

Supporting Information

Water-Soluble NHC-Stabilized Platinum Nanoparticles as Recoverable Catalysts for Hydrogenation in Water

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1. General procedures and characterization techniques

All operations were carried out under argon atmosphere using standard Schlenk tube or Fischer-Porter bottle techniques. Unless otherwise stated, reagents and solvents were used as received from commercial sources. Argon and H₂ (Alphagaz 1, Bot-L Smartop 50) were purchased from Air Liquide, phenylacetylene from Acros Organics, nitrobenzene from Scharlau, benzaldehyde from Panreac, acetophenone, 3-nitrostyrene, 3-nitrobenzaldehyde, and dialysis tubing cellulose membrane (average flat width 25mm, molecular weight cut-off = 14000 Dalton) from Sigma-Aldrich. Deionized water (type II quality) was obtained using a Millipore Elix 10 UV Water Purification System. Complexes *cis*-[Pt(CH₃)₂(dmsO)(NHC)] **1**,^[1] were synthesized as described in the literature. Phenylacetylene and acetophenone were purified before use by distillation at normal pressure and under vacuum, respectively. Benzaldehyde was purified before use by chromatography on silica (hexane:ethyl acetate 4:1).

Samples for Transmission Electron Microscopy (TEM) were prepared by deposition after evaporation on a covered holey copper grid of three drops of the nanoparticles in water (0.5 mL) dispersed in EtOH (2 mL), or a drop of the crude aqueous colloidal solution. TEM analyses were performed at the “Service Commun de Microscopie Electronique de l’Université Paul Sabatier” (TEMSCAN-UPS) by using a JEOL JEM 1011 CX-T electron microscope operating at 100 kV with a point resolution of 4.5 Å. The approximation of the particles mean size was made through a manual analysis of enlarged micrographs by measuring a large number of particles (> 250) using ImageJ software to analyse the images.

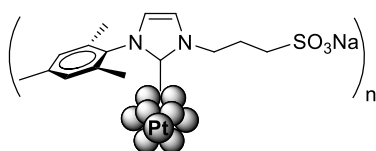
¹H NMR spectra in gas phase were recorded on a Bruker Avance 400 MHz spectrometer. Chemical shifts (δ , parts per million) are quoted relative to H₂O (¹H) residual signal from the water deposited externally on the NMR tube.

Gas chromatography coupled to mass spectrometry was performed using an Agilent GC-MS turbo system (5975-7820A model) equipped with an autoinjector, with an Agilent J&W HP-5MS non polar, (5%-Phenyl- methylpolysiloxane) low bleed capillary column of 30 m × 0.25 mm × 0.25 μ m. GC setting for the assessment of hydrogenation catalyses of phenylacetylene, benzaldehyde, nitrobenzene, 3-nitrostyrene and 3-nitrobenzaldehyde (acetophenone): 1.5 min (2.5 min) of solvent delay, 2.5 min at 70 °C (50 °C), then a ramp of 15 °C/min (5 °C/min) up to 230 °C (120 °C; then a second ramp of 25 °C/min up to 180 °C), and 2.5 min (0 min) at 230 °C (180 °C). Temperatures of injector and MS detector: 250 and 230 °C, respectively). Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

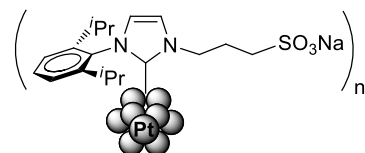
analyses were performed with a Perkin-Elmer ICP-MS NexION 300XX instrument at the elemental analysis unity at the SIdI of the Universidad Autónoma de Madrid. DLS were measured with a Nanotracs Ultra instrument.

2. Synthesis of water-soluble platinum nanoparticles 2a–d

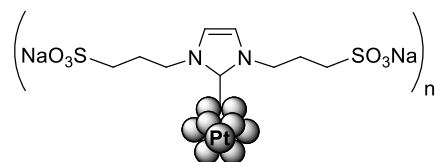
The platinum nanoparticles **2** were synthesized following the procedure described in the literature^[2] as follows: the corresponding platinum complex **1** (0.945 mmol) was introduced in a 50 mL Schlenk flask and dissolved in deionized water (5 mL). The resulting colorless to pale-yellow solutions were stirred at 1000 rpm, and heated at 80 °C for 18 h. The black solutions formed were left to reach room temperature slowly, filtered through a PTFE 0.2 µm filter in order to remove any eventual suspended solid, and the resulting solutions were dialysed in water using a cellulose membrane (MWCO = 14000 Dalton) for 36 h. The dialyses were monitored taking aliquots of the nanoparticle solutions and analyzing by ¹H-NMR the disappearance of dmsO and molecular species (*e.g.*, free imidazolium salts). Subsequent solvent removal under vacuum (50 °C, 100 mbar, 3 h) afforded black powders that were dried overnight under vacuum (room temperature, 10 mbar). The platinum nanoparticles were found to be stable in water under air, without precipitation over the time (> 12 months). The following features corresponds to the **PtNPs 2a-d** used for this work:



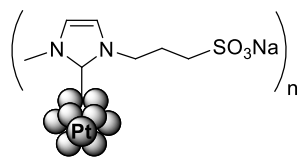
PtNPs 2a: TEM: NP mean size, 1.3 ± 0.4 nm. DLS: 1.6 ± 0.6 nm.
ICP-MS: Pt, 63.2%.



PtNPs 2b: TEM: NP mean size, 1.3 ± 0.4 nm. DLS: 1.6 ± 0.7 nm. ICP-MS: Pt, 61.6%.



PtNPs 2c: TEM: NP mean size, 1.6 ± 0.4 nm. DLS: 5.9 ± 1.8 nm.
ICP-MS: Pt, 43.4%. (After purification by dialysis, a molecular biscarbene Pt(II) complex still remained surrounding the NPs **2c** in a second coordination sphere. For details, please see ref. 2).



PtNPs 2d: TEM: NP mean size, 2.0 ± 0.3 nm. DLS: 2.3 ± 0.7 nm. ICP-MS: Pt, 56.6%.

3. TEM images of water-soluble platinum nanoparticles 2a–d

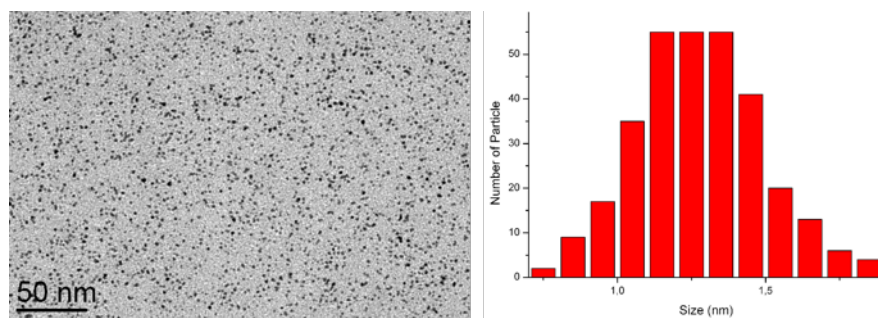


Figure S1. TEM image and the corresponding size distribution histogram of PtNPs **2a** (1.3 ± 0.4 nm).

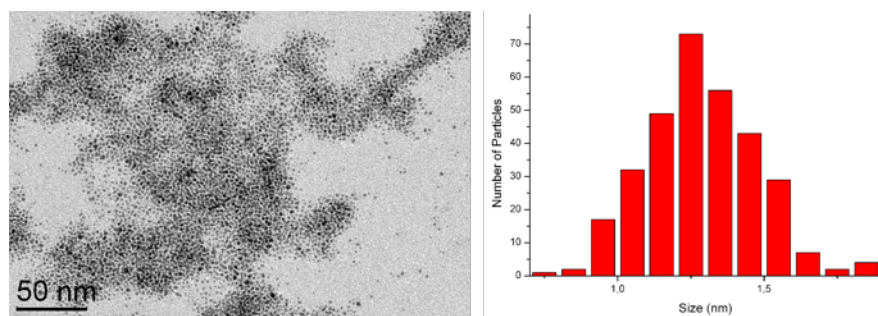


Figure S2. TEM image and the corresponding size distribution histogram of PtNPs **2b** (1.3 ± 0.4 nm).

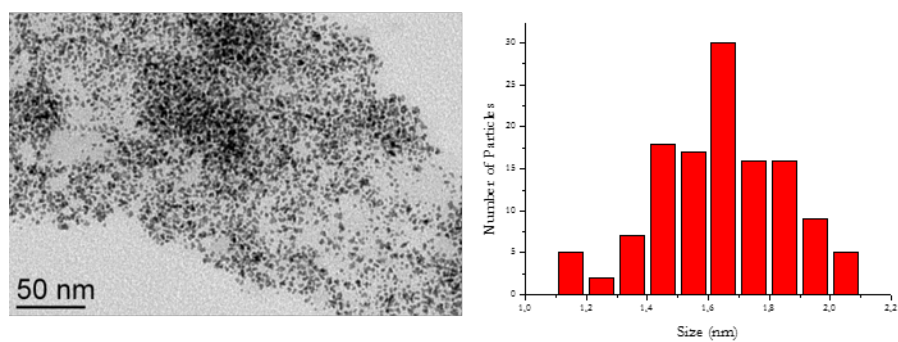


Figure S3. TEM image and size distribution histogram of PtNPs **2c** (1.6 ± 0.4 nm).

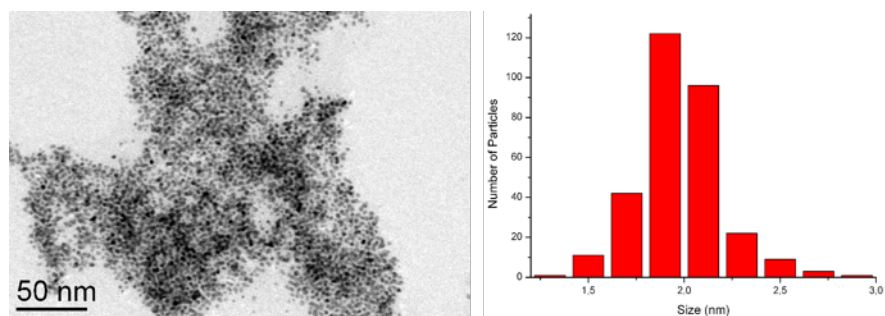


Figure S4. TEM image and the corresponding size distribution histogram of PtNPs **2d** (2.0 ± 0.3 nm).

4. Gas-phase ^1H NMR spectra of H_2 activation by PtNPs **2a**

In a high-pressure Teflon valve NMR tube, 9.5 mg of PtNPs **2a** NPs were introduced in solid state. After purging the system with several argon/vacuum cycles, the tube was filled with 2.0 bar of H_2 , and after sealing the valve the sample was left at room temperature for 24 h. Then, the gas-phase ^1H NMR was recorded. Afterwards, the excess of H_2 was removed under vacuum (10^{-6} bar) during 24 h. The gas-phase ^1H NMR spectrum was recorded again. Finally, 2.0 bar of D_2 were introduced into the NMR tube and left with the valve closed in contact with PtNPs **2a** overnight. The ^1H NMR spectrum reveals the presence of HD in the gas-phase, which formed as a consequence of the exchange between deuterium and hydrides on the nanoparticles.

5. Catalytic studies

Unless otherwise stated, all samples analysed by GC-MS were extracted with diethyl ether. Glassware material and magnetic stirring bars were previously treated with a mixture $\text{HCl}:\text{HNO}_3$ 3:1 (v/v) in order to remove possible traces of platinum that had remained on the material.

General procedure of a catalytic reaction: The substrate (1 mmol) was introduced in a 15 mL Fischer Porter flask containing 2.0 mL of an aqueous dispersion of PtNPs (concentration of PtNPs = 1.0 mg/mL; % of Pt(total): 63, 62, 43 and 57% for **2a**, **2b**, **2c**, and **2d**, respectively; total Pt loading 0.64, 0.64, 0.44 and 0.58 mol% [Pt] for **2a**, **2b**, **2c**, and **2d**, respectively; the effective Pt loadings at the surface, according to the magic number approach,^[3] are estimated to be 65% of Pt(total): 0.42, 0.41, 0.29 and 0.38 mol% [Pt] for **2a**, **2b**, **2c**, and **2d**, respectively). Afterwards, the mixture was cooled

down with liquid nitrogen and degasified with several vacuum/argon cycles. Once the system reached room temperature, the flask was filled with H₂ (2.0–5.0 bar depending on the substrate used). Then, the system was heated at 30 °C and stirred at 550 rpm during indicated time. After removal of the H₂, the organic phase was extracted with 3 × 1.0 mL of diethyl ether, unless otherwise stated.

Table S1. Optimization of the hydrogenation of phenylacetylene catalyzed by PtNPs **2a**.^a

Entry	T (°C)	P H ₂ (bar)	t (h)	Conv. (%) ^b	PhEt/St ^b
1	r.t.	1.0	2	49	27/73
2	r.t.	2.0	2	83	32/68
3	25	2.0	2	71	24/76
4	30	2.0	3	>99	31/69

(a) Reaction Conditions: 2.0 mg of NPs **2a** (2.0 mL of aqueous solution C = 1.0 mg/mL; 63% of Pt (total), 65% of Pt on the surface, 0.82 mg of accessible Pt on the surface, 0.4 mol% [Pt]), 1 mmol of phenylacetylene. (b) Determined by GC–MS. In these 4 entries, the organic phases had been extracted with toluene.

Table S2. Attempts to optimize the hydrogenation of acetophenone catalyzed by PtNPs **2a**.^a

Entry	T (°C)	P H ₂ (bar)	t (h)	% Conv (1 st) ^b	% Conv (2 nd) ^b	% Conv (3 rd) ^b
1	60	4.0	5	64	57	51
2	40	4.0	15	47	9	1
3	30	5.0	8	20-81	15-87	50-79

(a) Reaction Conditions: 2.0 mg of NPs **2a** (2.0 mL of aqueous solution C = 1.0 mg/mL; 63% of Pt (total), 65% of Pt on the surface, 0.82 mg of accessible Pt on the surface, 0.4 mol% [Pt]), 1 mmol of acetophenone. (b) Determined by GC–MS, measuring 80-95% of 1-phenylethanol; 1st, 2nd, and 3rd refers to the number of use of the catalyst in the recycling series.

In order to perform recycling experiments, all aqueous phases of PtNPs were previously evaporated under vacuum until neither organic products, nor organic solvents, were present in the solution. Afterwards, the remaining aqueous solution was treated with more substrate as above mentioned. The catalysts were recycled up to 10 times (11 uses with the initial run).

The kinetic profiles determined for the hydrogenation of phenylacetylene catalyzed by **2a**, were carried out in a Fischer-Porter tube equipped with a Teflon cannula connected to a T-3 port VICI Micro Valve, which was utilized to withdraw aliquots of the catalytic mixture at different times from the reaction flask.

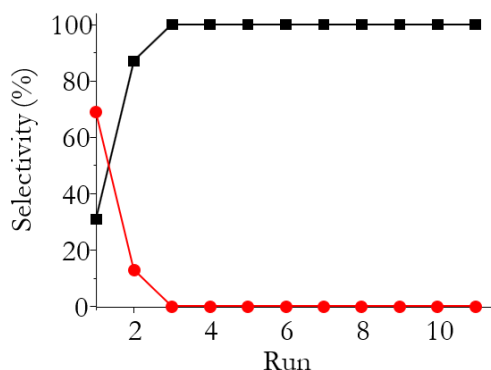


Figure S5. Evolution of ethylbenzene (■) and styrene (●) in the recycling experiments of hydrogenation of phenylacetylene catalyzed by PtNPs **2a**.

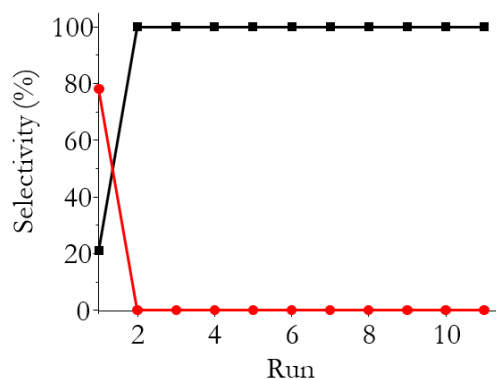


Figure S6. Evolution of ethylbenzene (■) and styrene (●) in the recycling experiments of hydrogenation of phenylacetylene catalyzed by PtNPs **2d**.

6. TEM images of PtNPs 2a–d after catalysis

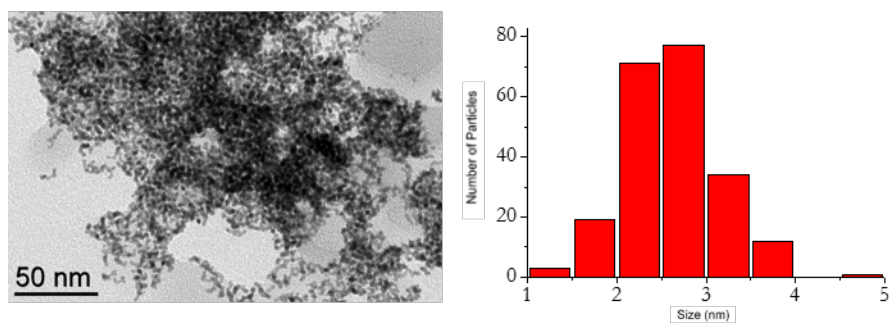


Figure S7. TEM image and the corresponding size distribution histogram of PtNPs **2a** after 11 cycles of hydrogenation of phenylacetylene (2.6 ± 0.5 nm).

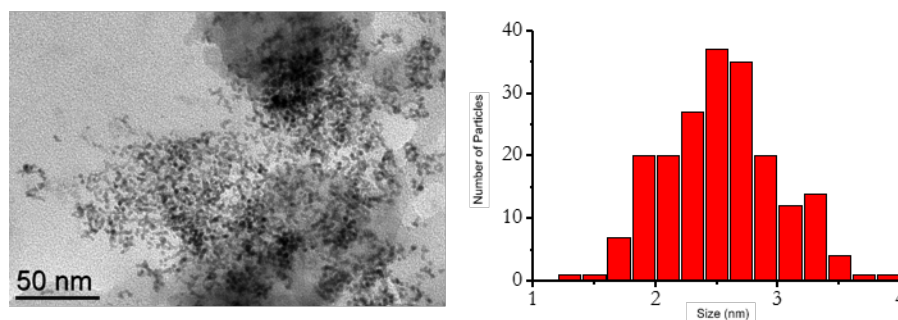


Figure S8. TEM image and the corresponding size distribution histogram of PtNPs **2b** after 11 cycles of hydrogenation of phenylacetylene (2.5 ± 0.5 nm).

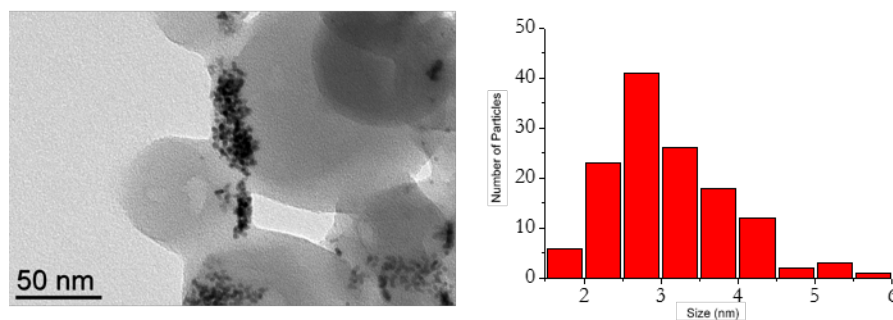


Figure S9. TEM image and the corresponding size distribution histogram of PtNPs **2c** after 11 cycles of hydrogenation of phenylacetylene (2.9 ± 0.6 nm).

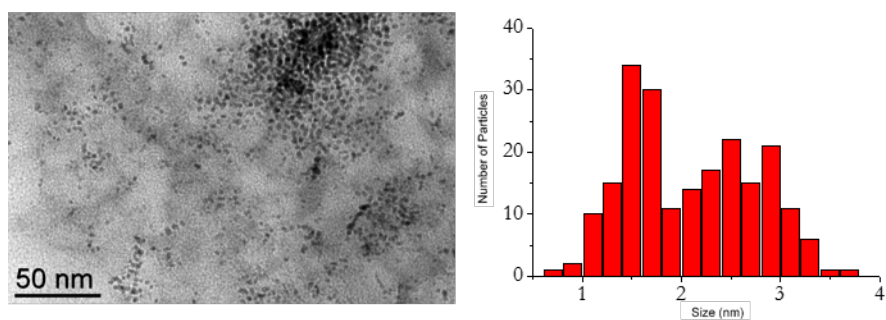


Figure S10. TEM image and the corresponding size distribution histogram of PtNPs **2d** after 11 cycles of hydrogenation of phenylacetylene (2.1 ± 0.7 nm).

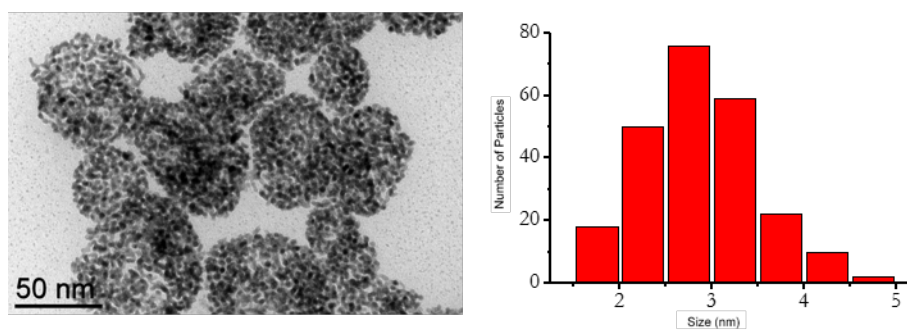


Figure S11. TEM image and the corresponding size distribution histogram of PtNPs **2a** after 11 cycles of hydrogenation of benzaldehyde (2.8 ± 0.6 nm).

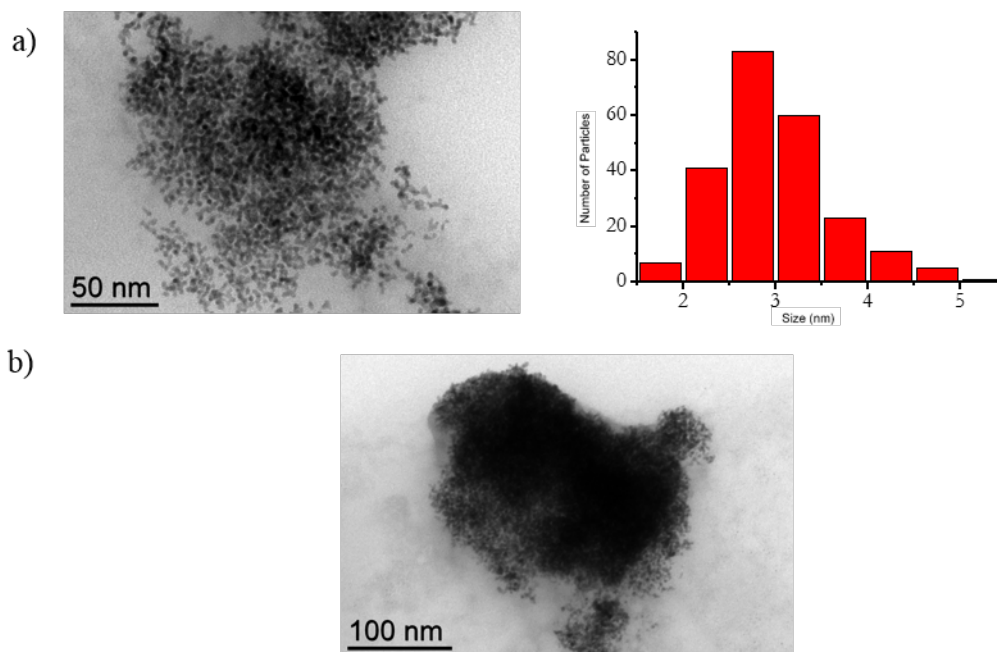


Figure S12. a) TEM image and the corresponding size distribution histogram of the solid precipitated after 11 cycles using PtNPs **2c** in the hydrogenation of benzaldehyde (2.9 ± 0.5 nm), and b) TEM image of the samples showing a large agglomerate.

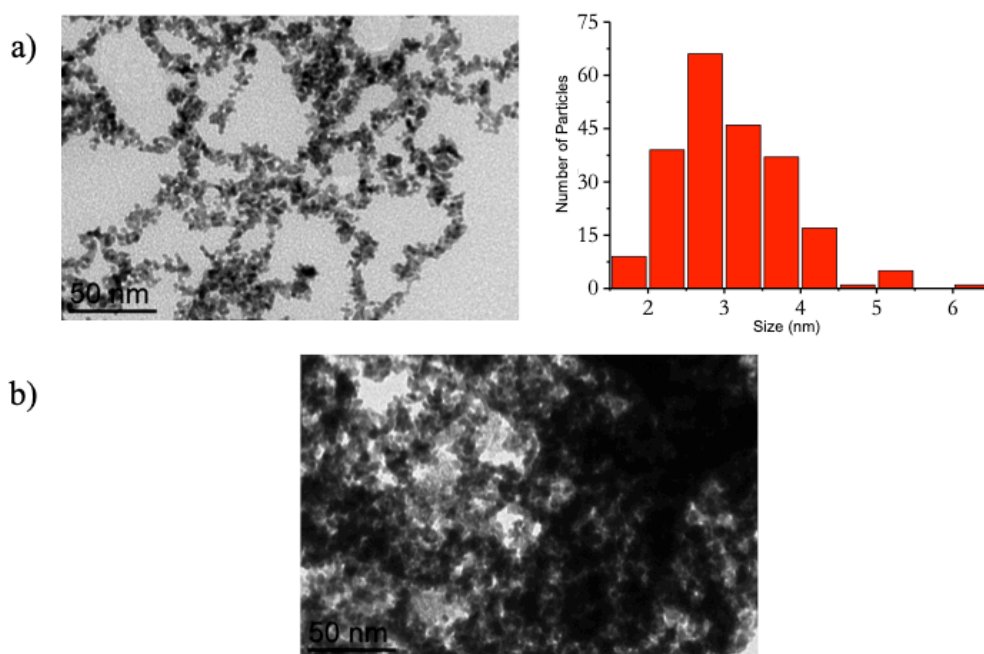


Figure S13. a) TEM image and the corresponding size distribution histogram of PtNPs **2a** after 11 cycles in the hydrogenation of acetophenone (3.0 ± 0.7 nm), and b) TEM image of the solid precipitated after the 11 uses of the NPs (4.4 ± 1.4 nm).

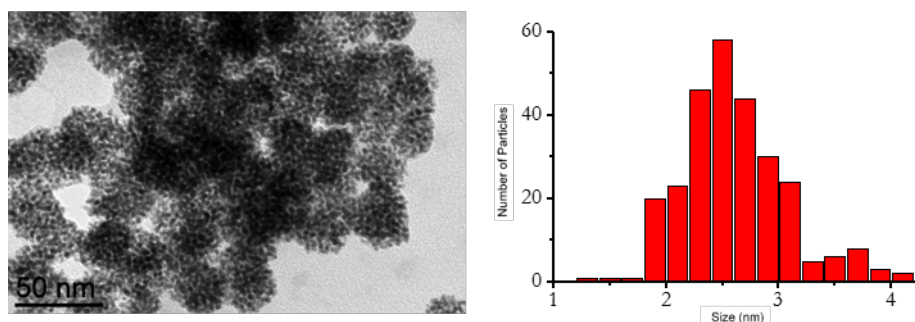


Figure S14. TEM image and the corresponding size distribution histogram of PtNPs **2a** after 11 cycles of hydrogenation of nitrobenzene (2.5 ± 0.4 nm).

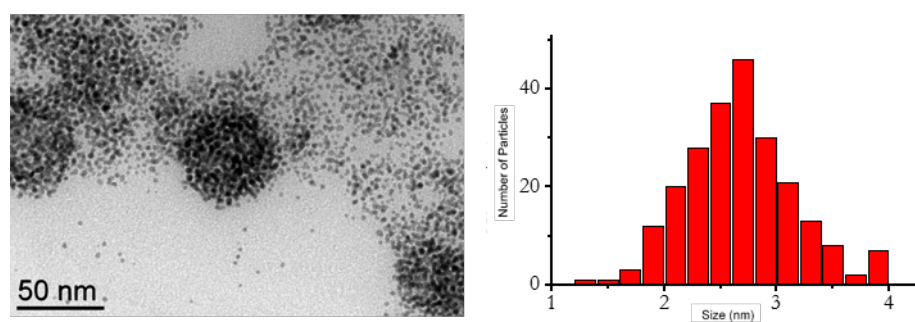


Figure S15. TEM image and the corresponding size distribution histogram of PtNPs **2c** after 11 cycles of hydrogenation of nitrobenzene (2.6 ± 0.4 nm).

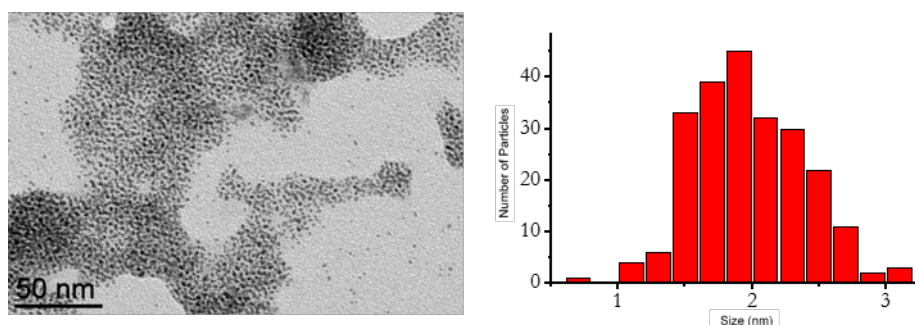


Figure S16. TEM image and the corresponding size distribution histogram of PtNPs **2a** after 1 cycle of hydrogenation of 3-nitrostyrene (1.9 ± 0.4 nm).

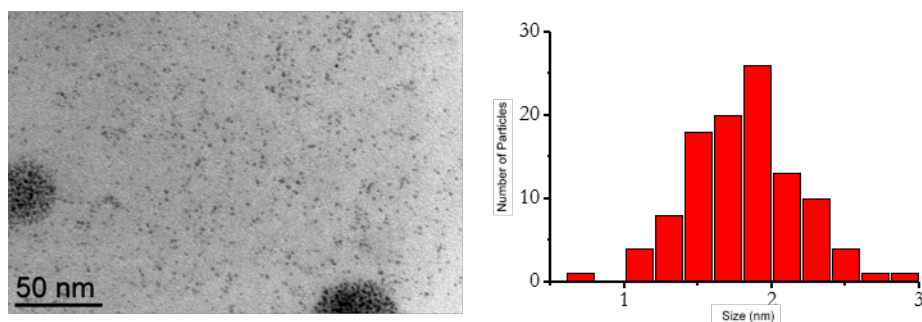


Figure S17. TEM image and the corresponding size distribution histogram of PtNPs **2a** after 1 cycle of hydrogenation of 3-nitrobenzaldehyde (1.8 ± 0.3 nm).

7. References

- [1] E. A. Baquero, J. C. Flores, J. Perles, P. Gómez-Sal and E. de Jesús, *Organometallics*, 2014, **33**, 5470–5482.
- [2] E. A. Baquero, S. Tricard, J. C. Flores, E. de Jesús and B. Chaudret, *Angew. Chem. Int. Ed.*, 2014, **53**, 13220–13224.
- [3] A. P. Umpierre, E. de Jesús and J. Dupont, *ChemCatChem*, 2011, **3**, 1413–1418.