Electronic Supplementary Information for Dalton Transactions

Electronic Supplementray Information

An organometallic approach for the synthesis of water-soluble ruthenium and platinum nanoparticles (ref B917749N)

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S 1. Experimental details and Protocol for the synthesis of Ru and Pt NPs

Experimental details:

The precursors Ru(COD)(COT) and $Pt(Me)_2(COD)$ were purchased from Nanomeps-Toulouse. PTA was synthesized following a published procedure [D.J. Daigle (M.Y. Darensbourg (Ed.), Inorg. Synth. 32 (1998) 40] by reaction of trishydroxymethylphosphine $P(CH_2OH)_3$ (which was previously obtained by *in situ* reaction between tetrakis(hydroxymethyl)-phosphonium chloride $[P(CH_2OH)_4]Cl$ (Aldrich) and sodium hydroxide) with formaldehyde and hexamethylenetetramine (also from Aldrich). All operations were carried out in Schlenk or Fischer-Porter glasware under argon or in a glove-box. Solvents were dried and distilled before use: THF over sodium-benzophenone and pentane over calcium hydride. All reagents and solvents were degassed before use by means of three freeze-pump-thaw cycles.

Samples for TEM analyses were prepared by slow evaporation of a drop of crude colloidal solution deposited onto holey carbon-covered copper grids under argon for THF solutions and under air for aqueous solution. The TEM, HREM and SEM-FEG analyses were performed at the "Service Commun de Microscopie Electronique de l'Université Paul Sabatier" (TEMSCAN). TEM images were obtained using a JEOL 1011 electron microscope operating at 100 kV with resolution point of 4.5 Å. HREM images were obtained using a JEOL JEM 2100F at 200 kV with resolution point of 2.3 Å. The size distributions were determined through a manual analysis of enlarged micrographs with Imagetool software to obtain a statistical size distribution and a mean diameter.

NMR analyses were performed at the NMR department of LCC on an Avance 500 apparatus.

Ru@PTA nanoparticles:

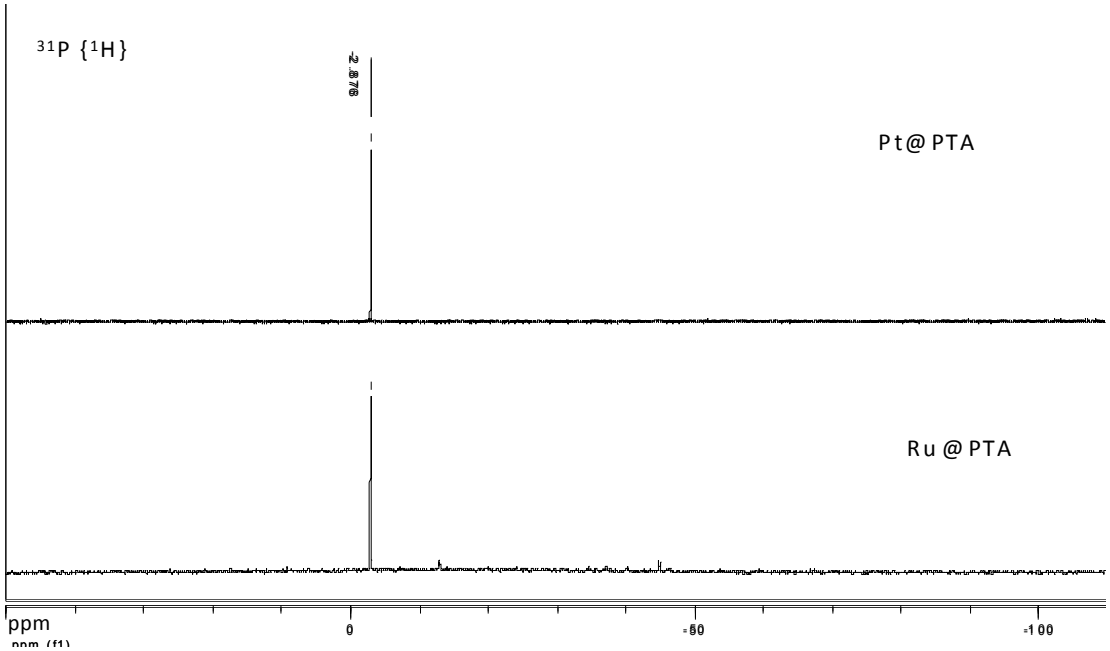
100 mg of [Ru(COD)(COT)] (0.317 mmol) were introduced in a Fisher-Porter bottle and left in vacuum during 0.5 h. 100 ml of THF, previously degassed by three freeze-pump cycles, were then added. The resulting yellow solution was cooled to 193K and a THF solution (100 ml) containing 40 mg of PTA (0.254 mmol, 0.8 eq./Ru) was introduced into the reactor. The Fisher Porter bottle was heated to 343K and then pressurized with 3 bars of dihydrogen. After 12 h, a homogenous brown colloidal solution is obtained. The volume of the solution was reduced to approximately 10 mL by solvent evaporation before its transfer onto a solution of deoxygenated pentane (100mL). A brown precipitate formed which was filtered and dried in vacuum, giving rise to the nanoparticles as a dark brown powder. In all cases, ruthenium colloids thus prepared were found to be stable with time and did not show any sign of decomposition under argon atmosphere.

Pt@PTA nanoparticles:

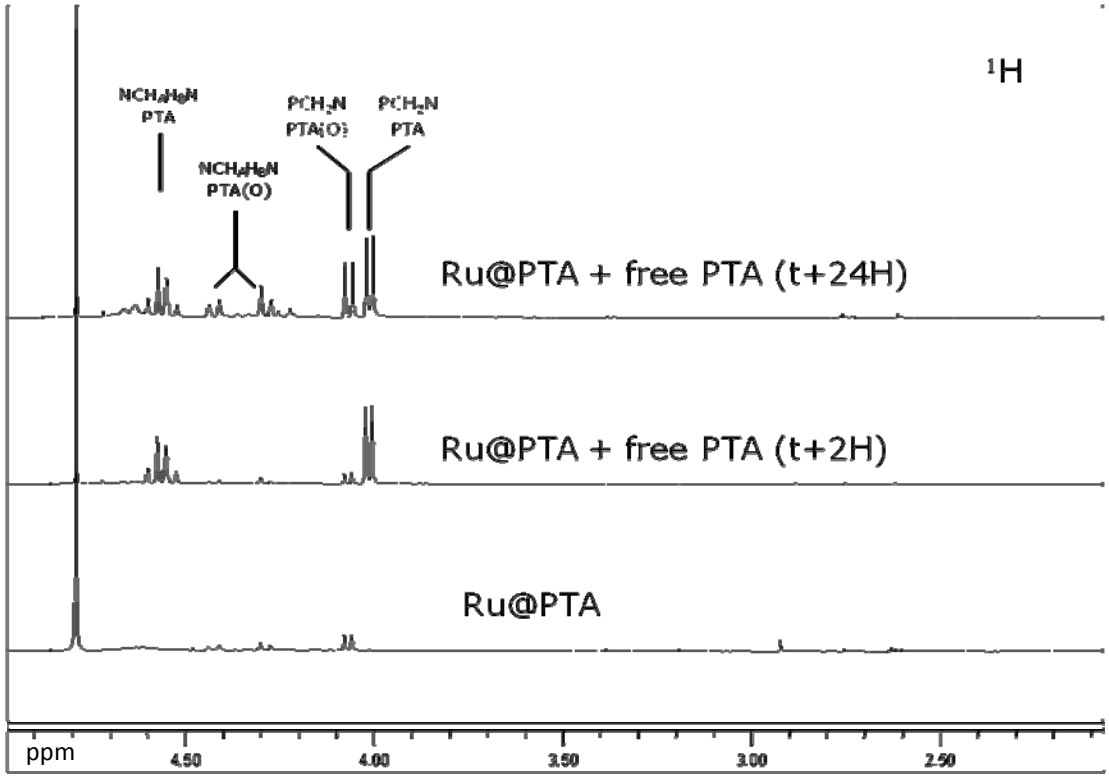
150 mg of $[PtMe_2(COD)]$ (0.45 mmol) were introduced in a Fisher-Porter bottle and left in vacuum during 0.5 h. 100 ml of THF, previously degassed by three freeze-pump cycles were then added. A solution of THF (100mL) containing 60 mg of PTA (0.38 mmol, 0.8 eq./Pt) was then introduced into the reactor. The Fisher-Porter bottle was heated to 343K and then

pressurized with 3 bars of dihydrogen. After 12 h, a homogenous brown solution is obtained. The volume of the solution was then reduced to approximately 10 mL before its transfer onto a solution of deoxygenated pentane (100mL). A dark brown precipitated formed which was filtered and dried in vacuum, giving rise to the nanoparticles as a dark brown powder. In all cases, platinum colloids were found to be stable with time and did not show any sign of decomposition under argon atmosphere.

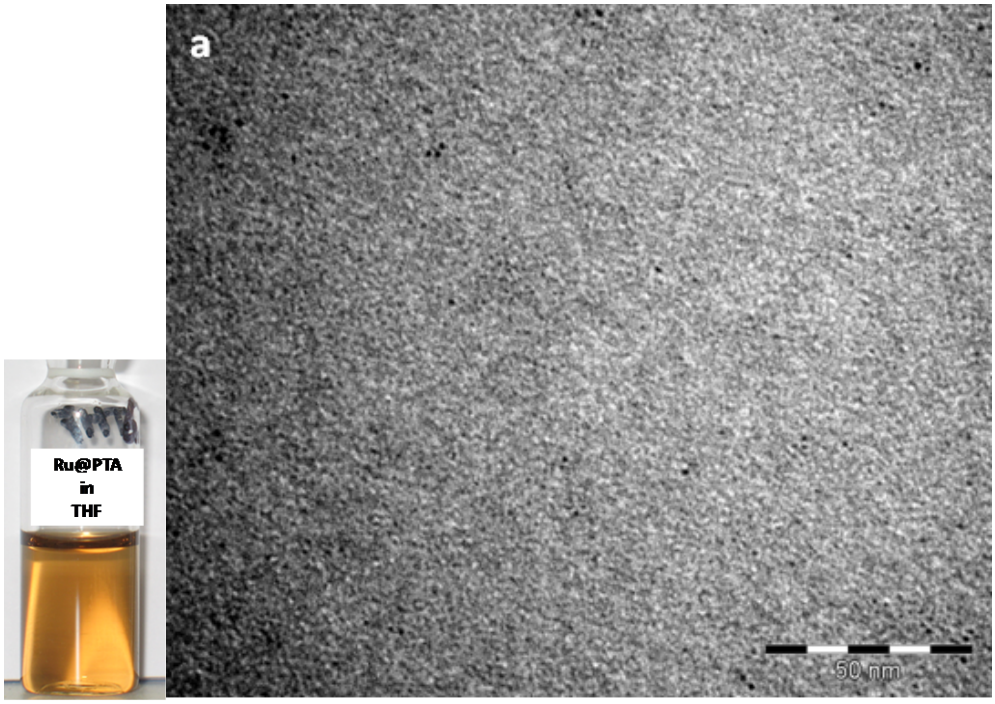
S 2. $^{31}P\{^{1}H\}$ NMR (Avance 500; 232.35 MHz; room temperature; D_2O) of Pt and Ru NPs water colloidal solutions

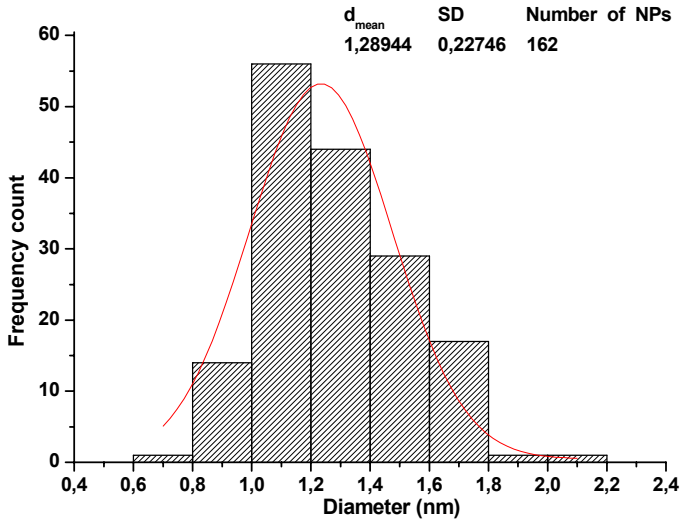


S 3. ^{1}H NMR (Avance 500; 500 MHz; room temperature; D_2O) of Ru and Pt NPs water colloidal solutions to follow their evolution with time and the formation of PTA oxide. Free PTA has been added as a standard.

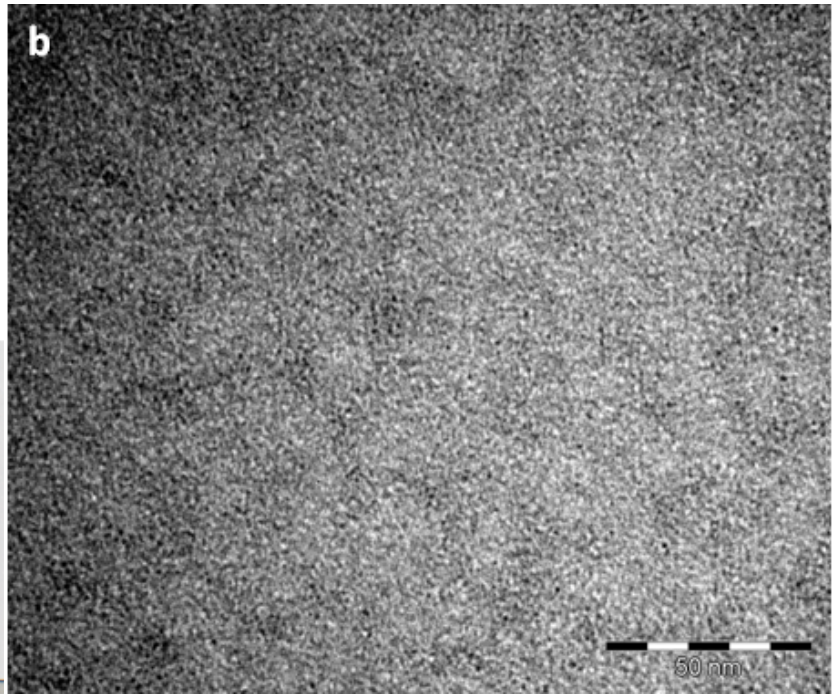


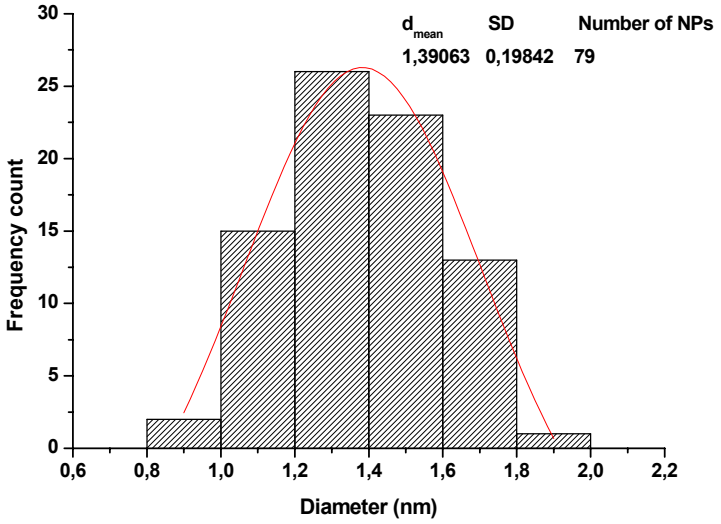
S 4. Pictures and TEM micrographs of Ru colloidal solution in THF (a) and in Water (b), and HREM micrograph of Ru colloidal solution in water (c)

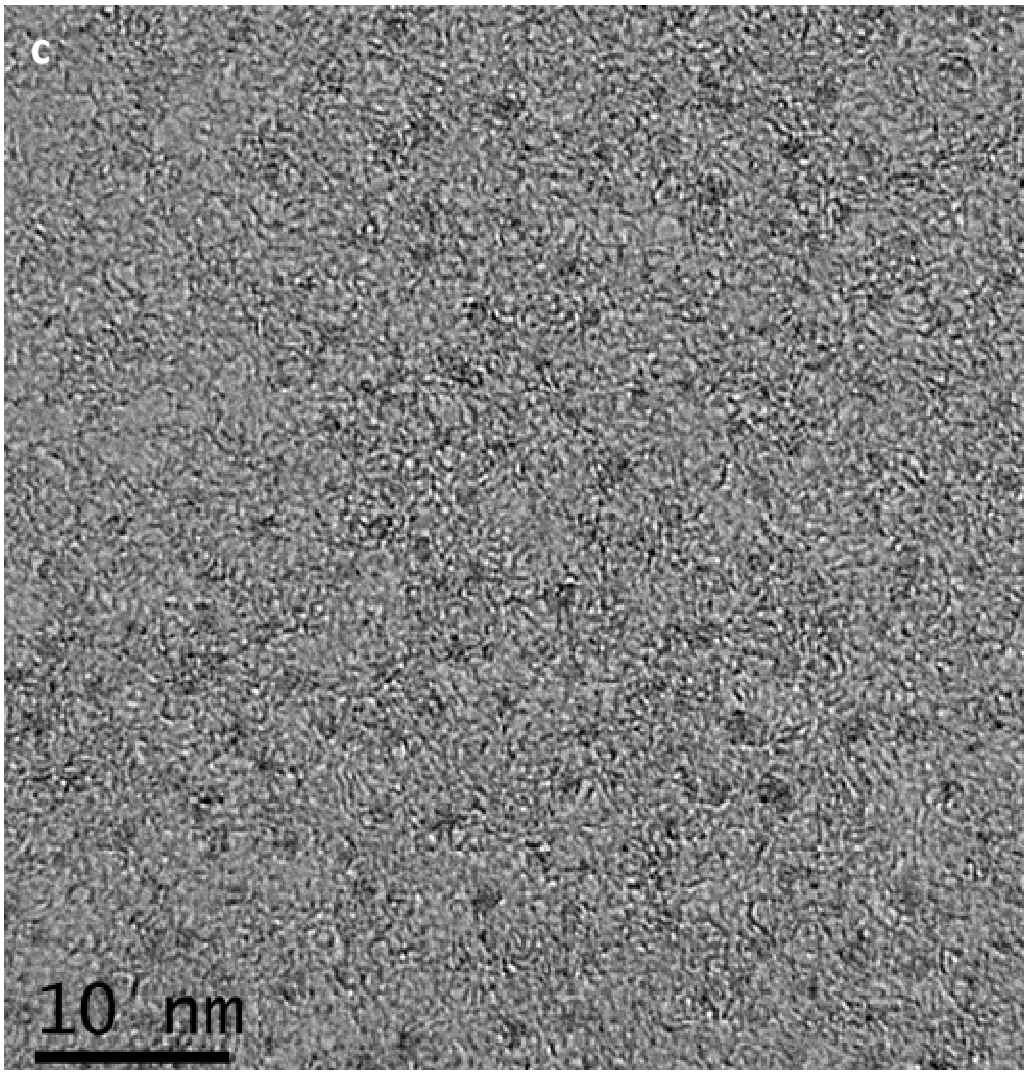





Ru@PTA
in
H2O


b
50 nm


d mean
SD
Number of NPs
1,39063
0,19842
79
Frequency count
Diameter (nm)
0
5
10
15
20
25
30
0,6
0,8
1,0
1,2
1,4
1,6
1,8
2,0
2,2



S 5. Pictures and TEM micrographs of Pt colloidal solutions in THF (a) and in Water (b), and HREM micrograph of Pt colloidal solution in water (c)