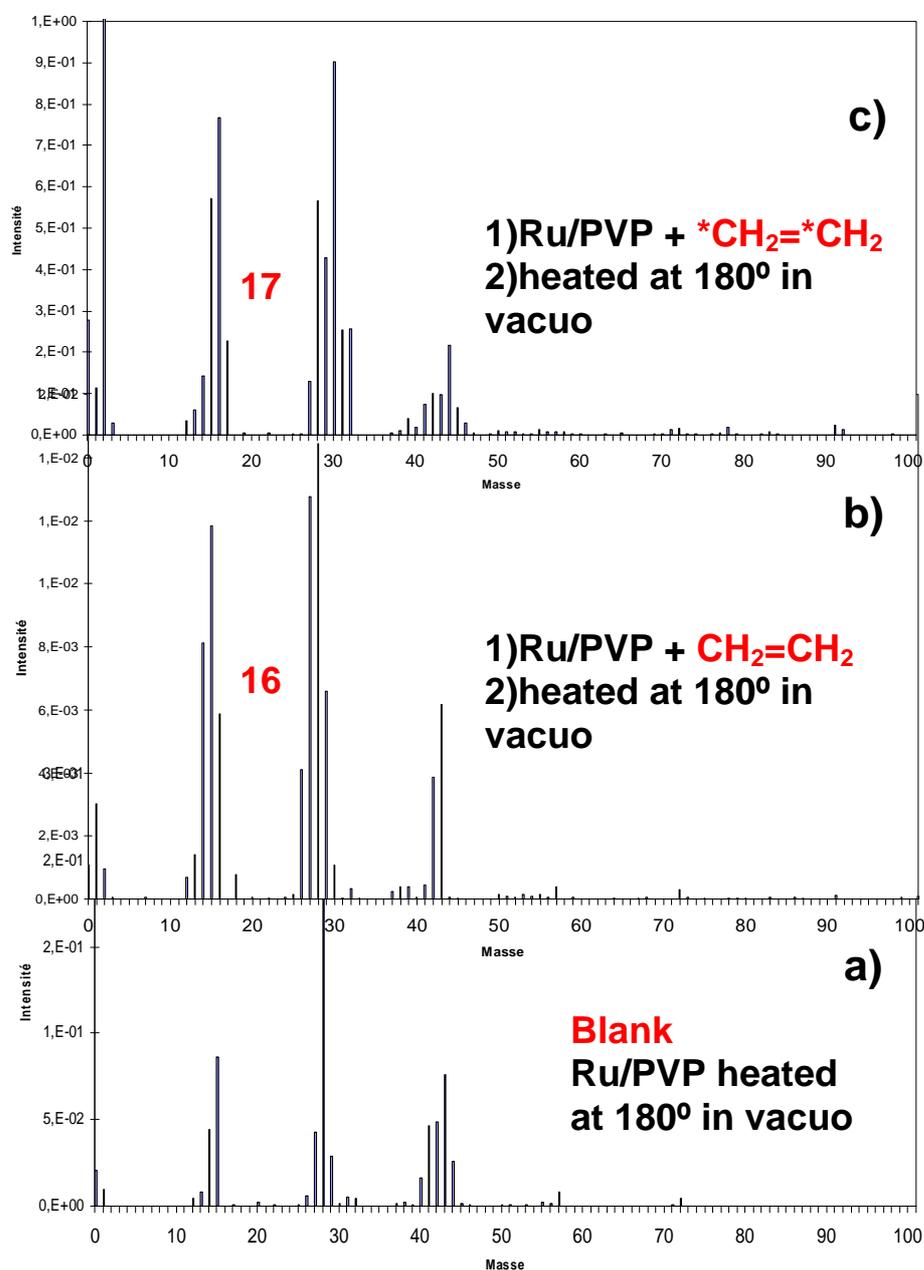
**Suppl Figure 3 :** CP  $^{13}\text{C}$  MAS and  $\{^1\text{H}\}^{13}\text{C}$  NMR spectra of the reaction of  $^{13}\text{C}$  ethylene with Ru/dppd nanoparticles.



**Suppl Figure 4 :** Gas phase  $^1\text{H}$  and  $^{13}\text{C}$  NMR after the reaction of Ru/PVP with  $^{13}\text{C}$ -ethylene and desorption at  $180^\circ\text{C}$  in vacuo.



**Suppl Figure 5 :** Mass spectra after the desorption experiments a) blank experiment; heating in vacuo of Ru/PVP at 180°C; b) reaction of Ru/PVP with ethylene and desorption at 180°C in vacuo; c) reaction of Ru/PVP with  $^{13}\text{C}$ -ethylene and desorption at 180°C in vacuo.



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