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Supporting Information

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

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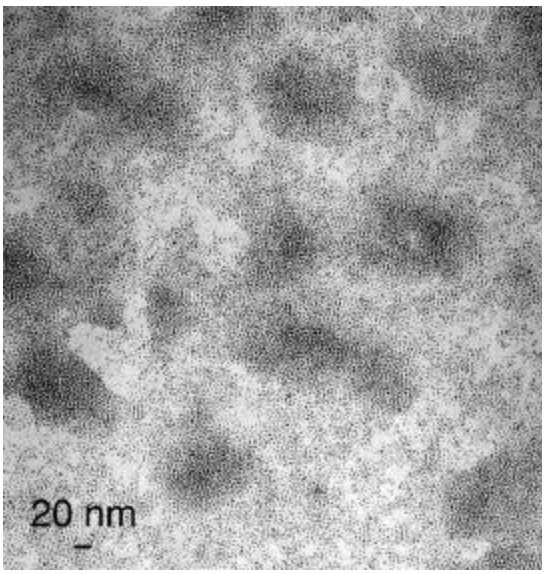
Synthesis and characterization of colloidal Ru-HDA nanoparticles

The nanoparticles for this study were prepared as previously reported through hydrogenation of $Ru(C_8H_{10})(C_8H_{12})$ under 3 bars H_2, at room temperature in THF in the presence of 0.2 eq./Ru of hexadecylamine (HDA) and characterized by TEM and WAXS as previously described (Figure S1). The brown colloidal powder thus obtained (**Coll-1**) could be used for solid state NMR experiments or could be redissolved in d^8-THF for solution studies.

A second sample (**Coll-2**) was prepared by exposure of solid **Coll-1** to gaseous D_2 (800 mbar, room temperature) for 1 day. A third sample (**Coll-3**) was prepared by treatment of **Coll-1** in THF under D_2.

Detection of H_2 removed from the particles by liquid State NMR

The ^1H solution NMR spectrum of **Coll-1** (d^8-THF) shows upon leaving the tube in the NMR apparatus for a few minutes, a new peak at 4.6 ppm exhibiting a longitudinal relaxation time of T_1 = 2.1 s, typical for free dissolved H_2 (Figure S2). This peak reached rapidly a maximum value, disappeared when the NMR tube was opened and appeared again when H_2 was bubbled into the NMR tube. The experiment was reproducible and suggests a partial desorption of H_2 from the ruthenium surface.



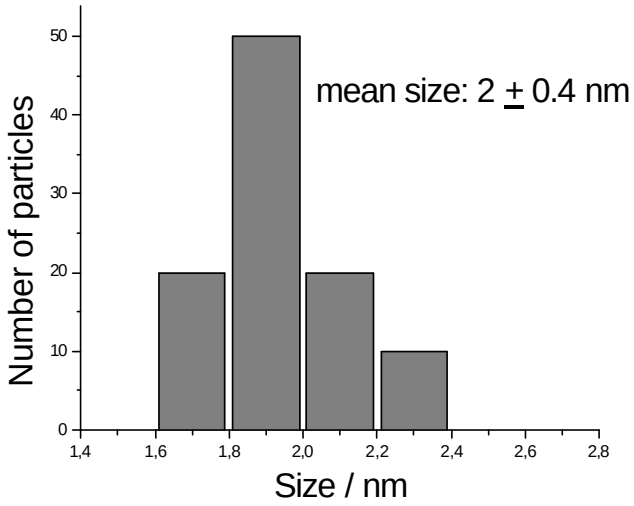


Figure S1 TEM micrograph and size histogram of Ru/HDA nanoparticles (**Coll-1**)

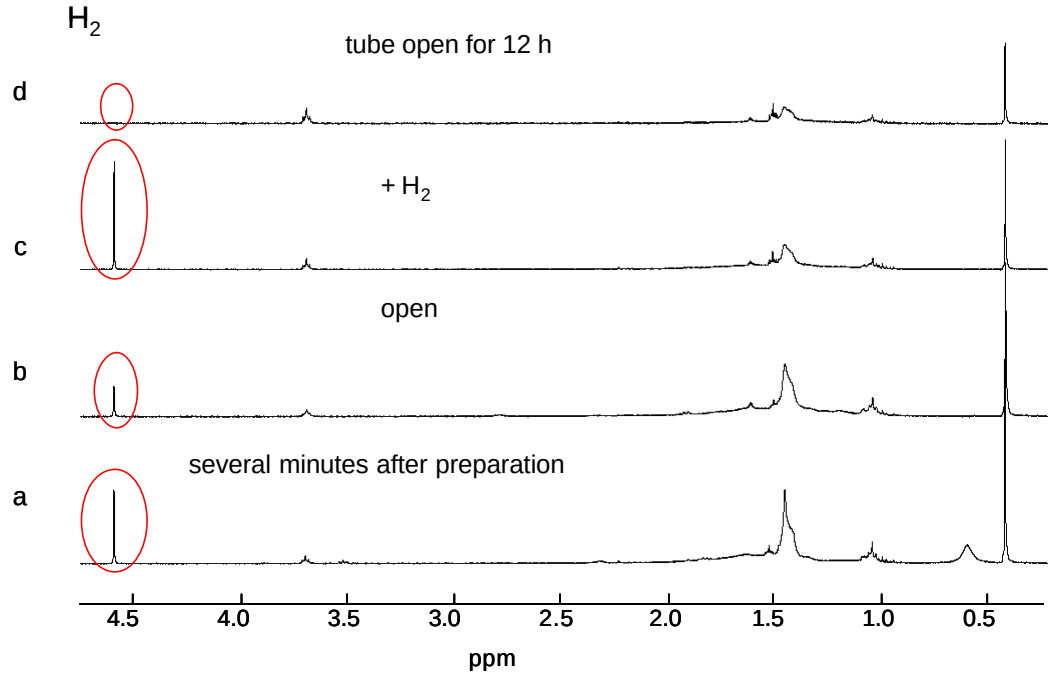


Figure S2 Liquid state ^{1}H NMR spectra of **Coll-1** (d^{8}-THF; 400 MHz) showing the evolution of the H_2 peak in the NMR tube containing Ru/HDA nanoparticles.

Solid State ^{1}H MAS and ^{13}C CPMAS NMR of Coll-1

All solid state MAS NMR measurements were performed at room temperature on a Varian InfinityPlus NMR spectrometer operating at a field of 14 T. Resonance frequencies are 599.97 MHz for ^{1}H and 150.87 MHz for ^{13}C. For all experiments, a triply tuned MAS-probe was employed (Chemagnetics 5 mm probe of T3 type). The powdered samples were glass sealed in vacuo and packed into zirconium oxide rotors. For MAS experiments, the sample spinning frequency was adjusted in the range of 1 to 4 kHz, respectively, and was stabilized to *ca.* ±2 Hz. Typical parameters for ^{1}H spectra: 8 scans, 90° pulse length: 3.4 µsec, sweep width 250 kHz.

Typical parameters for ^{13}C CPMAS NMR spectra: 30000 scans, 90° pulse ^{1}H: 3.4 µsec, contact time: 2 msec sweep width: 100 kHz. For Results of ^{1}H MAS NMR see Table 1.

Comment on ^{13}C spectrum: A very broad peak at 43.8 ppm in the was assigned to the carbon (α) located next to the -NH_2 group. In solution, this peak is absent. Probably, because of a moderately fast exchange between the free ligand exhibiting a long and the bound ligand exhibiting a short transverse relaxation time T_2 leading to a broad undetectable line. The short T_2 in the bound form arises from slow tumbling of the nanoparticle ligand. Therefore, the absence of the peak is not caused by a Ru- Knight shift.

Synthesis of deuterated Ru-HDA nanoparticles

Coll-1 was deuterated with D_2 gas in the solid state by treating a solid sample with D_2 gas (12 h, 400 mbar, RT) leading to **Coll-2** and in solution (2 hours, 1000 mbar, RT) followed by solvent (THF) evaporation leading to **Coll-3**.

^{2}H MAS of Coll-3

The solid state 92.1 MHz ^{2}H MAS NMR spectra (4.35 µsec 90° pulses, 200 scans on average, sweep width 25 kHz.) of **Coll-3** showed a single peak at 1.59 ppm (Figure S3), exhibiting a half height width of 120 Hz (Table 1). Spinning sidebands were either absent or hidden in the noise. *W* increased to 500 Hz when the spinning was stopped. This linewidth variation is very different from that observed either for the ligand signal or for D_2 gas sealed in a glass insert under otherwise similar MAS conditions (Table 1). These observations led to assign the peak at 1.59 ppm to deuterium atoms linked to ruthenium and undergoing a fast isotropic reorientation as the signal is sharp. The chemical shift of this signal is quite different from that

found for hydride ligands on molecular complexes (typically near – 10 ppm). Alternatively, this signal could arise from a fast exchange between surface deuterium atoms and D_2 in the gas phase.

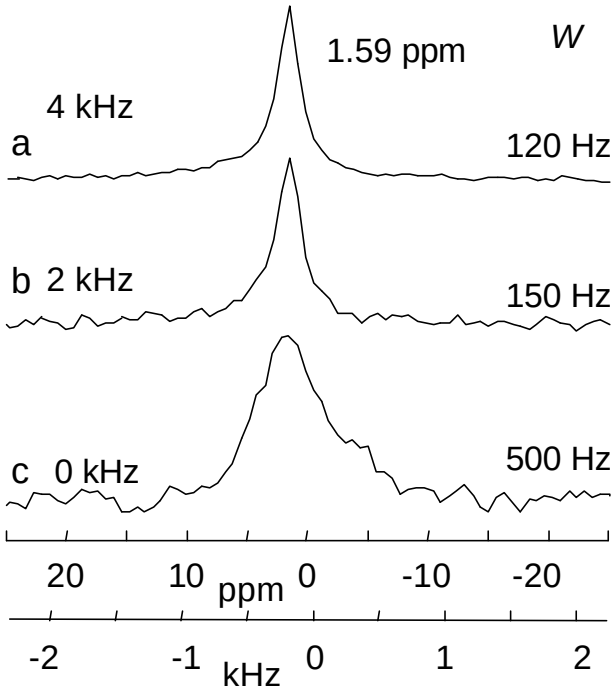


Figure S3 Solid state 91.4 MHz ^{2}H MAS NMR spectra of Ru/HDA particles (**Coll-3**) at various spinning speeds after H/D exchange performed in tetrahydrofuran.

Table 1 High-resolution solid state NMR signal line widths *W* of Ru/HDA particles at 14 Tesla.

MAS rotation frequency	*W*(^{1}H MAS) ligand	*W*(^{2}H MAS) Ru-D[a]	*W*(^{2}H MAS) of gaseous D_2
4 kHz	60 Hz[a]	120 Hz	120 Hz
2 kHz	65 Hz[a]	150 Hz	130 Hz
no rotation	7800 Hz[a]	500 Hz	145 Hz

[a] signal appearing at 1.59 ppm.

Details of the ^{2}H NMR of static samples of Coll-2 and Coll-3

The static ^{2}H experiments were performed at a field of 6.98 T, corresponding to a ^{2}H resonance frequency of 45.7 MHz on a standard Oxford wide bore magnet (89 mm) equipped with a room-temperature shim unit. For the ^{2}H channel a 2 kW class AB amplifier from AMT equipped with an RF-blanking for suppressing the noise during data acquisition was employed. The RF was fed through a crossed diode duplexer, connected to the detection preamplifier and through the filters into the probe. Typical ^{2}H pulse width was 5.0 μs. All experiments were performed using a home-built 5 mm ^{2}H NMR probe. The probe is placed in a dynamic Oxford CF1200 helium flow cryostat. The sample temperature was controlled employing an Oxford ITC 503 temperature controller. During cooling and before and after data acquisition the sample temperature was directly controlled via a Cernox sensor placed in the direct vicinity of the sample.

All spectra were recorded using the solid echo technique, with an echo spacing of 30 μs and a full 16-step phase cycle. Before Fourier transformation, the echo-signal was phase corrected and the imaginary part zeroed to give fully symmetric spectra. A repetition time of 5 s recycle delay was used. The number of accumulations was between 6208 and 12448 scans per spectrum.