A new and specific mode of stabilization of metallic nanoparticles†

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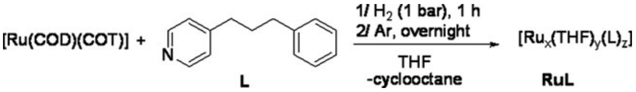
We report in this paper the stabilization of ruthenium nanoparticles using a very simple ligand (4-(3-phenylpropyl)pyridine), through strong π-coordination of the phenyl moiety.

An ever-increasing interest has been devoted in recent years to metal nanoparticles (NPs) because of their small size and electronic configuration giving rise to attractive properties in various areas.[1] For the past few years, our research has been focused on the preparation of well-defined metallic nanoparticles stabilized by different classical ligands.[2] One of our objectives is to better understand how the ligand can affect the stabilization of the NPs depending on its interaction with the metallic surface. To our knowledge, this point has been little studied even if the true nature of active catalytic species represents a recurrent discussion in colloidal catalysis. Most investigations concern nanoparticles stabilized by cinchonidine which is considered as a specific ligand for the stabilization of NPs.[3] We have recently observed that Pd nanoparticles can display a specific reactivity in enantioselective allylic alkylation processes depending on the ligand or the substrate involved. For example, in this reaction, PdNPs show a full selectivity towards substrates containing phenyl groups.[4] This fact points to a strong interaction of aromatic moieties with NP surfaces. It is then of prime importance to determine the coordination mode of ligands at the NP surface in order to design specific ligands for them.

For that purpose, the use of tools from molecular chemistry such as IR or NMR spectroscopy seems to be particularly appropriate. For example, the interaction of a carbene ligand with Ru nanoparticles has been recently evidenced by ^{1}H NMR.[5] Using classical stabilizers for the synthesis of metallic NPs such as carboxylic acids, thiols or amines, we proved that the heterodonor atom interacts by σ-type coordination with the metallic surface.[6]



Scheme 1 Synthesis of Ru nanoparticles **RuL** stabilized by L.

In order to elucidate π-interactions between the ligand and metallic surface, we decided to look for specific NPs stabilizers. 4-(3-phenylpropyl)pyridine was chosen for its simple structure containing a pyridine group, which, upon σ-coordination, can favour the flat phenyl approach to the metallic surface. Ruthenium was selected because of its absence of a Knight-shift so allowing NMR investigations.

Ruthenium nanoparticles (**RuL**) were prepared through decomposition of [Ru(COD)(COT)] (COD = 1,5-cyclooctadiene; COT = 1,3,5-cyclooctatriene), in the presence of 4-(3-phenylpropyl)pyridine (**L**) under dihydrogen, according to a previously reported methodology.[7] Optimized conditions led to reproducible NP syntheses (Scheme 1).[8]

Under these conditions, small and homogeneously dispersed nanoparticles showing a quite narrow size distribution around a mean diameter of 1.3 ± 0.3 nm, were obtained (Fig. 1). This result contrasts with the formation of large and agglomerated particles that we observed using simple pyridine as stabilizer (see Fig. S1 in ESI†) and which was in agreement with previous reports concerning gold particles containing pyridine.[9] This suggests that the presence of a phenyl group in 4-(3-phenylpropyl)pyridine participates in the stabilization of the particles and favours their dispersion probably as a result of the coordination of the phenyl group on the metallic surface.

It is noteworthy that no signal was observed in the far IR region (400–200 cm^{-1}) suggesting the absence of covalent Ru–N or Ru=O bonds.[10]

A ^{13}C CP-MAS NMR spectrum of **RuL** shows narrow aliphatic peaks together with a broad signal in the aromatic region (see Fig. S2 in ESI†). As shown in previous work, RuNPs prepared under dihydrogen atmosphere contain

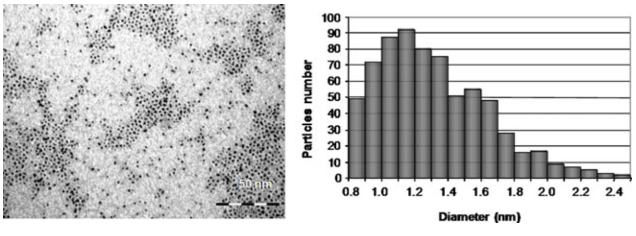


Fig. 1 TEM micrograph of **RuL** nanoparticles and size distribution histogram (ϕ_{mean} = 1.27 ± 0.33 nm for 696 particles).

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† Electronic supplementary information (ESI) available: Fig. S1: TEM micrograph of RuNPs stabilized by pyridine. Fig. S2: ^{13}C CP-MAS NMR spectrum of **RuL**. Fig. S3: ^{2}H MAS NMR spectra of preformed **RuL** exposed to D_2 and followed by vacuum treatment. Fig. S4: ^{1}H NMR spectra corresponding to 4-(3-phenylpropyl)pyridine–dodecanethiol exchange monitoring for **RuL**. Fig. S5: TEM micrographs corresponding to the monitoring of **RuL** formation. See DOI: 10.1039/b804402c

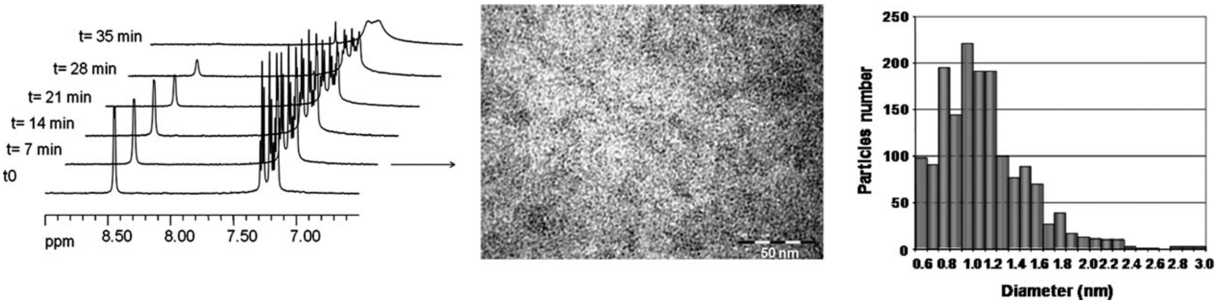

Fig. 2 Left: ^{1}H NMR (aromatic region, 500 MHz, 298 K, THF-d_8) monitoring **RuL** formation. The signal at *ca.* 8.5 ppm corresponds to pyridinyl *ortho* protons and those at 7.2–7.4 ppm correspond to the other aromatic protons. Right: TEM image corresponding to sample analysed after 7 min of H_2 addition ($\phi_{mean} = 1.10 \pm 0.32$ nm for 1603 particles).

hydrides at the metallic surface which can be exchanged with ligand hydrogen atoms.[5] Therefore preformed nanoparticles **RuL** were exposed to 3 bar of deuterium before recording the ^{2}H MAS NMR spectra. The ^{2}H MAS NMR spectrum (see Fig. S3 in ESI†) showed two signals: one attributed to Ru–D bonds and the other attributed to C–D bonds with a 120 kHz quadrupolar splitting, in agreement with reported data.[11] This analysis evidences the presence of organic stabilizers at the NPs surface able to exchange their hydrogen with surface deuterides.

The presence of **L** at the surface of the particles and its stability in the reductive conditions employed, was checked by a ligand exchange reaction with dodecanethiol, taking advantage of the known affinity of sulfur derivatives for noble metal surfaces.[12] A quantitative release of unreduced 4-(3-phenylpropyl)pyridine (monitored by ^{1}H NMR) was achieved after 24 h of reaction (see Fig. S4 in ESI†). This fact reveals (i) the effective presence of the ligand at the surface of the particles and (ii) a strong interaction of the ligand with the metallic surface.

The ligand coordination to **RuL** was studied by ^{1}H NMR monitoring under preparative conditions, using undecane as quantitative internal reference.[13] Disappearance of the [Ru(COD)(COT)] signals and the appearance of resonances of COD, cyclooctene and cyclooctane were observed, without detecting other peaks. Moreover, ligand signal broadening was observed after a few minutes under dihydrogen. This phenomenon could be related to the interaction of the ligand with the metallic surface as observed for gold nanoparticles.[14] TEM micrographs corresponding to samples taken during the NMR monitoring, revealed the extremely fast formation of **RuL** (Fig. 2), showing a mean diameter close to that observed under preparative conditions (Fischer–Porter bottle scale).

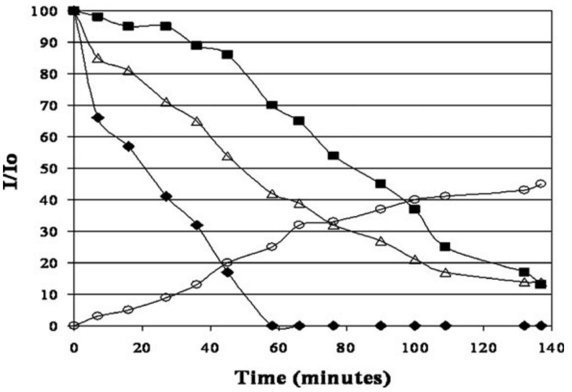

Fig. 3 Relative ^{1}H NMR signal integral *vs.* time corresponding to **RuL** formation (H phenyl (■); [Ru(COD)(COT)] (△); H *ortho*-pyridine (◆); cyclooctane (○)).

From the kinetic curves (Fig. 3), we could observe that the signal broadening was faster for the *ortho*-pyridinyl protons than that observed for the all other aromatic protons. Thus, the ligand seems to interact with the metallic surface by the N atom of pyridinyl group in a first stage, moving on to a π-interaction with the surface, consistent with the absence of an Ru–N absorption band in the IR spectrum.

In summary, we demonstrate here that 4-(3-phenylpropyl)-pyridine efficiently stabilizes small Ru nanoparticles. The presence of this ligand at the surface of the particles is evidenced by H/D exchange and ligand substitution reactions. The mode of stabilization involves π-coordination of the phenyl group at the particle surface. This can be considered as a new and specific mode of ligand coordination at nanoparticle surfaces although such coordination has previously been proposed, in particular for the coordination of cinchonidine on Pt nanoparticles.[3]

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8. Synthesis of **RuL**: A solution of 4-(3-phenylpropyl)pyridine in THF (2 cm^3 of a solution 0.02 M of ligand in THF, 0.04 mmol) was introduced in a Fischer–Porter bottle. Then the solvent was evaporated and a solution of [Ru(COD)(COT)] (60 mg, 0.2 mmol) in THF (80 cm^3) was introduced under argon atmosphere. The system was then pressurised with dihydrogen (1 bar) and stirred at room temperature for 1 h. The hydrogen was then replaced by argon and the mixture was stirred overnight. The solvent was evaporated *in vacuo* and the isolated particles were further washed with pentane (3×10 cm^3). The organic phase was concentrated and analyzed by ^{1}H NMR proving the absence of free ligand. The black solid was dried under reduced pressure; $\phi_{mean} = 1.27 \pm 0.33$ nm (images obtained by Transmission Electron Microscope JEOL1011 running at 120 kV). IR absorptions: ν_{max}/cm^{-1} 2917 and 2841 (C–H), 1612 and 1550 (C=N), 1402 and 1384 (C=C), 1258, 1089, 1019 and 798 (CO and CC of the THF). Elemental analysis (found: Ru, 41.39; C, 22.99; H, 3.32; N, 1.44. $Ru_5C_{22}H_{33}NO_{23}$ requires Ru, 41.26; C, 21.57; H, 5.96; N, 1.14%).
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12. The NMR spectrum was recorded with 5 mg of **RuL** synthesized in THF-d_8 in the presence of 12 mg of dodecanethiol.
13. Procedure for ^{1}H NMR monitoring of RuNP formation: 4-(3-phenylpropyl)pyridine (0.3 μL, $\rho = 1.024$ g cm^{-3}, 1.52×10^{-3} mmol), [Ru(COD)(COT)] (2.6 mg, 8.25×10^{-3} mmol) and undecane (0.2 μL, $\rho = 0.74$ g cm^{-3}, 1.28×10^{-3} mmol) were dissolved in 0.6 cm^3 of THF-d_8 in the NMR tube (Wilmad NMR tube w/J. Young valve, 5 mm). The system was then pressurised with dihydrogen (2 bar) and introduced to NMR probe. NMR spectra were recorded on a Avance 500 Bruker equipped with a CryoFlowProbe.
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