## **+** Electronic Supplementary Information (ESI)

# Ruthenium nanoparticles canopied by heptagoncontaining saddle-shaped nanographenes as efficient aromatic hydrogenation catalysts

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## S1. Experimental Procedures

## 1.1. General considerations and starting materials

All chemical operations were carried out using standard Schlenk tubes, Fischer–Porter bottle techniques or in a glove-box under nitrogen atmosphere. Solvents were purified before use; THF (Sigma-Aldrich) by distillation under argon atmosphere through filtration in the column of a purification system (SPS). Ru(COD)(COT) was purchased from Nanomeps, and acetophenone (99 %), 1-methylindole (> 97 %), benzaldehyde (> 99 %), styrene (99 %), naphtalene (99 %), biphenyl (> 99 %), 5-hydroxymethylfurfural (99 %) and dodecane (99 %) from Sigma Aldrich. All reagents were used without purification, except for HMF which was purified by filtering with an equimolar silica:alumina mixture, and after that it was stored in a refrigerator.

Transmission Electron Microscopy (TEM) and High resolution TEM (HRTEM). Ru-NPs were observed by TEM and HRTEM after deposition of a drop of a solution of the isolated nanoparticles after dispersion in THF on a copper grid. TEM analyses were performed at the "Servicio de Microscopia Electrónica" of Universitat Politècnica de València (UPV) by using a JEOL JEM 1400 Flash electron microscope operating at 120 kV with a point resolution of 3.8 Å. The approximation of the particles mean size was made by measuring a number of particles on a given grid. HRTEM observations were carried out with a JEOL JEM 2010 electron microscope working at 200 kV with a resolution point of 2.35 Å. FFT (Fast Fourier Transform) treatments have been carried out with Digital Micrograph Version 3.7.4.

<u>Inductively Coupled Plasma (ICP).</u> ICP analyses of **Ru@1** and **Ru@2** were performed at "Mikroanalytisches Labor Kolbe" in Mülheim, Germany.

<u>X-ray Photoelectron Spectroscopy (XPS).</u> XPS analyses were performed using a SPECS device equipped with a Phoibos 150-9MCD detector using in all spectra recorded Al-K $\alpha$  radiation (hv: 1486.61 eV), with a pass energy of 30 eV. (Mg-K $\alpha$  radiation (hv: 1235.6 eV) and Al-K $\alpha$  radiation (hv: 1483.6 eV) from a dual source. The pressure during the measurements was kept under 10<sup>-9</sup> Torr. The quantification and titration of the spectra was done with the help of the software CASAXPS version 2.3.244PR1.0, referencing them in base of C1s = 284.5 eV.

<u>Thermogravimetric Analyses (TGA).</u> TGA analyses were carried out in a Netzsch TGA/STA 449 F3 Jupiter device; using a heating rate of 10 °C in an air stream of 100 mL/min until a temperature of 700 °C was reached.

<u>Gas Chromatography (GC).</u> The spectra of the reactants and their hydrogenated products were recorded with an Agilent Technologies 7890A GC-system with Flame ionization detector and a HP-5 column. The method used start with the injection temperature T0. After holding this temperature for 2 min, the column is heated to temperature T1 (10 °C/min) and finally, the column is heated to T3 (30 °C/min) and hold for 1 min (T0 = 80 °C, T1 = 160 °C, T2 = 280 °C). On the other hand, HMF and derivatives spectra were recorded with a Varian CP-3800 equipment with an automatic injector Varian CP-8400 and a Carbowax column. The method used starts with an injection temperature of 50 °C. After hold the temperature for 1 minute, the column is heated to a 240 °C (20 °C/min) maintaining this temperature 3.5 minutes. Dodecane has been used as standard.

<u>Gas Chromatography coupled to Mass Spectrometry (GC/MS).</u> GC-MS analyses were carried out in an Agilent 6890N chromatograph equipped with a column HP-5 (30 m, 0.32 mm, 0.25  $\mu$ m) coupled to an electron impact mass spectrometer Agilent 5973N.

<u>X-ray powder diffraction (XRD)</u>. XRD analysis was performed using a PANanlytical CubiX diffractometer using Cu-K $\alpha$  (1.5406 Å) radiation and an autosampler handler. XRD measurement was performed under inert atmosphere, placing **Ru@2** in the centre of a specific sample holder for air-unstable samples sealed with a Kapton foil inside a glove-box.

## Synthesis of nanographenes:

Heptagon-Containing Saddle-Shaped Nanographenes 1 and 2 were prepared following the protocol described in: I. R. Márquez, N. Fuentes, C. M. Cruz, V. Puente-Muñoz, L. Sotorrios, M. L. Marcos, D. Choquesillo-Lazarte, B. Biel, L. Crovetto, E. Gómez-Bengoa, M. T. González, R. Martin, J. M. Cuerva and A. G. Campaña, *Chem. Sci.*, 2017, 8, 1068
Compounds 1 and 2 were previously reported in: A. H. G. David, S. Míguez-Lago, C. M. Cruz, J. M. Cuerva, V. Blanco and A. G. Campaña, *Org. Mat.*, 2021, 3, 51-59.

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#### Synthesis of ruthenium nanoparticles.

**Ru@1**. A Schlenk flask was charged with **1** (51.9 mg, 0.078 mmol) and dissolved in 10 mL THF. After that the solution was added to a 250 mL Fischer–Porter bottle charged with a cooled solution (-80 °C) of Ru(COD)(COT) (250 mg, 0.78 mmol) in 50 mL of THF (previously degassed by three freeze-pump cycles). The Fischer-Porter was then pressurized with 3 bar of H<sub>2</sub>, and the solution was allowed to reach the room temperature while it was stirred vigorously. A black homogeneous dispersion was immediately formed and the stirring was continued for 20 h at room temperature. After that, the remaining H<sub>2</sub> pressure was released, and 50 mL of anhydrous pentane was added to the suspension to favour the precipitation of Ru NPs. The resulting black precipitate was dried overnight under vacuum. The size of the NPs was measured by TEM on a sample of at least 100 nanoparticles, which afforded a mean value of  $1.6 \pm 0.4$  nm. ICP gave the following Ru content: 61.0 % for Ru@1.

*Ru@2.* Same procedure as previously described for **Ru@1** has been followed, with the difference that the ligand used was **2** (52.4 mg, 0.078 mmol). The size of the nanoparticles was measured by TEM, analyzing a sample of the catalyst with at least 100 nanoparticles, obtaining an average value of  $1.6 \pm 0.5$  nm. The metallic content has been quantified by ICP, giving an experimental Ru content: 60.6 %.

#### 1.2. Hydrogenation reactions

The reactor was equipped with a magnetic stirring bar and filled with Ru NPs (2 mg). The corresponding substrate (0.15 mmol) and anhydrous THF were added (2 mL) under argon before the atmosphere of the vial was exchanged by carefully pressurizing/depressurizing the reactor with hydrogen for three times. Then, the indicated pressure was adjusted (10 bar) and the reaction mixture stirred at 50 °C for 20h. Finally, the catalyst was separated by filtration, and the products of the reaction mixture were analyzed by GC using dodecane as internal standard, and confirmed with GC-MS.

## 1.2.2. Isolation of cyclohexanol

After 20 h reaction, the reactor was slowly depressurized and the sample was filtered through a silica plug and evaporated to dryness at 150 mbar using a rotary evaporator at room temperature. The residue was first weight to calculate the yield and dissolved in CDCl<sub>3</sub> to analyzed it by <sup>1</sup>H NMR (see Figure S23).

#### **1.3. Kinetic experiments**

For the kinetic experiments, the reactor was charged, pressurized and heated at the required conditions and aliquots were taken from the reaction medium and analyzed by GC, using dodecane as internal standard.

#### 1.4. Multiple Addition Experiment

For the multiple addition experiment, the reactor was charged, pressurized and heated at the required conditions for anisole hydrogenation (50 °C, 10 bar  $H_2$ , 2 mL THF). Each 12 hours an aliquot was taken from the reaction medium and new starting material (i.e. anisole) was added to the reactor. The aliquots were analyzed by GC using dodecane as internal standard, and confirmed by GC-MS. The activity and selectivity remained over 8 catalytic cycles confirming the stability of the Ru NP catalysts.

#### 1.5. VASP - DFT calculations of metal nanoclusters.

Software: Vienna ab initio simulation package, VASP [a) G. Kresse and J. Furthmüller, *Phys. Rev. B* 1996, **54**, 11169; b) G. Kresse and J. Furthmüller, *Comput. Mater. Sci.*, 1996, **6**, 15.] spin polarized DFT; exchange-correlation potential approximated by the generalized gradient approach proposed by Perdew, Burke, and Ernzerhof (PBE);[a) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; b) J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1997, **78**, 1396] Van der Waals interactions were taken into account through the D3 correction method of Grimme *et al.*; [S. Grimme, J. Antony, S. Ehrlich, and S. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.] projector augmented waves (PAW) full-potential reconstruction; [a) P. E. Blöchl, *Phys. Rev. B* 1994, **50**, 17953; b) G. Kresse and D. Joubert, *Phys. Rev. B* 1999, **59**, 1758.] PAW data sets for Ru treating the (n-1)p, (n-1)d and ns states (i.e. 14 valence electrons); kinetic energy cutoff: 525 eV; G-centered calculations; [H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* 1976, **13**, 5188] Gaussian smearing (s) of 0.02 eV width, energies being therefore extrapolated for s = 0.00 eV; geometry optimization threshold: residual forces on any direction less than 0.02 eV/Å; supercell size: 33Å~33.5Å~34 Å<sup>3</sup> for all species (ensures a vacuum space of at least *ca.* 10 Å between periodic images of the nanoclusters).

DOS, COHP and Mulliken Population Analysis (MPA) calculated after projection of the PAW wavefunction by the Lobster software, using the pbeVASPfit basis set.[S. Maintz.; V. L. Deringer.; A. L. Tchougreeff and R. Dronskowski, *J. Comput. Chem.*, 2016, **37**, 1030] The charge spilling, a criterion that assesses the quality of the projection was systematically lower than 1.0%. A comparison of such MPA charges with other electronic density decomposition schemes (AIM-Bader, Natural Population Analyzis, CM5) can for example be found in [I. C. Gerber and R. Poteau, *Theor. Chem. Acc.*, 2018, **137**, 1]. d-band center (dbc) values were calculated from the projected DOS (pDOS) obtained with LOBSTER, see details in [L. Cusinato; I. del Rosal and R. Poteau, *Dalton Trans.*, 2017, **46**, 378]. Slater-Type Orbitals

(STOs) of Figures S9 and S12 are obtained from Lobster and adapted to the jmol format thanks to the selectLOBSTER in-house utility (freely available at <u>http://romuald-poteau.blogspot.com/p/my-tools.html</u>).

#### 1.6. Gaussian – NMR Calculations

All DFT calculations were carried out with the Gaussian 09 suite of programs.[Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013] Geometries were fully optimized in gas phase without symmetry constraints, employing the PBE functional, for the sake of consistency with the VASP calculations.[a) J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865; b) J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1997, 78, 1396.] The nature of the extrema was verified by analytical frequency calculations. The calculation of electronic energies and enthalpies of the extrema of the potential energy surface (minima and transition states) were performed at the same level of theory as the geometry optimizations. For C and H, Pople's double- $\zeta$  basis set augmented by a polarization and diffuse function was used 6-31+G(d,p).[a) R. Ditchfield, W. J. Hehre and J. A. Pople, J. Chem. Phys., 1971, 54, 724; b) W. J. Hehre, R. Ditchfield and J. A. Pople, J. Chem. Phys., 1972, 56, 2257; c) P. C. Hariharan and J. A. Pople, Theor. Chim. Acta 1973, 28, 213; d) M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, J. Chem. Phys., 1982, 77, 3654.]. Dispersion corrections were treated with the D3 version of Grimme's dispersion with Becke-Johnson damping [S. Grimme, S. Ehrlich and L. J. Goerigk, Comp. Chem., 2011, 32, 1456]. In all cases, among the various theories available to compute chemical shielding tensors, the Gauge Including Atomic Orbital (GIAO) method has been adopted for the numerous advantages it presents.[J. R. Cheeseman, G. W. Trucks, T. A. Keith and M. J. Frisch, J. Chem. Phys., 1996, 104, 5497.] Typically, in order to compare our calculations with experimental values, <sup>1</sup>H chemical shielding have been converted to chemical shifts using the usual equation:  $\delta_{iso} = \sigma_{iso,ref} - \sigma_{iso,sample}$  where  $\sigma_{iso,ref}$  is the isotropic <sup>1</sup>H chemical shielding in TMS calculated at the same level of theory.

#### S2. X-ray powder diffraction (XRD)

**Figure S1** shows two broad peaks, a first one located at ca. 20°, which is associated to the Kapton foil used to performed the analysis under inert atmosphere; and another centred at 43° that is attributed to hcp-Ru and confirms that Ru NPs are predominantly as Ru<sup>0</sup>. Due to the small size of the nanoparticles (~ 1.6 nm observed by TEM) the signal is very broad. However, knowing the values of the position (20) and width at half height (FWHM) of the peak, it is possible to approximately know the size of the nanocrystal through the Scherrer equation (crystallite-size = (k· $\lambda$ )/( $\beta$ ·cos $\theta$ )). Applying this equation to our signal (FWHM of 8.723 °) the crystallite size was calculated for Ru@2, and it is approximately of 1 nm, which is in close agreement with TEM analysis.



Figure S1. XRD diffractogram of Ru@2. The peak with asterisk corresponds to Kapton foil.

Table S1. Compositions of Ru@1 and Ru@2.										
Ru NP <sup>[a]</sup>	Size (nm)	% Ru <sup>[a]</sup>	Ru <sub>x</sub> :L <sub>y</sub> <sup>[b]</sup>	Ru <sub>x</sub> /L <sub>y</sub>	Ru(s) <sup>[c]</sup>	% Ru(s) <sup>[c]</sup>	Ru(s) <sub>x</sub> /L <sub>y</sub>			
Ru@1	1.6 ± 0.4	58.8	163:17	9.6	99	60.7	5.8			

#### S3. ICP-AES and TGA

Ru@2	1.6 ± 0.5	57.6	163:18	9.0	99	60.7	5.5
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[a] % of Ru obtained by TGA [b] The total number of atoms is determined calculating the unit cell of Ru (hcp) per nanoparticle based on the diameter measured by TEM. [c] Number of surface atoms were estimated by using the atom's magic number approach (*ChemCatChem* 2011, **3**, 1413).



Figure S2. Thermogravimetric analysis (TGA) curve for Ru@1.



Figure S3. Thermogravimetric analysis (TGA) curve for Ru@2.



## S.4 MAS-NMR

Figure S4. <sup>13</sup>C MAS NMR spectra of Ru@1 (a, blue) and Ru@2 (b, red).



**Figure S5.** <sup>13</sup>C CP-MAS NMR spectra of **Ru@1** (a, blue) and **Ru@2** (b, red) after exposure to <sup>13</sup>CO (1 bar, 20 h, r.t.). The signals with asterisk correspond to spinning side bands.





**Figure S6.** DRIFT spectra of **Ru@1** before (blue) and after (red) CO adsorption (bubbling CO into a THF solution during 5 min). The bands with asterisk correspond to THF.



**Figure S7.** DRIFT spectra of **Ru@2** before (blue) and after (red) CO adsorption (bubbling CO into a THF solution during 5 min). The bands with asterisk correspond to THF.

S6. XPS



Figure S8. X-ray photoelectron spectroscopy (XPS) of the O 1s signals of (a) 1 and (b) Ru@1.



Figure S9. X-ray photoelectron spectroscopy (XPS) of the Ru 3p signal of (a) Ru@1 and (b) Ru@2.



Figure S10. X-ray photoelectron spectroscopy (XPS) survey spectrum of (a) Ru@1 and (b) Ru@2.

## **S7. DFT studies**



**Figure S11**. <sup>1</sup>H NMR chemical shielding and chemical shifts of **1** (top) and **2** (bottom) calculated at the DFT-PBE level of theory (see computational details).



c)  $\Delta E (Ru_{57}H_{37}) = -93.8 \text{ kcal.mol}^{-1} / \text{ ligand}$ 

d)  $\Delta E (Ru_{57}H_{47}) = -77.1 \text{ kcal.mol}^{-1} / \text{ ligand}$ 

Figure S12. Hydrogen coverage effect on the coordination energy on  $RuH_{37}@1$  (a and c) and  $RuH_{47}@1$  (b and d).



**Figure S13**. Density of States (DOS) and Crystal Orbital Hamilton Population (COHP) plots for the **Ru**<sub>57</sub>**H**<sub>37</sub>**@1** and **Ru**<sub>57</sub>**H**<sub>37</sub>**@2** models. With the exception of the CO states in **Ru@1**, the profiles for the two compounds are very similar. The position of the bottom of the d-band of the metal moiety is also shown, in addition to the Fermi energy and to the d-band centers of the surface and core metal atoms. An interesting feature in the COHP profiles is the presence of strongly coupled metal-1 or metal-2 states below the bottom of the d-band (blue and green filled peaks). This is typical of metal-to-ligand charge transfer (CT) states. The strong

interaction between the ligands and the metal surface thus originates both from a mixing of d orbitals and  $\sigma/\pi$  molecular orbitals of the ligands (blue and green COHP profiles above the bottom of the d-band) and from CT. This CT is in line with the quite strong electron-withdrawing strength of the **1** and **2** ligands, revealed by a charge analysis (see also next figure, **S12**). dbc values of **Ru@1** and **Ru@2** models are, respectively: 2.92 eV (surface) and 3.41 eV (core) *vs*. 2.91 eV (surface) and 3.43 eV (core). The MOs shown on the right are responsible for some high COHP(Ru-C) values (energies given w.r.t. The Fermi energy). Given the weak d DOS at *ca*. -10 eV (i.e. -7 eV wrt to the Fermi energy), MOs that lie at such energy also mainly have a CT character.



Figure S14. 3D MPA colour map of Ru<sub>57</sub>H<sub>37</sub>@1 and Ru<sub>57</sub>H<sub>37</sub>@2. Surface ruthenium atoms, in blue, are oxidized by all hydrides and by the protecting ligands. The oxidizing strength of 1 is slightly higher than that of 2. Hydrides exhibit the typical charge previously found in other systems (see for example the ESI of M. Cardona, P. Lecante, C. Dinoi, I. del Rosal, R. Poteau, K. Philippot and M. R. Axet, *Green Chem.*, 2021, 23, 8480; or in R. González-Gómez, L. Cusinato, C. Bijani, Y. Coppel, P. Lecante, C. Amiens, I. del Rosal, K. Philippot and R. Poteau, *Nanoscale* 2019, 11, 9392).



**Figure S15.** Second sphere of coordination through  $\pi$ - $\pi$  interactions between the aromatic rings of the nanographenes. Interaction energies between the second coordination sphere ligand and the **Ru@1** or **Ru@2** models are given below.



**Figure S16**. Coronene (a), dibenzosuberone (b) and benzophenone (c) adsorbed on the Ru<sub>57</sub>H<sub>37</sub> NP surface, on the same coordination sites as **1** and **2** in the **Ru@1** and **Ru@2** models. Average coordination energies per ligand are given below.



**Figure S17**. Electronic structure analysis of  $\mathbf{Ru}_{57}\mathbf{H}_{37}(\text{coronene})_3$ : pDOS and pCOHP profiles, to compare to Figure S9. The MOs shown on the right are responsible for some high COHP(Ru-C) values (energies given w.r.t. The Fermi energy). The two high-energy lying MOs were identified by the LCAO coefficient of the Ru atoms involved in the coordination. The 3D MPA colour map is inserted in the pDOS part (same scale as used in Figure S10).  $q_{Ru}$ : +0.21|*e*|;  $q_{Hi}$ : -0.22|*e*|;  $q_{coronene}$ : +1.32|*e*|. dbc values: 2.89 eV (surface) and 3.41 eV (core).



## S8. Liquid-NMR

Figure S18. <sup>1</sup>H-<sup>1</sup>H gCOSY expansion of the aromatic region of **Ru@1**.



**Figure S19.** <sup>1</sup>H-<sup>13</sup>C gHMBC spectra of **1** (top) and **Ru@1** (down), highlighting in red the signal corresponding to C=O group.



**Figure S20.** <sup>1</sup>H NMR spectra of **1** (red) and **Ru@1** (blue) in THF(d<sup>8</sup>). Cyclooctane comes from the reduction of Ru(COD)(COT) during the synthesis of RuNPs.



Figure S21. <sup>1</sup>H-<sup>1</sup>H gCOSY expansion of the aromatic region of Ru@2.



**Figure S22.** <sup>1</sup>H NMR spectra of **2** (red) and **Ru@2** (blue) in THF(d<sup>8</sup>). Cyclooctane comes from the reduction of Ru(COD)(COT) during the synthesis of RuNPs.



**Figure S23.** <sup>1</sup>H NMR spectrum of isolated cyclohexanol obtained after hydrogenation of phenol using Ru@2 as catalyst. The signal with \* correspond to the residual peak of CDCl<sub>3</sub>. The signal with # correspond to water traces present in CDCl<sub>3</sub>.



**Figure S24.** TEM pictures (a, b) after decomposition of Ru(COD)(COT) under 3 bar H<sub>2</sub> in the presence of 0.5 equiv. of coronene (20h, THF, r.t.).



**Figure S25.** TEM pictures (a-c) and size histograms (d) of RuNPs obtained after the decomposition of Ru(COD)(COT) under 3 bar  $H_2$  in the presence of 0.5 equiv. of benzophenone (20h, THF, r.t.).



**Figure S26.** TEM pictures (a,b) and size histogram (c) of RuNPs after decomposition of Ru(COD)(COT) under 3 bar H<sub>2</sub> in the presence of 0.5 equiv. of dibenzosuberone (20h, THF, r.t.).



**Figure S27**. HRTEM (a) and TEM (b) micrographs with the corresponding size histogram (c) of **Ru@1** after hydrogenation of acetophenone. Conditions: acetophenone (0.15 mmol), RuNPs (2 mg), THF (2 mL), hydrogen (10 bar), 50 °C, 20h.



**Figure S28**. HRTEM (a) and TEM (b) micrographs with the corresponding size histogram (c) of **Ru@2** after hydrogenation of acetophenone. Conditions: acetophenone (0.15 mmol), RuNPs (2 mg), THF (2 mL), hydrogen (10 bar), 50 °C, 20h



**Figure S29**. TEM micrographs (a, b) and the corresponding size histogram (c) of **Ru@1** after multiple addition experiment at 50 °C (96 h reaction). Conditions: anisole (0.15 mmol), RuNPs (2 mg), THF (2 mL), hydrogen (10 bar), 50 °C, 12h. Each 12 hours, anisole (0.15 mmol) was added to the reaction mixture.



**Figure S30**. TEM micrographs (a, b) and the corresponding size histogram (c) of **Ru@2** after multiple addition experiment at 50 °C (96 h reaction). Conditions: anisole (0.15 mmol), RuNPs (2 mg), THF (2 mL), hydrogen (10 bar), 50 °C, 12h. Each 12 hours, anisole (0.15 mmol) was added to the reaction mixture.



**Figure S31**. Multiple addition experiments for the hydrogenation of anisole catalyzed by **Ru@1** (a) and **Ru@2** (b). Conditions: anisole (0.15 mmol), RuNPs (2 mg), THF (2 mL), hydrogen (10 bar), 50 °C, 12h. Each 12 hours, anisole (0.15 mmol) was added to the reaction mixture. Conversions and selectivities were determined by GC using dodecane as internal standard, and confirmed by GC-MS.

## S.11 Catalytic studies



**Figure S32**. Hydrogenation of toluene under neat conditions using **Ru@2** as catalyst. Reaction conditions: 2 ml toluene, 2 mg **Ru@2** (7.2  $_{x}$  10<sup>-3</sup> mmol Ru assuming ~ 60% Ru from TGA/ICP and ~ 60% Ru(s)), 10 bar H<sub>2</sub>, 50 °C, 20 h.