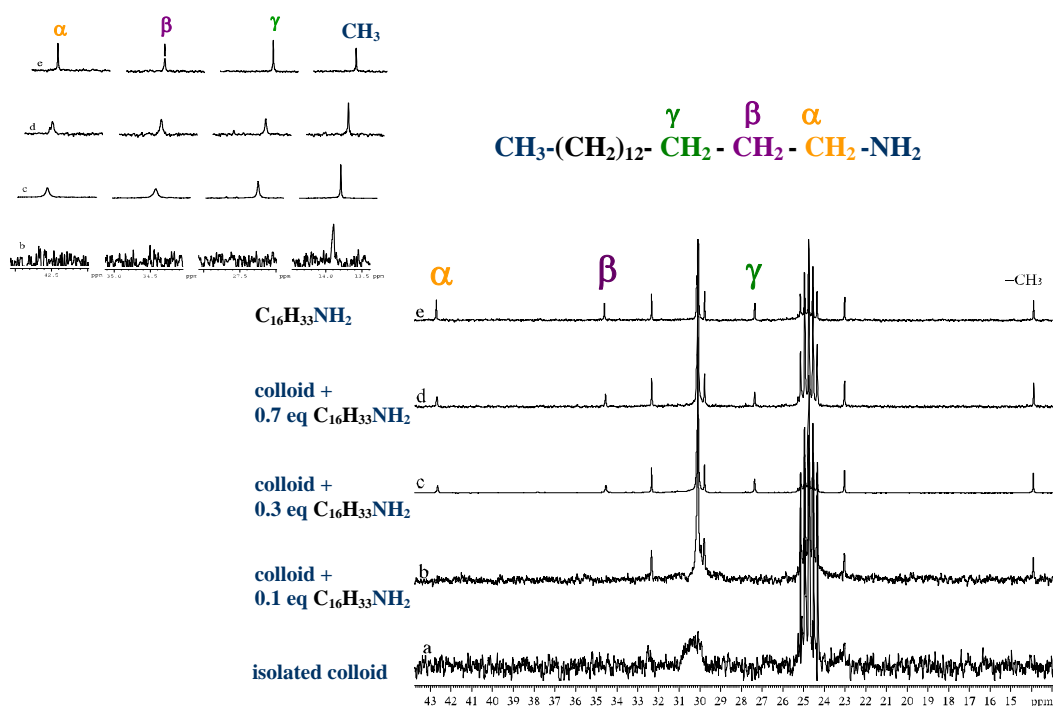


## Interest of NMR solution studies for the characterization of metal nanoparticles

In our laboratory, metal nanoparticles are considered as large **organometallic objects**, and a great interest is devoted to their **characterization** through the use of usual techniques of molecular chemistry, and most particularly **NMR**, with the objective to get precise information on their surface state.

At this day, NMR is a tool which is poorly used in the world scientific community working in this domain for the NPs characterization although this technique allows obtaining very interesting information about their surface state. This is mainly due to the bad quality of the obtained spectra related to the **Knight-shift phenomenon** induced by the metal core proximity giving rise to strongly shifted or no visible signals (Pd and Pt for example) in one hand and the **slow tumbling** of the NPs in solution since they have great sizes in the other hand. Nevertheless, very interesting results are now emerging.

The ligands used as stabilizers of the NPs, in particular when they bear long alkylchain, can serve as **probes** and their behaviour onto the NPS surface can be studied. As example, solution  $^{13}\text{C}$  NMR studies have been carried out onto various ligand stabilized Ru NPs, and it clearly appeared that thiol ligands are strongly coordinated onto the Ru NPs surface while amine ones are labile and can be rapidly exchanged at the NMR time scale with free amine molecules present in the solution. This exchange phenomenon has been observed for other NPs systems such as Pd and Pt ones. In addition, the adsorption of organosilane ligands onto the surface of Ru NPs could be shown through NMR studies.



$^{13}\text{C}$  NMR spectra of hexadecylamine stabilized Ru NPs ( $\text{THF-d}_8$ ): the signals of the  $\alpha$ ,  $\beta$  and  $\gamma$  carbon atoms of the hexadecylamine chain are not visible on the spectrum registered for the purified Ru NPs; these signals become apparent when amine is added in the NMR tube but large half height width are observed which are characteristic of a rapid exchange phenomenon at the NMR time scale between coordinated and free amine molecules.

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