

† Electronic Supplementary Information (ESI)

Tailoring graphene-supported Ru nanoparticles by functionalization with pyrene-tagged N-heterocyclic carbenes

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1. TEM

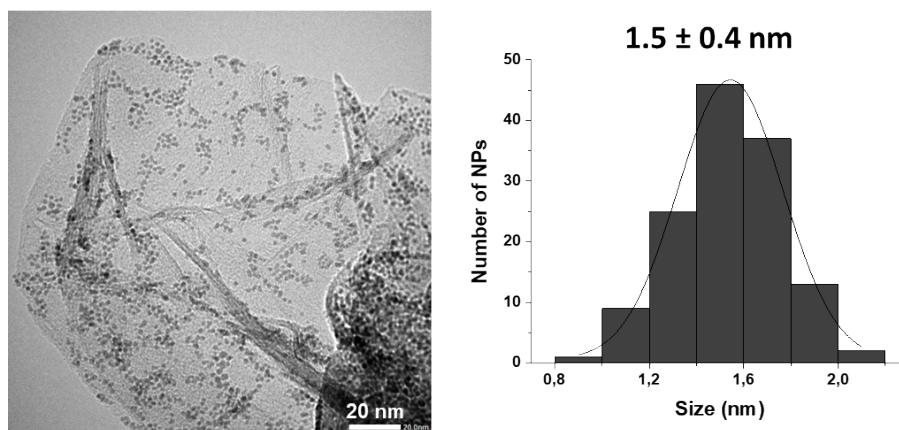


Figure S1. TEM image and size distribution histogram of Ru@rGO/pyr-IMes_{0.2}.

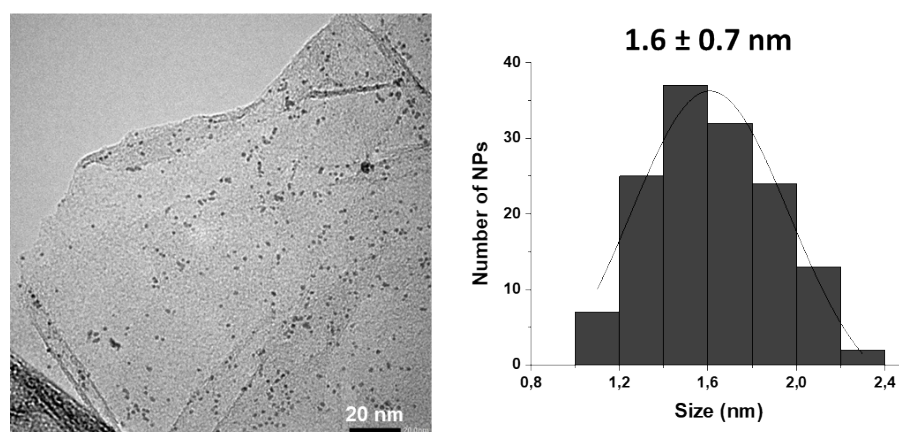


Figure S2. TEM image and size distribution histogram of Ru@rGO/pyr-IMes_{0.8}.

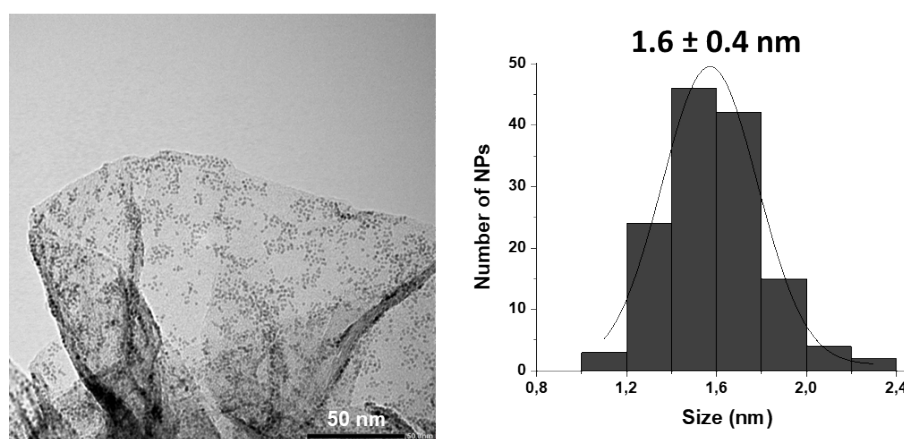


Figure S3. TEM image and size distribution histogram of Ru@rGO/pyr-IMes₁.

2. HRTEM

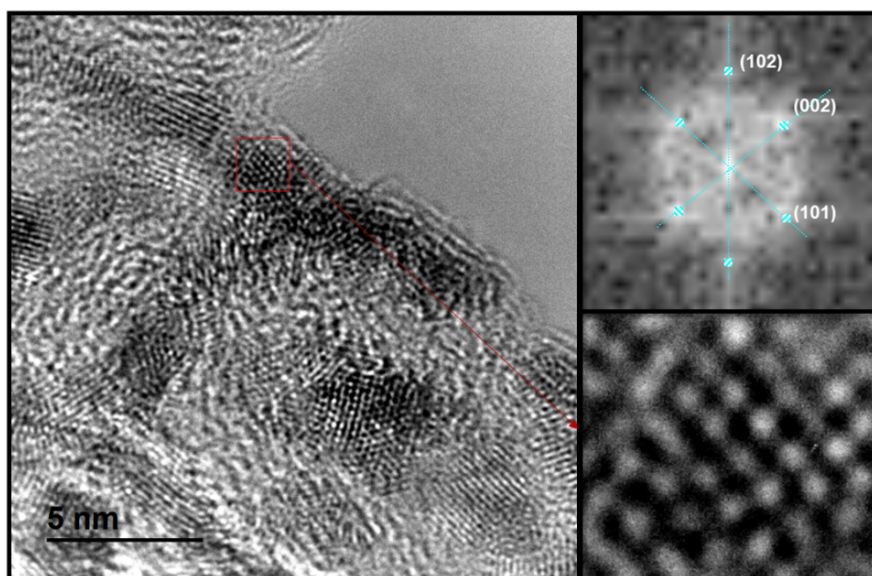


Figure S4. HRTEM micrographs of **Ru@rGO** (left, right bottom) and Fourier Transform Analysis with the planar reflections (right, top).

3. Raman

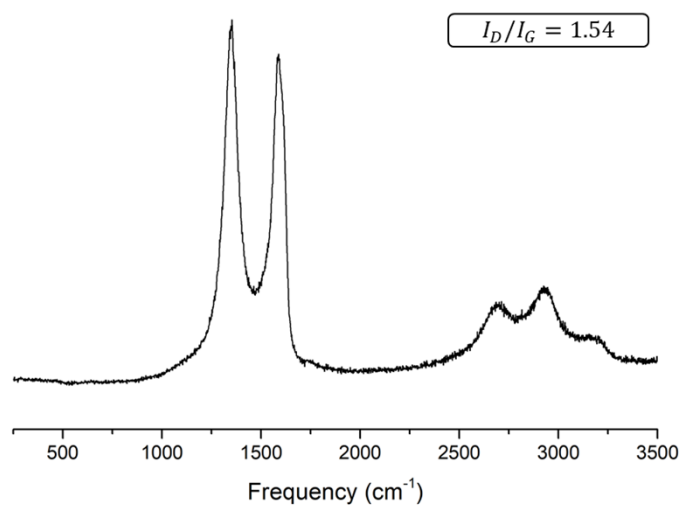


Figure S5. Raman spectrum and I_D/I_G ratio of **rGO**.

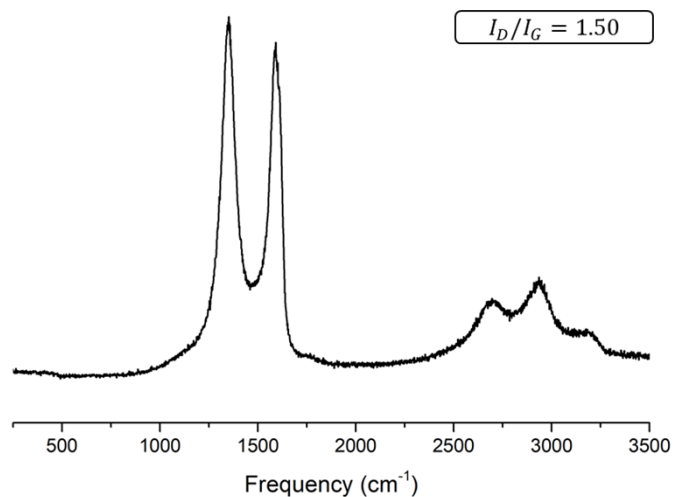


Figure S6. Raman spectrum and I_D/I_G ratio of **Ru@rGO**.

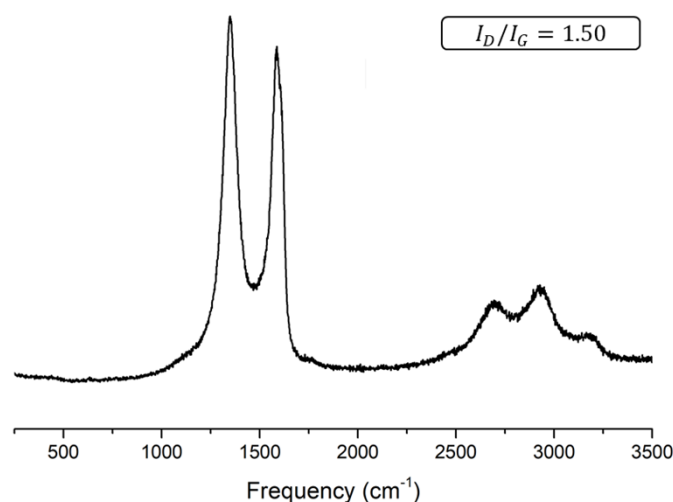


Figure S7. Raman spectrum and I_D/I_G ratio of **Ru@rGO/pyr-IMes_{0.5}**.

4. EA and BET surface area

Table S1. Elemental analysis (EA) and BET surface area of **Ru@rGO/pyr-IMes_x**. Determination of the precise number of equiv. of pyr-IMes incorporated to **Ru@rGO**.

	Ru@rGO/pyr-IMes_x			
	X = 0.2	X = 0.5	X = 0.8	X = 1
BET Surface area of Ru@rGO (nm²/100 mg)	$3.32 \cdot 10^{19}$	$3.32 \cdot 10^{19}$	$3.32 \cdot 10^{19}$	$3.32 \cdot 10^{19}$
EA (wt% N)	2.38	5.94	9.50	11.88
% N incorporated	49.61	52.47	49.58	50.34
pyr-IMes molecules per nm²	0.053	0.141	0.214	0.271
Actual n° equiv. of pyr-IMes	0.099	0.262	0.397	0.503

5. TEM of ligand-stabilized Ru NPs

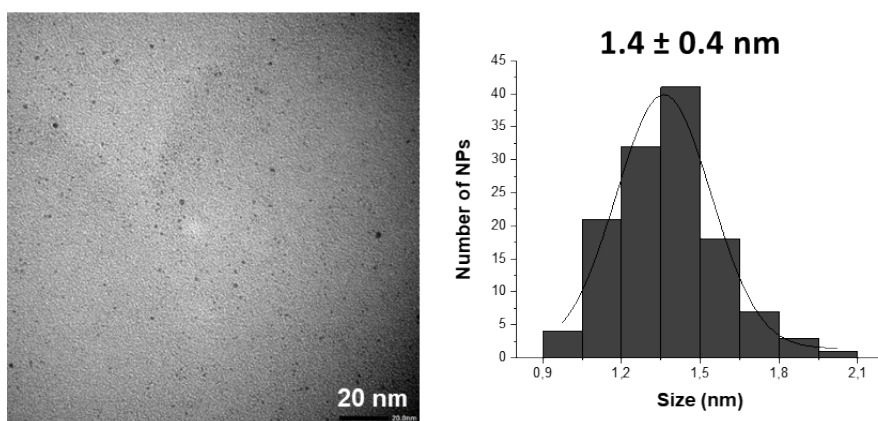


Figure S8. TEM image and size distribution histogram of **Ru/pyr-IMes_{0.2}**.

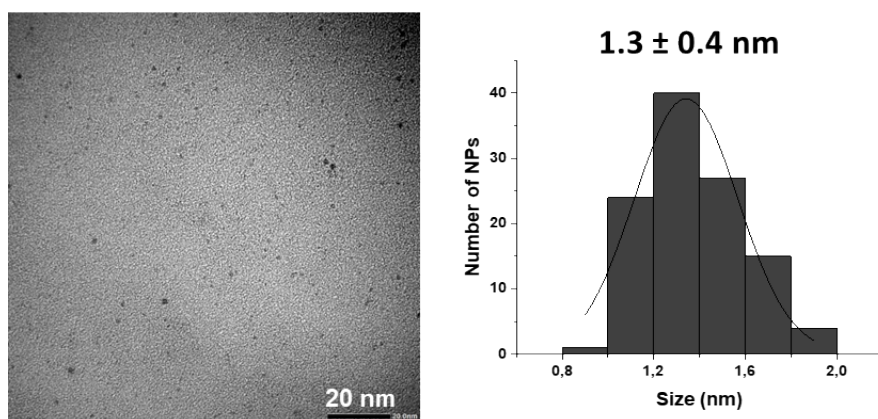


Figure S9. TEM image and size distribution histogram of **Ru/pyr-IMes_{0.5}**.

6. HRTEM of ligand-stabilized Ru NPs

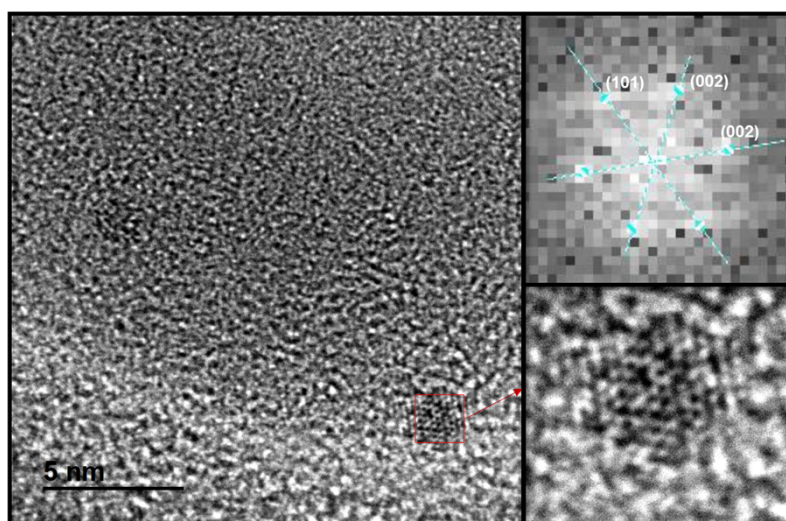


Figure S10. HRTEM micrographs of **Ru/pyr-IMes_{0.5}** (left, right bottom) and Fourier Transform Analysis with the planar reflections (right, top).

7. ICP-AES

Table S2. ICP analysis for **Ru/pyr-IMes_{0.2}** and **Ru/pyr-IMes_{0.5}**.

	Size (nm)	Ru (wt%) ^[a]	Ru _x :L _y ^[b]	Ru _x /L _y	Ru _(s) ^[c]	Ru _{(s)x} /L _y
Ru/pyr-IMes_{0.2}	1.4 ± 0.4	55.7	91:18	5	73	4.06
Ru/pyr-IMes_{0.5}	1.3 ± 0.4	33.2	132:44	2	62	1.41

[a] % of Ru obtained by ICP analysis. [b] The total number of atoms was determined calculating the unit cell of Ru (hcp) per MNP, based on the mean diameter measured by TEM. [c] Number of surface atoms. Approximate values obtained from ref.1.

8. DRIFT

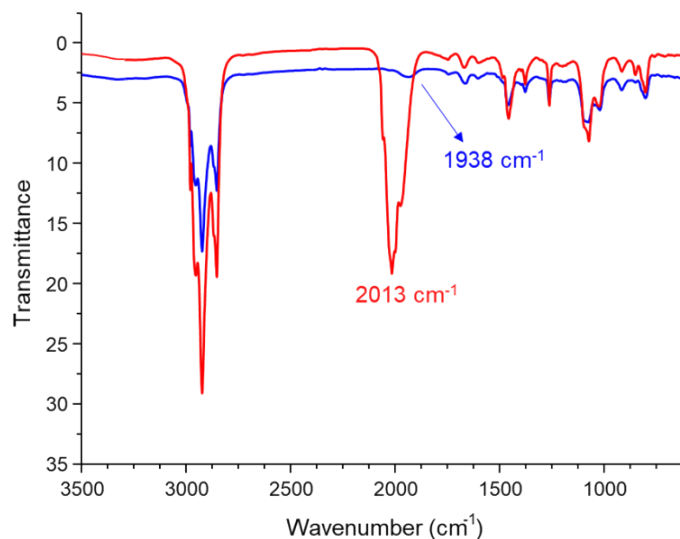


Figure S11. DRIFT spectra of a sample of **Ru/pyr-IMes_{0.2}** before (blue) and after (red) exposure to CO (bubbling CO into a THF solution for 5 min).

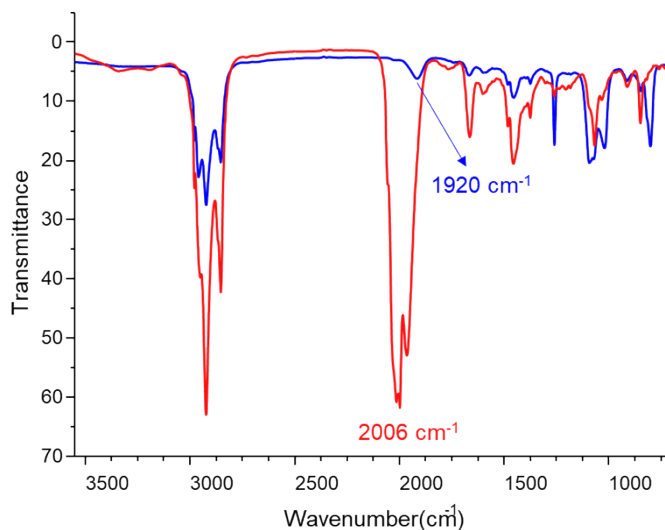


Figure S12. DRIFT spectra of a sample of **Ru/pyr-IMes_{0.5}** before (blue) and after (red) exposure to CO (bubbling CO into a THF solution for 5 min).

9. MAS-NMR

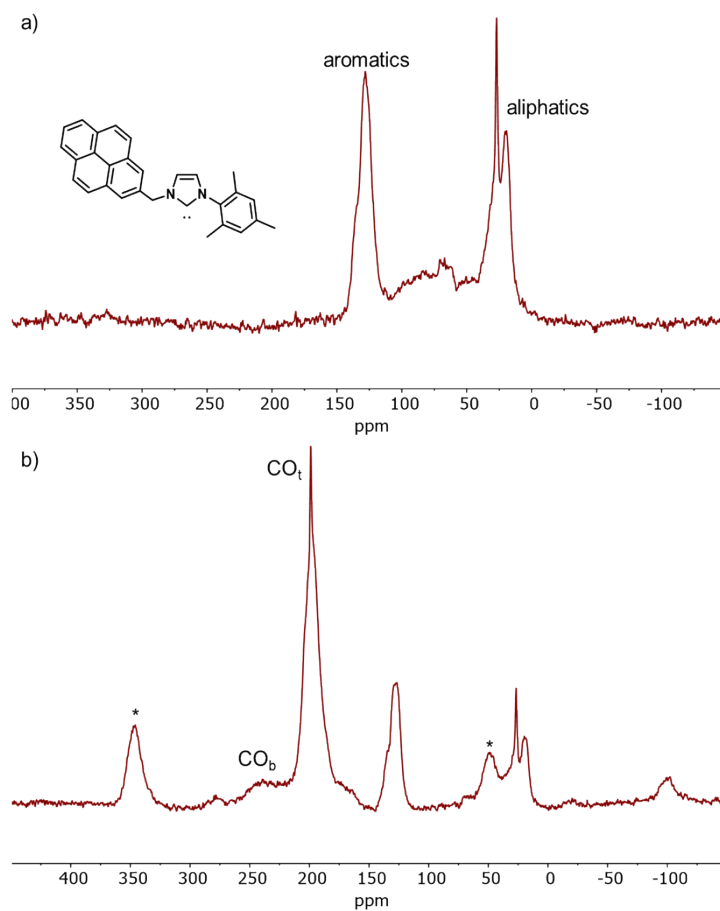


Figure S13. $^{13}\text{C}\{^1\text{H}\}$ CP-MAS NMR spectra for Ru/pyr-IMes_{0.2} (a) before and (b) after exposure to ^{13}CO (1bar, ^{13}CO , 20h, r.t.). Asterisks mark the positions of spinning side bands (*).

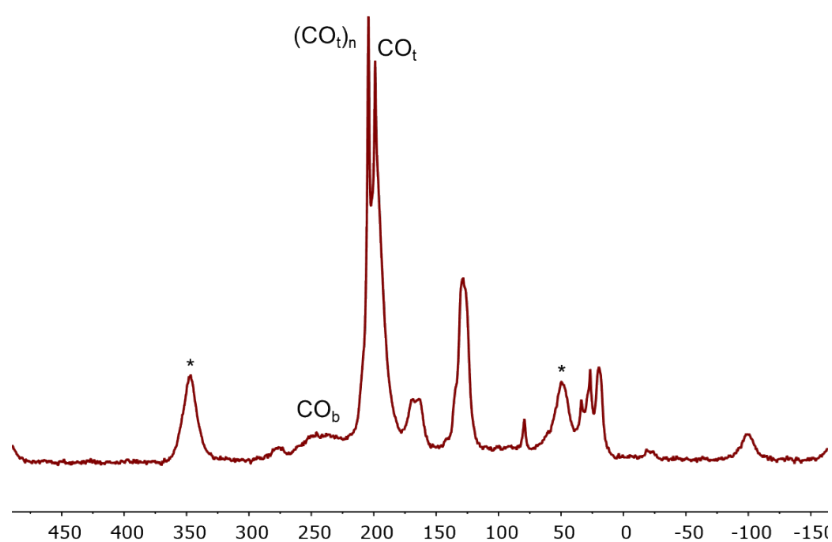


Figure S14. C-MAS NMR spectra for Ru/pyr-IMes_{0.5} after exposure to ^{13}CO (1bar ^{13}CO , 20h, r.t.). Asterisks mark the positions of spinning side bands (*).

10. XPS

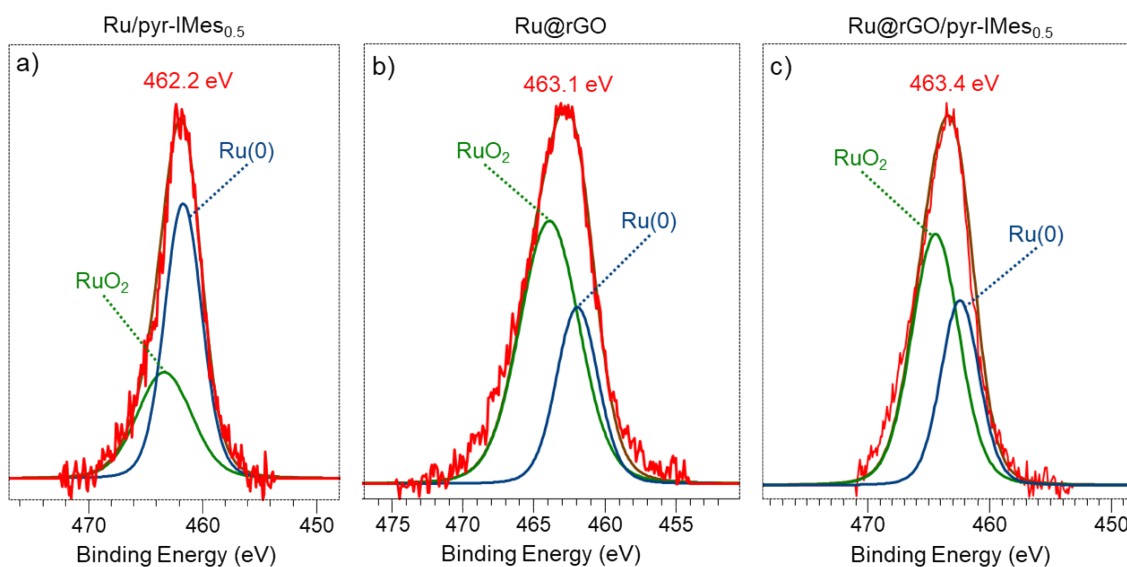


Figure S15. X-ray photoelectron spectroscopy (XPS) of the Ru 3p_{3/2} signals of (a) Ru/pyr-IMes_{0.5}, (b) Ru@rGO and (c) Ru@rGO/pyr-IMes_{0.5}.

11. TEM after catalysis

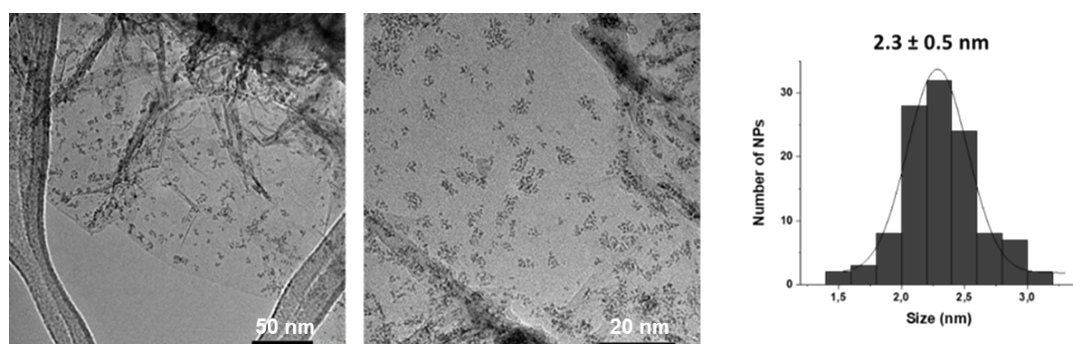


Figure S16. TEM images and size histogram of Ru@rGO after catalysis.

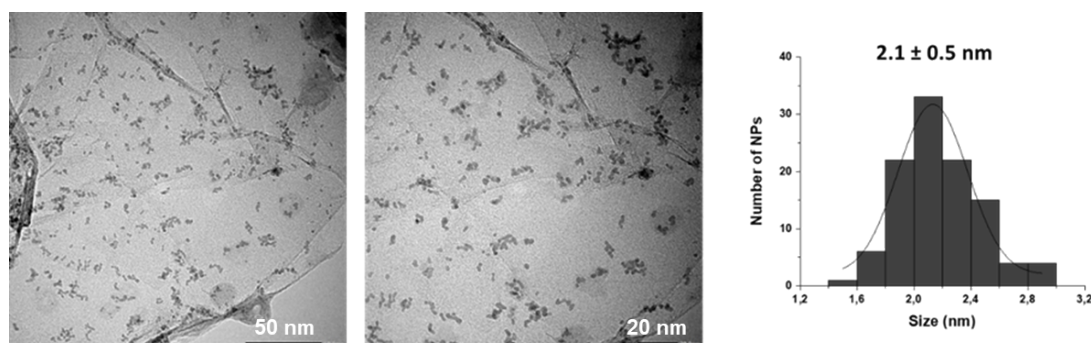


Figure S17. TEM images and size histogram of Ru@rGO/pyr-IMes_{0.2} after catalysis.

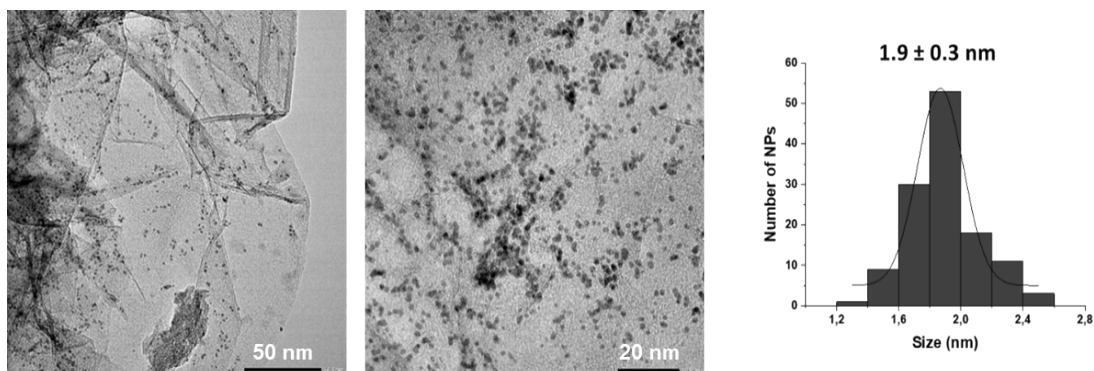


Figure S18. TEM images and size histogram of Ru@rGO/pyr-IMes_{0.5} after catalysis.

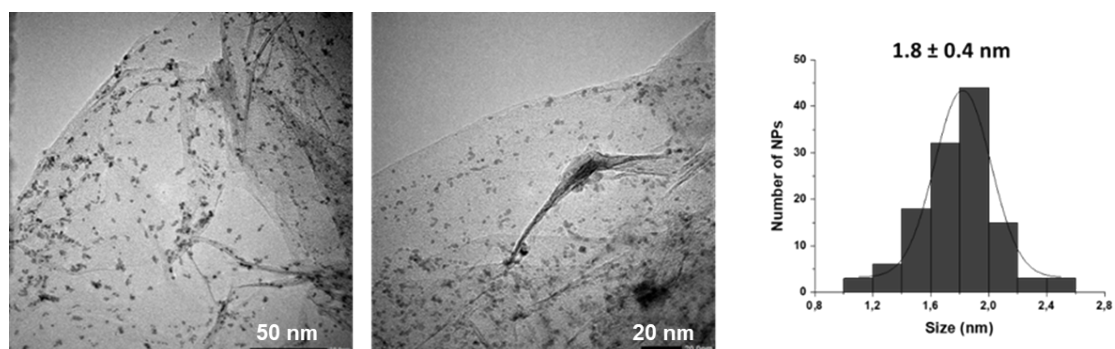


Figure S19. TEM images and size histogram of Ru@rGO/pyr-IMes_{0.8} after catalysis.

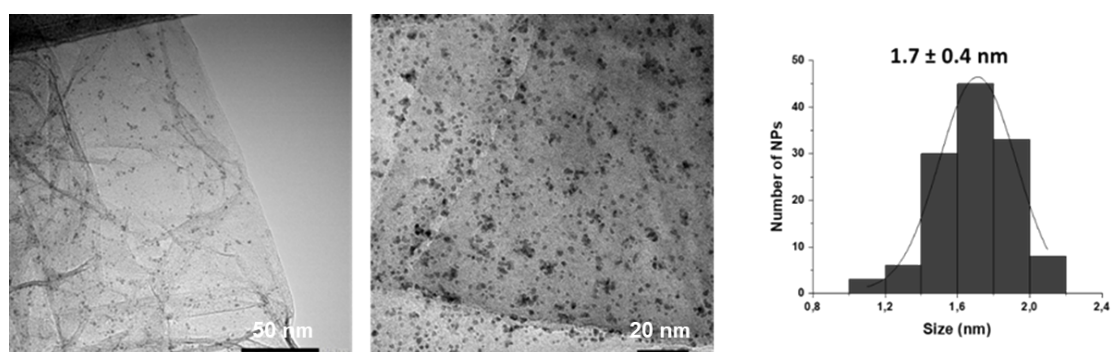


Figure S20. TEM images and size histogram of Ru@rGO/pyr-IMes₁ after catalysis.

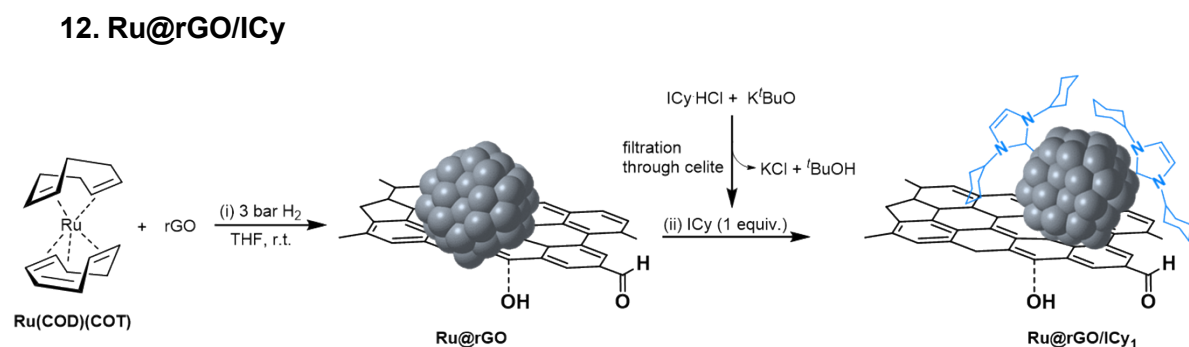


Figure S21. Two-step synthetic route followed for the synthesis and subsequent functionalization of Ru@rGO with ICy.

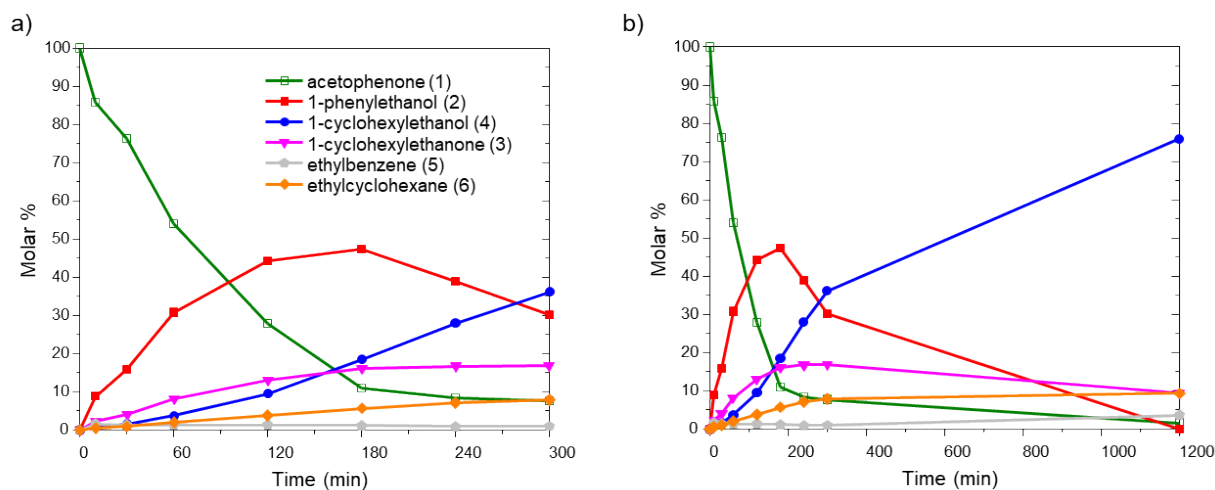


Figure S22. Hydrogenation of acetophenone using Ru@rGO/ICy₁ as catalysts at short (a) and long (b) reaction times.

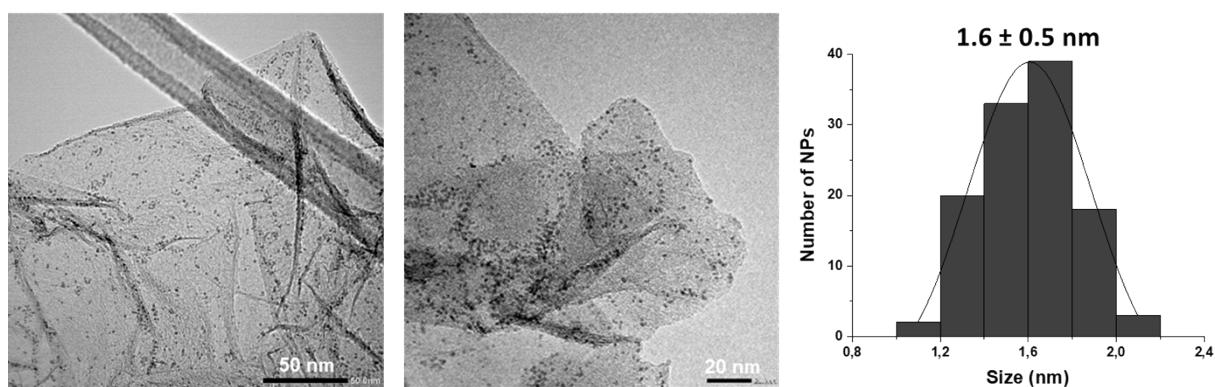


Figure S23. TEM images and size histogram of Ru@rGO/ICy₁.

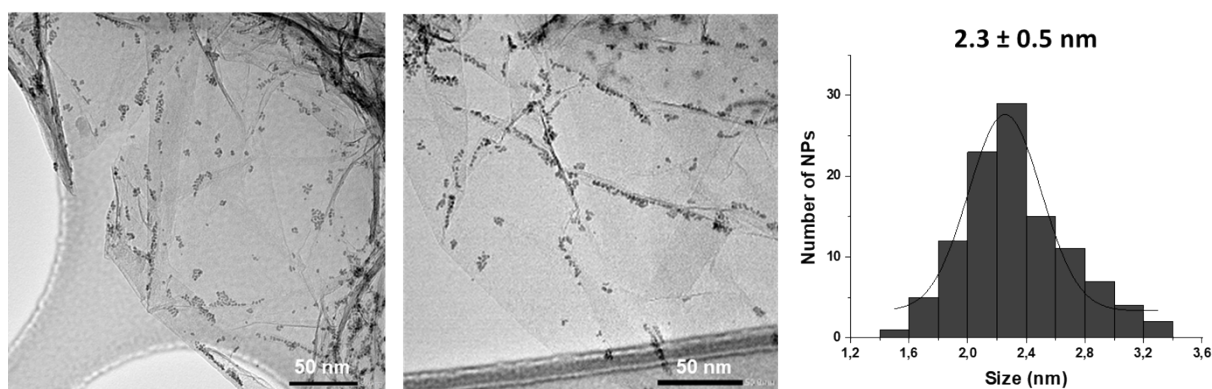


Figure S24. TEM images and size histogram of Ru@rGO/ICy₁ after catalysis.

13. Multiple addition experiment

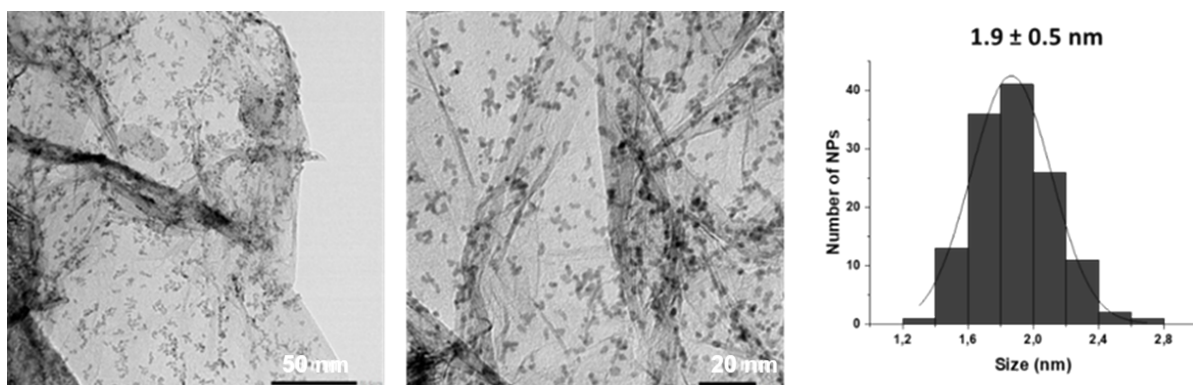


Figure S25. TEM images and size histogram of **Ru@rGO/pyr-IMes_{0.5}** after multiple addition catalysis.

14. “Hot Filtration”

Table S3. Conversions of **Ru@rGO/pyr-IMes_{0.5}** in acetophenone hydrogenation after thermal filtration^a and in the presence of catalyst.^b

Catalyst	2h	4 h
Ru@rGO/pyr-IMes_{0.5}^a	59 %	59 %
Ru@rGO/pyr-IMes_{0.5}^b	57 %	88%

¹ A. P. Umpierre, E. de Jesús and J. Dupont, *ChemCatChem*, 2011, **3**, 1413.