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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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Graphical abstract

Ruthenium nanoparticles prepared by hydrogenation of an organometallic precursor accommodate at their surface over one hydride per surface ruthenium together with various ligands such as amines or phosphines as evidenced by gas, liquid and solid state NMR as well as titration by olefins; they react with ethylene at room temperature to give ethane and surface methyl species.
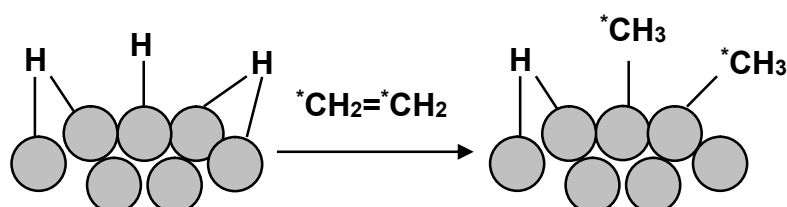
Introduction

Metal nanoparticles have been used for a long time for their ability to catalyse chemical reactions in heterogeneous and in homogeneous phases.[1] Traditional heterogeneous and homogeneous catalysis require very different analytical techniques which are difficult to combine for the study of metal nanoparticles, where it is difficult to distinguish colloidal and molecular catalysis.[2] Thus, many questions concerning their reactivity are still open, in particular the nature of intermediate surface species. Knowledge of the latter is important for the development of new nanocatalysts and new catalytic transformations. Recently, some of us have used solid state NMR for this purpose.[3] Using this method, we have now discovered a new reactivity of ruthenium nanoparticles reported in this communication.

The synthesis of this type of particles has been developed for about ten years by some of us through hydrogenation of organometallic precursors in the presence of organic ancillary ligands such as amines, thiols or carboxylic acids as stabilizing.[4] In particular, using the organometallic precursor [Ru(COD)(COT)] (COD = 1,5-cyclooctadiene; COT = 1,3,5-cyclooctatriene) nearly monodisperse ruthenium nanoparticles of very small size can be obtained which display a remarkable surface coordination chemistry. This system and similar ones involving Pd, Pt or Rh nanoparticles catalyze a number of chemical reactions such as olefins hydrogenation, C-C coupling reactions, or aromatic hydrocarbons hydrogenation.[5] The former two reactions are also catalyzed in homogeneous phases by molecular complexes.

Some of us have shown independently that palladium nanoparticles stabilized by asymmetric phosphite groups were good enantioselective catalysts for an alkylation reaction.[6] This result is a strong evidence for the direct coordination of the phosphite groups on the palladium surface which could however not be confirmed by spectroscopic methods.

Thus, an important element controlling the properties of nanoparticles is the way how ligands are attached to surface metal atoms. The most studied ligand which can be coordinated to clean metal surfaces as well as to nanoparticles in solution is CO.[7] Using NMR techniques, we have provided evidence for the coordination of the stabilizing ancillary amines at the surface of ruthenium particles as well as their dynamic behaviour in solution.[8] In a similar way, also the grafting of organosilanes[9] fragments was studied.

Especially important is the coordination of hydrogen to metal nanoparticles. Hydrogen binding to clean metal surfaces has been well established by surface science and is one of the major issues in heterogeneous catalysis. It is generally admitted that one H is adsorbed per surface metal atom.[10] Recently, using a combination of ^{1}H NMR gas phase and ^{2}H solid state NMR some of us have demonstrated the presence of mobile hydrides on the surface of amine protected ruthenium nanoparticles[3] which are in slow exchange with gaseous dihydrogen. However, during a catalytic process other species like alkenes or arenes may adsorb on the surface or give rise to new reactive intermediates, e.g. alkyl groups, carbenes, etc… The question then arises is to know whether, like on organometallic complexes, these groups are stable and can be detected spectroscopically.

We describe in this communication (*i*) the synthesis of a new class of phosphine protected ruthenium nanoparticles, (*ii*) the characterization of phosphine coordination by NMR techniques, (*iii*) the presence and the quantification of hydrides on the surface of ruthenium nanoparticles stabilized by a polymer (PVP), diphosphines (dppb; dppd) or amines (HDA) and (*iv*) finally our exploration of the reactivity of these nanoparticles by NMR which led to the discovery of a novel and unexpected reaction.

The ruthenium nanoparticles were prepared as previously described by hydrogenation of the organometallic precursor [Ru(COD)(COT)] in THF at room temperature. The new particles stabilized by the diphosphines dppb (bis(diphenylphosphino)butane) and dppd (bis(diphenylphosphino)decane) were synthesized in the same way upon adding 0.1 molar equivalent of diphosphine per introduced ruthenium. The nanoparticles could be isolated upon addition of pentane and redissolved in THF for solution NMR studies. They display a mean size of respectively 1.5 (±0.3) nm (dppb) and 1.9 (±0.5) nm (dppd) (Figure 1) as well as the hcp structure of bulk ruthenium as demonstrated by WAXS studies.

Coordination of the phosphine groups was assessed by NMR spectroscopy. In solution in d^8-THF no signal is visible in the ^{31}P NMR spectrum of Ru/dppb nanoparticles. However, addition of drops of H_2O_2 leads to the immediate appearance of new peaks near 4, 33 and 58 ppm which were attributed respectively to a non oxidized diphenyl-phosphino moiety, and to phenyl and alkyl phosphine oxide moieties (see Suppl Figure 1). This experiment demonstrates first the coordination of the phosphine groups to the nanoparticles and their

release after oxidation and secondly, the absence of both free phosphine and exchange processes at the NMR time-scale in the initial solution. In addition, this experiment evidences the hydrogenation of some phenyl groups during the synthesis process. The absence of NMR signals in solution for the nuclei coordinated to a nanoparticle has previously been observed and discussed and may result from several factors including Knight shift, fast T_2 relaxation resulting from the slow tumbling of the particles in solution and surface anisotropy.[11] In order to distinguish between these factors, the nanoparticles were characterized by CP-MAS solid state NMR. The ^{13}C MAS NMR spectra of Ru/dppb and Ru/dppd exhibit respectively peaks corresponding to alkyl carbons at 26 ppm and aromatic carbons at 130 ppm for Ru/dppb and only signals characteristics of alkyl carbons near 30 ppm for Ru/dppd. Accordingly, the ^{31}P MAS NMR spectrum of Ru/dppb shows two broad signals near 50 and 25 ppm, while that of Ru/dppd exhibits an intense broad signal at 55 ppm with a shoulder near 30 ppm (Suppl Figure 2), in agreement with the coordination of respectively dialkyl- and diphenyl-phosphino groups at the surface of the particles. From this study, it results that: i) the absence of signal in solution cannot be attributed to a magnetic effect, the ruthenium nanoparticles of such small sizes appear perfectly diamagnetic; ii) the lack of homogeneity of the surface causes an important broadening of the signals but does not prevent their observation: the absence of signal in solution is therefore clearly due to a relaxation problem, as previously observed by ^{13}C NMR on the alkyl chains of thiol stabilized gold nanoparticles.[11]

As mentioned above, the presence of hydrides on the surface of Ru nanoparticles stabilized by hexadecylamine has previously been established by a combination of methods, namely ^{1}H solution, ^{1}H gas phase and ^{2}H static solid state NMR.[3] Using these methods we could also detect mobile hydrogens on ruthenium nanoparticles stabilized by PVP or by diphosphine ligands.[12] However, only a qualitative indication about the adsorption of hydrogen onto the Ru nanoparticles surface could be obtained by this way, while quantitative information would shed some light on the real Ru nanoparticles surface coverage. Since ruthenium nanoparticles are very active hydrogenation catalysts, we set out a titration of the surface hydrides by olefins involving a measure of alkane formation by GC analysis according to the following equation:

$$R^1HC=CHR^2 + [Ru_xH_y] \rightarrow R^1H_2C\text{-}CH_2R^2 + [``Ru"]$$

Two olefins of different structures, namely 1-octene and norbornene, and two different concentrations of each olefin (1 eq. and 5 eq. per total Ru present in the particles) were used in order to avoid artefacts. Three different nanoparticle systems were tested, namely Ru/HDA previously shown to contain hydrides,[3] Ru/PVP and Ru/dppd, namely particles in a polymer displaying limited interactions and particles firmly attached to phosphine ligands. 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 (Table). 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.

In order to determine spectroscopically the fate of the ruthenium nanoparticles ("Ru") after the hydrogenation process and the nature of the adsorbed species on their surfaces, we performed the following experiments. In a way similar to that described previously for the Vaska complex[13] we let gaseous ethylene react with solid Ru/dppb nanoparticles in a NMR

sample tube closed with a Teflon needle valve, in the absence of any solvent. By ^{1}H gas phase NMR we observed the presence both of gaseous ethylene and of ethane. When we performed the reaction using tetradeutero-ethylene, a mixture of respectively d1-d3 ethylene and d1-d5 ethane was observed. In the next step, we studied the resulting ruthenium nanoparticles by solid state ^{2}H NMR under the condition of slow magic angle spinning (3.0 kHz). Figure 2a depicts a spectrum obtained at room temperature which was simulated as shown in Figure 2b using the SIMPSON programme.[14] The envelope of the spinning sideband pattern indicates the presence of three spectral components. The major component is a relatively narrow side band spectrum with a quadrupole coupling constant q_{cc} of about 50-55 kHz. This value is characteristic for the presence of methyl groups exhibiting fast 3-fold 120° jumps. The latter reduce the intrinsic q_{cc} of 167 kHz to the observed value.[15] The rotation axis itself may be subject to a slow rotational diffusion or shortly "reorientation" in the second to millisecond timescale. We assign this spectral component to "surface methyl groups" bound to the nanoparticles. The second broad component exhibiting a lower intensity is characterized by a large quadrupole coupling constant of 160-170 kHz. We assign this component to immobilized –CD groups in PVP, formed by H/D exchange with surface deuterons prior to the reaction with ethylene, as described previously for other ligands.[3] Finally, we observe a sharp component in the signal center indicating the presence of fast reorientating deuterons. Candidates for this line are mobile surface deuterons[3] or mobile deuterated ethane in the particles.

In order to corroborate the presence of the postulated surface methyl groups by ^{13}C MAS NMR we let Ru/PVP and Ru/dppd particles react with gaseous di-^{13}C ethylene. In order to avoid signal intensity problems arising from cross polarization all ^{13}C magnetization was created directly by 90° pulses. Figure 3a depicts a spectrum of Ru/PVP obtained using ^{1}H decoupling prior to the reaction. Only signals of PVP are observed which were not further analyzed. By contrast, after addition of di-^{13}C ethylene two new narrow signals are observed at 3 and 7 ppm (Figure 3b).

These signals were further characterized in an experiment without ^{1}H decoupling (Figure 3c). We observe that the minor signal at 3 ppm is split into a quartet exhibiting a CH-coupling constant of $J_{C-H} \cong 120$ Hz. We also note that the signal is not present in the corresponding CP MAS NMR spectrum. These NMR parameters are typical for a methyl group exhibiting both fast 120° jumps as well as a fast rotational diffusion. Thus, this signal contributes to the sharp center line in the ^{2}H NMR spectrum. This behavior is expected for mobile ethane in the nanoparticles. By contrast, no CH coupling can be resolved for the broader signal at 7 ppm.

Its chemical shift also indicates a methyl group created by ethylene. The signal line width does not allow for an unresolved ^{1}H-^{13}C coupling larger than 75 Hz. We assign this signal to the same species giving rise to the major signal component in the ^{2}H MAS NMR spectrum. As the dipolar CH-coupling is reduced by the 120° jumps, and as the ^{13}C chemical shift anisotropy of methyl groups is only about 20 ppm,[16] both interactions are averaged out by MAS, which should lead to only one or two weak rotational sidebands. We could not detect the latter, but they might be lost in the noise because of rotational diffusion which also contributes to the remaining center band.

In other words, we assign the signal at 7 ppm to surface methyl groups which might be subject to slow jumps from one Ru to another. The observation that the CH-coupling constant must be much smaller than for a organic methyl group corresponds to the usual observation for molecular agostic complexes.[17]

In order to identify the nature of the surface species containing these methyl groups, desorption experiments were carried out on the Ru/PVP system, the less likely to generate artefacts. Only at 180°C in vacuo did we observe a desorption which rules out the presence of an adsorbed gas such as ethane. Gas phase ^{13}C NMR allowed the detection of a species showing a resonance at -9.9 ppm correlated with a broad singlet at 1.6 ppm in ^{1}H NMR and clearly corresponding to methane (see Suppl Figure 4).[18] Other signals for C2 and higher hydrocarbons were also observed. The gas mixture was also analysed by mass spectrometry. After comparing with a blank experiment carried out on the same nanoparticles but not treated with ethylene or ^{13}C-ethylene (Suppl Figure 5 a)), we found predominantly the presence of methane (m/e16 and m/e17 when using labelled ethylene) and ethane (m/e 30, respectively 32) as well as traces of higher hydrocarbons (Suppl Figure 5 b) and c)).

The most likely hypothesis to explain the presence of methyl groups at the surface of the ruthenium particles was initially to consider the isomerisation of ethylene into surface vinylidene fragments of the type Ru≡^{13}C-^{13}CH$_3$.[19] However, no signal was observed around 45 ppm as expected for the methyl group in this fragment.[20] Furthermore, we did not succeed to find the corresponding signal of the carbon bound to Ru which was fully enriched with ^{13}C, whereas, as illustrated on Suppl Figure 2, a corresponding phosphine group linked to the surface is visible by MAS ^{31}P NMR. Furthermore, the chemical shift of the methyl groups and the desorption experiments, showing unambiguously by gas phase NMR and mass spectroscopy the presence of methane and ethane, all agree with the presence of methyl ligands on the ruthenium surface This implies an activation of a C-C bond in very mild

conditions in the three types of nanoparticles studied, namely Ru/PVP, Ru/HDA and Ru/dppd. The reaction mechanism is so far unknown but a reasonable pathway would involve insertion of ethylene into a remaining surface hydride to give a surface ethyl species followed by β-alkyl transfer on the surface as illustrated on the scheme. The following step could be rehydrogenation of the surface methylene moiety by remaining surface hydrogens.

The direct and facile observation of these methyl groups by NMR was totally unexpected but the characterization of surface methyl ligands after a hydrogenation process has previously been published. Interestingly the work aimed at characterizing the deactivation process of an industrial heterogeneous palladium hydrogenation catalyst and correlates well with our observation of the stability of these surface bound methyl groups.[21]

In summary, we report in this communication the characterization of phosphine coordination by NMR which has no real precedent and the presence and stability of hydrides on different types of Ru nanoparticles. In each case do we find a ratio hydride/surface Ru larger than 1. In addition, we clearly demonstrate the presence of surface methyl groups by a combination of NMR and desorption methods. The presence of these groups arises from a facile carbon-carbon bond cleavage at room temperature which may be an important reaction during hydrogenation processes. The reactivity of these novel methyl groups must now be explored.

Captions to Scheme and Figures :

Table: Conversion of olefins into alkanes with the different Ru nanoparticles systems.

Figure 1: TEM images of Ru nanoparticles stabilized by dppb (A) and dppd (B).

Figure 2 : (a) ^{2}H-MAS Spectrum of Ru/dppb nanoparticles after reaction with $D_2C=CD_2$; (b) SIMPSON simulation of the spectrum employing a mobile –CD3 group (Qcc=55kHz), an immobile -CD group (Qcc=173kHz) and two liquid like Lorentzian lines in the center.

Figure 3: a) $^{13}C\{^1H\}$ MAS NMR spectrum of Ru/PVP; b) $^{13}C\{^1H\}$ MAS NMR spectrum of Ru/PVP + ^{13}C ethylene; c) ^{13}C MAS NMR spectrum of Ru/PVP + ^{13}C ethylene.

Supplementary Figures:

Suppl Figure 1 : Solution (d^8-THF) ^{31}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 H_2O_2 (oxidation of the phosphines and release of partially or fully oxidized phosphine in the solution).

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

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

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

Table

Reaction time		2 hours		18 hours		24 hours		Olefin
[olefin]/initial [Ru] ratio		1 eq.	5 eq.	1 eq.	5 eq.	1 eq.	5 eq.	
NPs systems	Ru/PVP	0.47	0.49	0.50	0.50	0.51	0.49	1-octene
	Ru/HDA	0.29	0.29	0.34	0.34	0.33	0.35	
	Ru/dppd	0.24	0.31	0.26	0.32	0.27	0.31	
	Ru/PVP	0.44	0.42	0.49	0.47	0.50	0.48	norbornene
	Ru/HDA	0.26	0.32	0.30	0.32	0.30	0.32	
	Ru/dppd	0.21	0.32	0.26	0.30	0.26	0.31	

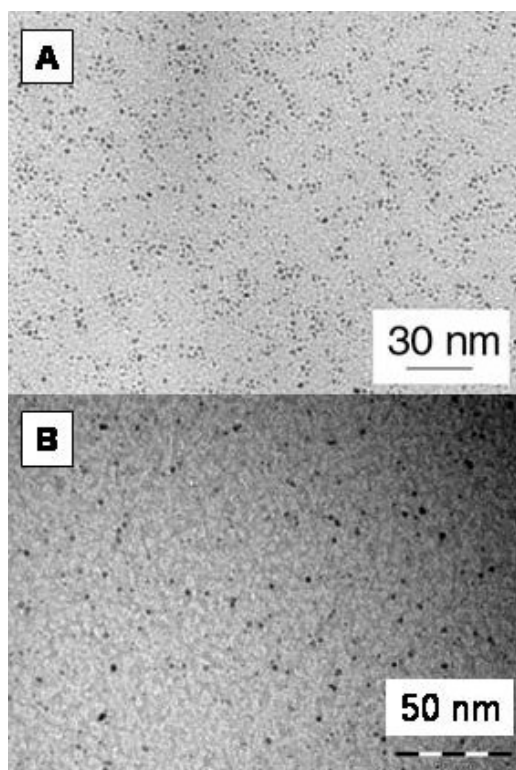**Figure 1 :** Figure 1: TEM images of Ru nanoparticles stabilized by dppb (A) and dppd (B).

Figure 2 : (a) ^{2}H-MAS Spectrum of Ru/dppb nanoparticles after reaction with $D_2C=CD_2$; (b) SIMPSON simulation of the spectrum employing a mobile –CD3 group (Qcc=55kHz), an immobile -CD group (Qcc=173kHz) and two liquid like Lorentzian lines in the center.

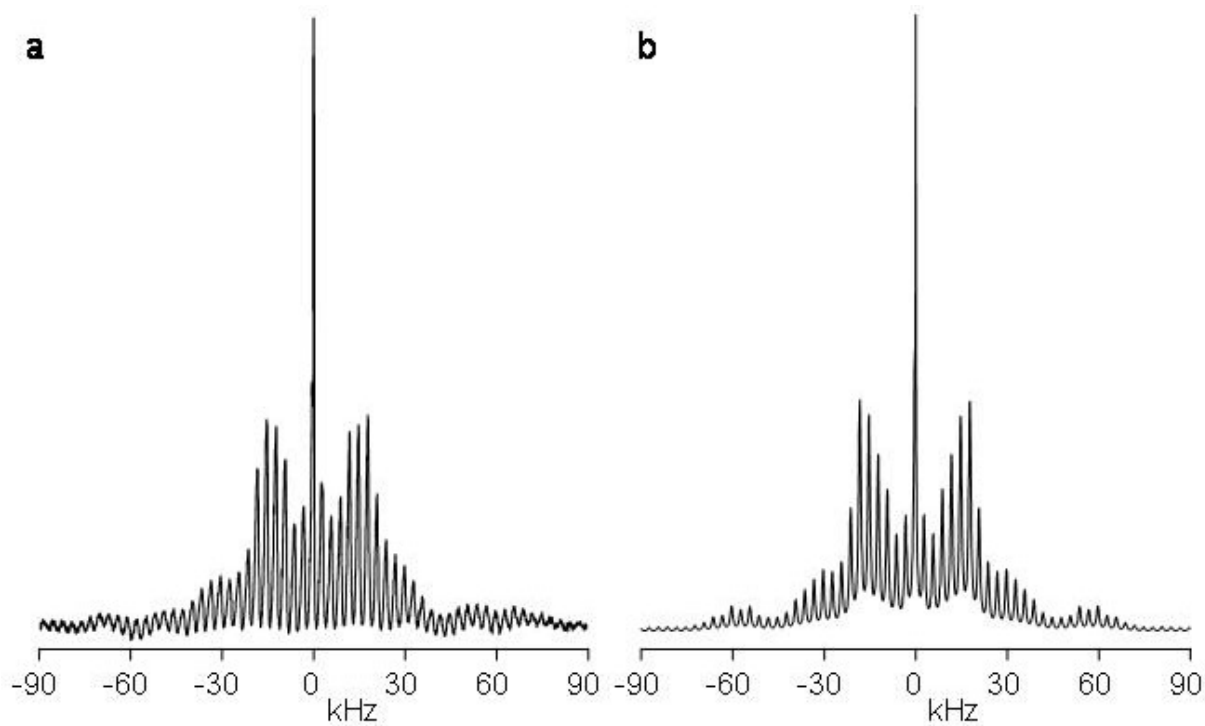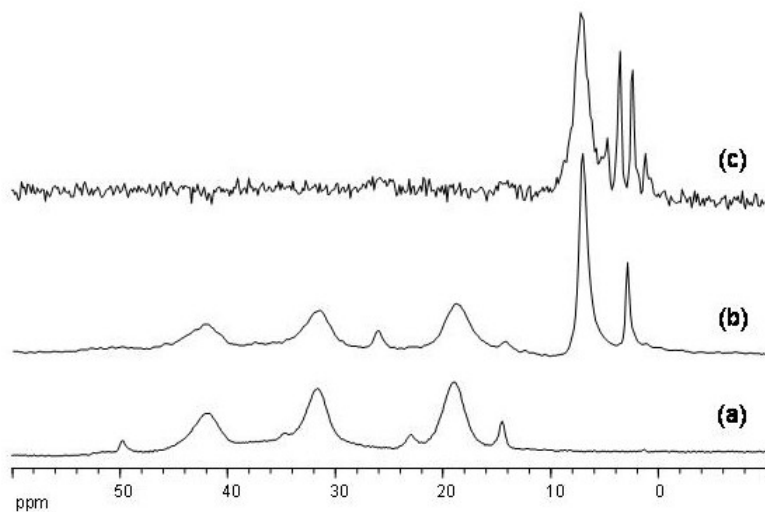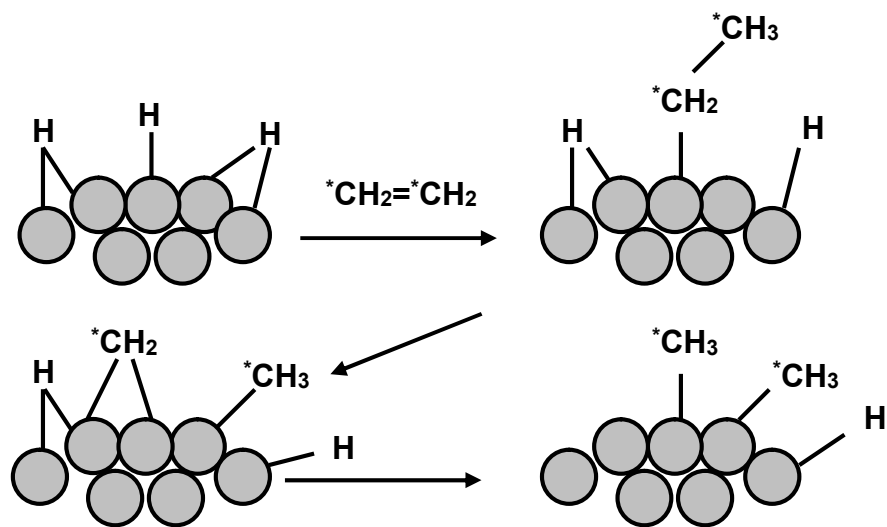**Figure 3 :** a) $^{13}C\{^1H\}$ MAS NMR spectrum of Ru/PVP; b) $^{13}C\{^1H\}$ MAS NMR spectrum of Ru/PVP + ^{13}C ethylene; c) ^{13}C MAS NMR spectrum of Ru/PVP + ^{13}C ethylene.

Scheme

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