Direct NMR Evidence for the Presence of Mobile Surface Hydrides on Ruthenium Nanoparticles

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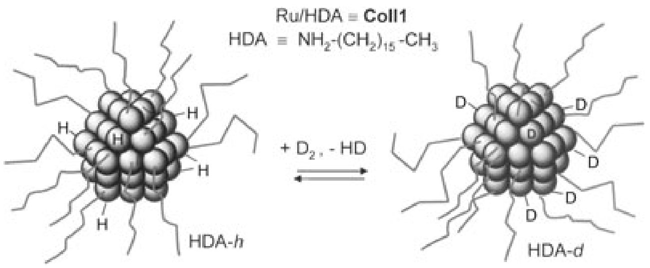

Scheme 1. *Ruthenium nanoparticles showing hydrogen–deuterium exchange between surface and ligand sites.*

Metal colloids consist of an inner core of metal atoms stabilised by surface ligands such as aliphatic alcohols, amines or thiols.[1] The particles may catalyse interesting organic transformations, including asymmetric hydrogenation and C–C coupling reactions.[2,3] The mode of coordination and the strength of binding of ancillary organic surface ligands has been studied by infrared (IR) and liquid-state NMR spectroscopy.[4,5] However, little is known about ligands such as hydrogen or hydride species which constitute active partners of the catalytic behaviour of metal nanoparticles.

In the past, the interaction of hydrogen with defined metal surfaces such as ruthenium has been studied using established methods of surface science.[6] However, although these methods provide the best possible information concerning the type of binding of H atoms to the metal, they are difficult to apply to nanoparticles. If the latter are charged and paramagnetic, electron paramagnetic resonance (EPR) methods are useful if hyperfine interactions between the unpaired electrons and surface hydrogen species can be observed as shown recently for Pt clusters in zeolites.[7]

Herein, we use a combination of various NMR methods, in particular solid-state ^{2}H NMR spectroscopy, for a better understanding of the interactions of hydrogen with ruthenium nanoparticles. This method has been proven to be useful in the study of the motions of hydrogen in the coordination sphere of transition metal complexes.[8] The reactivity of the hydrogen detected on the nanoparticles is demonstrated by the finding of hydrogen–deuterium exchange between surface and ligand sites (Scheme 1).

The Ru nanoparticles studied are stabilised by hexadecylamine (HDA) as a protecting ligand (**Coll-1**); they were prepared and characterised as reported previously.[5,9] The ^{1}H NMR spectra of **Coll-1** in [D$_8$]THF, recorded directly after sample preparation,[10] suggested the presence of hydrogen in this material[5e] because a signal at 4.6 ppm was detected, corresponding to dissolved H$_2$ released by the nanoparticles. A direct detection of hydrogen bound to ruthenium failed, probably because of line broadening due to slow tumbling of the nanoparticles in solution.

In the first part of this study we, therefore, tried to detect the assumed Ru–H species directly by high-resolution ^{1}H magic-angle spinning (MAS) NMR spectroscopy of the solid particles in the absence of solvents. Unfortunately, only the signals of the ligand could be observed, which were also characterised by ^{13}C cross-polarisation (CP) MAS NMR spectroscopy.[10] However, an indirect detection was obtained. **Coll-1** was introduced into an empty NMR tube equipped with a teflon needle valve and evacuated at 10^{-6} bar for two days at 298 K. After this procedure the valve was closed and a gas-phase ^{1}H NMR spectrum was recorded. Only a signal at 0.77 ppm was observed which corresponds to gaseous water outside the tube (Figure 1 a). This signal could be removed by flushing the probe with gaseous nitrogen;[11] however, we preferred to keep this signal as an external intensity standard. No signal arising from thermally desorbed H$_2$ could be observed by ^{1}H NMR spectroscopy, even after heating additionally the sample outside the spectrometer to 360 K for one day.

However, when the NMR tube was filled with D$_2$ gas (800 mbar, room temperature), a new gas-phase peak appeared at 4.5 ppm, typical for gaseous H$_2$ and HD. The signal intensity increased with time and remained constant after three h (Figures 1 b–1 d). The peak exhibited a linewidth of 230 Hz. In order to distinguish between H$_2$ and HD, two separately sealed 800-mbar samples of both gases were prepared and their gas-phase ^{1}H NMR spectra measured at room temperature. A line width of 1200 Hz was found for H$_2$ and of 200 Hz for HD. This difference is in agreement with previous findings.[12] Thus, we assign the major part of the new peak to HD, where the H atom in HD has to come from **Coll-1**. In other words, D$_2$ is activated by the nanoparticle and recombination with bound H atoms leads to desorption as HD as indicated in Scheme 1, and hence to a deuteration of **Coll-1**. In the following, we label the sample deuterated in this way as **Coll-2**.

In order to prove the deuteration process, we recorded a broad band 46.1 MHz ^{2}H NMR spectrum of **Coll-2** (Figure 2 a). Indeed, a strong signal for the deuterons introduced was ob-

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Supporting information for this article is available on the WWW under http://www.chemphyschem.org or from the author.

DOI: 10.1002/cphc.200400621

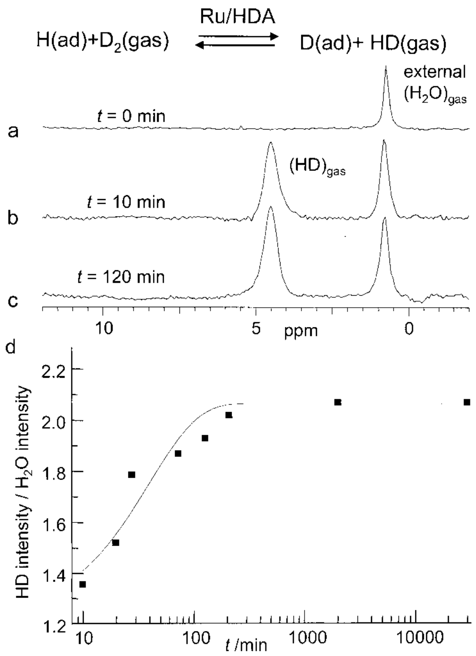

Figure 1. *Gas-phase 500 MHz ^{1}H NMR spectra showing the production of HD from the reaction of Ru/HDA nanoparticles (**Coll-1**) containing adsorbed H atoms with gaseous D_2 in a glass-sealed NMR tube. a) Evacuated NMR tube above the solid. The peak at 0.77 ppm arises from gaseous water outside the NMR tube. b) After exposure to D_2 during 10 minutes. c) After exposure to D_2 during 120 minutes. d) Semi-logarithmic plot of the evolution of the HD concentration as a function of time. The solid line corresponds to an exponential time dependence.*

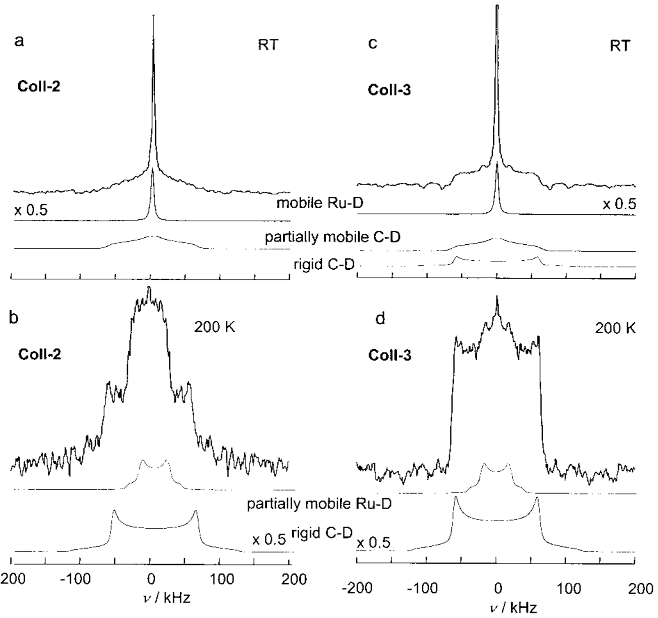

Figure 2. *Solid-state 45.7 MHz ^{2}H NMR spectra of static samples of Ru/HDA particles after H–D exchange performed in the solid state (**Coll-2**) and in solution (**Coll-3**). The experimental spectra correspond to the sum of the corresponding subspectra, calculated as described previously.[8a,b] Here, Q_{CC} is the quadrupole coupling constant, and $Q_{ZZ}=3/4\,Q_{CC}$, and the $\eta=[Q_{YY}-Q_{XX}]/Q_{ZZ}$ the asymmetry parameter. a) Spectrum of **Coll-2** at room temperature (RT) with the following parameters: mobile Ru–D: $Q_{zz}<1$ kHz, partially mobile CD: $Q_{zz}=68$ kHz, $\eta=0.86$. b) spectrum of **Coll-2** at 200 K with the following parameters; partially mobile Ru–D: $Q_{zz}=50$ kHz, $\eta=0.3$; rigid CD: $Q_{zz}=120$ kHz, $\eta=0.02$. c) Spectrum of **Coll-3** at room temperature with the following parameters; mobile Ru–D: $Q_{zz}<1$ kHz, rigid CD: $Q_{zz}=120$ kHz, $\eta=0.02$; partially mobile CD: $Q_{zz}=68$ kHz, $\eta=0.86$. d) Spectrum of **Coll-3** at 200 K with the following parameters; partially mobile Ru–D: $Q_{zz}=50$ kHz, $\eta=0.3$; partially mobile Ru–D: $Q_{zz}=50$ kHz, $\eta=0.3$.*

served. We observed a centre line exhibiting a linewidth of about 500 Hz as well as a broad component. The corresponding subspectra of the two components calculated using known procedures[13] are included in Figure 2a. Under MAS conditions, the width of the centre line which appears at 1.6 ppm is reduced to 120 Hz.[10] By contrast, the linewidth ($\approx$120 Hz) of the signal of gaseous D_2 at 4.6 ppm, filled in a sealed glass insert ($\approx$500 mbar), embedded in a MAS rotor did not depend on the spinning rate as expected. In the spectrum recorded at 200 K (Figure 2b), both signal components are transformed into typical Pake lineshapes as illustrated by the subspectra. The narrow centre signal exhibits now a quadrupole coupling constant of $Q_{CC}=63$ kHz. This value is comparable with those of Ru–D binding in molecular complexes.[8] Therefore, we assign the centre line in Figure 2a to mobile deuterons bound to Ru, subject to an isotropic reorientation. The broad component exhibits now a value of 160 kHz, typical for immobilised (*rigid*) C–D groups,[14] but too small for rigid N–D groups.[15] We therefore assign the broad signal component to deuterons which have been incorporated into the aliphatic chains of the HDA ligand. Now, we were able to understand their room-temperature line shape contributions (Figure 2a): they are typical for a superposition of C–D groups exhibiting a different flexibility, that is, local order parameter of their fast anisotropic reorientation. As such a line shape depends on many parameters, it was approximated by an effective reduced Pake pattern as indicated in Figure 2a.

In order to know whether it is possible to manipulate the ratio of the two deuteron environments, we prepared a third sample (**Coll-3**) where gaseous D_2 was introduced in solution directly after the synthesis of the nanoparticles in THF. Again, strong deuteron signals consisting again of Ru–D and C–D components were found, as depicted in Figures 2c and 2d. The main difference to **Coll-2** is the much larger amount of the C–D compared to the Ru–D signal component. Moreover, even at room temperature, a small component of *rigid* C–D component is now observed. The incorporation of D into the HDA ligand was further corroborated by liquid-state ^{2}H NMR spectroscopy of **Coll-3** in THF, although at this stage we were not yet able to determine whether the ligand deuteration is uniform or whether specific sites are preferentially deuterated.

Therefore, the spectra of Figure 2 provide the first detection of reactive D atoms bound to metal nanoparticles, although it is difficult to derive at present further information about the binding sites and the type of bonding between D and Ru atoms from the observed value of $Q_{CC}=63$ kHz. Q_{CC} values reflect the size of the local electric field gradients, but may be reduced by local anisotropic motions, in particular at higher temperatures. For a Ru-η-D_2 complex we have recently measured a value of 107 kHz at low temperatures.[8b] By ^{2}H NMR relaxation measurements of deuterated transition metal complexes in solution, effective *Q*cc values between 15 and 155 kHz have been obtained, where the smaller values probably arise again from local motions.[16] By contrast, the HD molecule exhibits an intrinsic value of 227 kHz.[17] In order to characterise further the Ru–D bonding situation in nanoparticles and to determine whether the value of 63 kHz for the Ru–D component corresponds to the rigid limit, we plan additional ^{2}H NMR measurements of model complexes at different temperatures.

Independent of the outcome of these experiments, one can estimate that the nanoparticles contain several hundred metal atoms, where about one half are located in the surface shell. Therefore, it is tempting to assign the observed signals to Ru–D species occupying surface sites (Scheme 1). However, hydrogen may also be bound to inner Ru atoms. In this context we note an interesting result of Christmann and co-workers[6a] who found evidence that dihydrogen does not dissolve into Ru metal at usual pressures and temperatures. More recently, it was shown that dihydrogen dissociates on Ru surfaces and binds as single atom to three surface Ru atoms. In any case, we think that the surface D species observed here are bound as atoms to one or more Ru atoms and are rapidly jumping from one site to another. Recent calculations by Honkala and Nørskov indeed suggest a low diffusion barrier for surface hydrides.[18] The observed isotropic reorientation of the Ru–D component at room temperature is then compatible with a diffusion of D atoms in the curved surface of the Ru nanoparticles. The binding to the surface also explains why it is not possible to remove hydrogen from the surface by vacuum treatment, but only to carry out H–D exchange with deuterium gas.

Our experiments demonstrate therefore that the organometallic synthetic method used leads to Ru nanoparticles where a coordinated ancillary ligand, in the present case a long chain amine, coexist with mobile and reactive H or D ligands. These surface species are also able to perform H–D exchange reactions with the alkyl chain of HDA. We think that this process takes place through a classical oxidative addition/reductive elimination process. At present, the spectra of Figure 2a indicate that only mobile CD groups can react in this way, whose number is much smaller in the solid as compared to the liquid state. This explains why the deuterium fraction in the aliphatic sites is larger for the particles deuterated in solution as compared to those resulting from gas–solid deuteration.

In conclusion, we describe herein the first direct NMR evidence for the presence of mobile and reactive hydride ligands coordinated to a metal nanoparticle, in the present case, ruthenium. Our investigations extend previous work evidencing the coordination of ancillary ligands such as amines or thiols to nanoparticles and gives a view of these nano-objects as very large organometallic species displaying a rich surface reactivity.

Acknowledgements

The authors thank the DFG-CNRS foundations for funding and Prof. Nørskov and Dr. Honkala for interesting discussions. H.H.L. thanks the Fonds der Chemischen Industrie, Frankfurt, for financial support.

Keywords: C–H activation · hydrogen · nanoparticles · NMR spectroscopy · ruthenium

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[10] see Supporting Information.

[11] Values of about 0.8 ppm are typical for mixtures of water clusters where the monomer dominates. This value is also observed for the gas phase above liquid water.

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Received: December 14, 2004