Supporting Information
for

Heterometal nanoparticles from Ru-based molecular
clusters covalently anchored onto functionalized carbon
nanotubes and nanofibers

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Additional Experimental Data

Table S1: Characterization of clusters.

| Cluster | Synthesis yield (%) | IR ν_{CO} (cm\(^{-1}\))\(^{a,b}\) | Elemental analysis (%) (calculated values) | Ref. |
|---------|---------------------|----------------------------------|------------------------------------------|------|
| [Ru\(_6\)C(CO)\(_{17}\)] (1) | 71 | 2068 (s), 2047 (s) (hexane) | Not determined | [30] |
| [Ru\(_6\)C(CO)\(_{15}\)] (2) | 89 | 2068 (s), 2034 (m), 2018 (w) (hexane) | Not determined | [30] |
| [Ru\(_6\)PtC(CO)\(_{16}\)(COD)] (3) | 31 | 2078 (m), 2035 (s), 2002 (m), 1975 (w), 1943 (w) 1821 (w) | C 20.59 (21.92), H 1.50 (0.88) | [31] |
| [Ru\(_5\)PtC(CO)\(_{14}\)(COD)] (4) | 67 | 2077 (m), 2050 (s), 2033 (s), 2011 (s), 1989 (w), 1966 (w) 1818 (w) | C 22.43 (22.78), H 1.10 (1.00) | [31] |
| [Ru\(_6\)C(CO)\(_{16}\)(Au\{PPh\(_3\}\})\(_2\)] (5) | 84 | 2067 (w), 2049 (s), 2017 (vs), 1965 (w), 1821 (m) | C 32.15 (32.07), H 1.64 (1.52) | [32] |
| [Ru\(_5\)C(CO)\(_{14}\)(Au\{PPh\(_3\}\})\(_2\)] (6) | 75 | 2065 (m), 2035 (m), 2020 (s), 2008 (s), 1975 (m), 1845 (w) | C 33.31 (33.51), H 1.64 (1.65) | [33, 34] |
| [Ru\(_4\)C(CO)\(_{12}\)(Au\{PPh\(_3\}\})\(_2\)] (7) | 67 | 2064 (vw), 2032 (s), 2022 (s), 2008 (w), 1990 (m), 1954 (w) | C 34.94 (35.22), H 1.71 (1.81) | [34] |
| [Ru\(_5\)PtC(CO)\(_{15}\)(Au\{PPh\(_3\}\})\(_2\)] (8) | 73 | 2068 (m), 2038 (s), 2015 (vs), 1968 (m), 1859 (m), 1834 (m) | C 30.55 (30.45), H 1.70 (1.47) | [35] |
| (PPN)[Ru\(_5\)Co(CO)\(_{13}\)] (9) | 57 | 2069 (w), 2019 (vs), 1824 (w), 1793 (w) | C 44.05 (46.53), H 2.57 (2.40), N 1.11 (1.11) | [36] |

\(^{a}\)Abbreviations: s = strong, m = medium, w = weak, br = broad and sh = shoulder

\(^{b}\)Infrared spectra of the clusters were recorded in dichloromethane solution, unless otherwise stated.
Table S2: Thermogravimetric analysis under N₂.

| Cluster                                      | Weight loss (%) | Final decomposition temperature (°C) | Calculated weight loss (%) | Weight loss at selected activation temperature (%)^a |
|----------------------------------------------|-----------------|--------------------------------------|-----------------------------|-----------------------------------------------|
| [Ru₆C(CO)₁₇] (1)                             | 44              | 300                                  | 44                          | 44                                            |
| [Ru₅C(CO)₁₃] (2)                             | 47              | 300                                  | 45                          | 47                                            |
| [Ru₆PtC(CO)₁₆(COD)] (3)                      | 38              | 300                                  | 41                          | 38                                            |
| [Ru₅PtC(CO)₁₄(COD)] (4)                      | 38              | 300                                  | 41                          | 38                                            |
| [Ru₆C(CO)₁₆(Au{PPh₃})₂] (5)                  | 48              | 750                                  | 49                          | 32                                            |
| [Ru₅C(CO)₁₄(Au{PPh₃})₂] (6)                  | 49              | 900                                  | 50                          | 26                                            |
| [Ru₅C(CO)₁₄(Au{PPh₃})₂] (7)                  | 53              | 900                                  | 52                          | 34                                            |
| [Ru₅PtC(CO)₁₅(Au{PPh₃})₂] (8)                | 45              | 800                                  | 46                          | 30                                            |
| (PPN)[Ru₃Co(CO)₁₃] (9)                        | 57              | 900                                  | 71                          | 36                                            |

^a300 °C for clusters 1 to 4, 350 °C for clusters 5 to 8 and 400 °C for cluster 9.
Table S3: Loading and XPS results for the incorporation of clusters 1 to 8 on CNFs and MWNTs.

| Cluster | Support   | Metal loading (wt %)\(^a\) | XPS | M/C\(_{\text{calc}}\)\(^b\) (×100) | M/C\(_{\text{exp}}\) before act. (×100) | M/C\(_{\text{exp}}\) after act. (×100) |
|---------|-----------|-----------------------------|-----|-----------------------------------|---------------------------------------|---------------------------------------|
| 1       | CNF–PPh\(_2\) | 2.0                         | Ru  | 0.25                             | 0.85                                  | 0.97                                  |
|         | MWNT–PPh\(_2\) | 4.2                         | Ru  | 0.53                             | 0.36                                  | 0.30                                  |
| 2       | CNF–PPh\(_2\) | 2.3                         | Ru  | 0.28                             | 1.45                                  | 1.14                                  |
|         | MWNT–PPh\(_2\) | 3.0                         | Ru  | 0.37                             | 0.36                                  | 0.24                                  |
| 3       | CNF–PPh\(_2\) | 2.2                         | Ru  | 0.19                             | 0.83                                  | 0.69                                  |
|         |           | Pt                          |     | 0.04                             | 0.25                                  | 0.27                                  |
|         | MWNT–PPh\(_2\) | 3.1                         | Ru  | 0.28                             | 0.22                                  | 0.16                                  |
|         |           | Pt                          |     | 0.06                             | 0.10                                  | 0.10                                  |
| 4       | CNF–PPh\(_2\) | 2.8                         | Ru  | 0.24                             | 1.08                                  | 0.94                                  |
|         |           | Pt                          |     | 0.06                             | 0.34                                  | 0.39                                  |
|         | MWNT–PPh\(_2\) | 4.4                         | Ru  | 0.38                             | 0.40                                  | 0.29                                  |
|         |           | Pt                          |     | 0.09                             | 0.12                                  | 0.14                                  |
| 5       | CNF–PPh\(_2\) | 2.2                         | Ru  | 0.14                             | 0.73                                  | 0.49                                  |
|         |           | Au                          |     | 0.07                             | 0.39                                  | 0.17                                  |
|         | MWNT–PPh\(_2\) | 2.8                         | Ru  | 0.20                             | 0.15                                  | 0.09                                  |
|         |           | Au                          |     | 0.08                             | 0.11                                  | 0.04                                  |
| 6       | CNF–PPh\(_2\) | 2.6                         | Ru  | 0.17                             | 0.61                                  | 0.62                                  |
|         |           | Au                          |     | 0.08                             | 0.45                                  | 0.13                                  |
|         | MWNT–PPh\(_2\) | 2.8                         | Ru  | 0.18                             | 0.14                                  | 0.09                                  |
|         |           | Au                          |     | 0.09                             | 0.12                                  | 0.05                                  |
| 7       | CNF–PPh\(_2\) | 1.1                         | Ru  | 0.06                             | 0.18                                  | 0.21                                  |
|         |           | Au                          |     | 0.04                             | 0.13                                  | 0.05                                  |
|         | MWNT–PPh\(_2\) | 2.0                         | Ru  | 0.12                             | 0.06                                  | 0.04                                  |
|         |           | Au                          |     | 0.07                             | 0.05                                  | 0.03                                  |
| 8       | CNF–PPh\(_2\) | 2.3                         | Ru  | 0.11                             | 0.47                                  | 0.33                                  |
|         |           | Pt                          |     | 0.03                             | 0.16                                  | 0.11                                  |
|         |           | Au                          |     | 0.07                             | 0.47                                  | 0.08                                  |
|         | MWNT–PPh\(_2\) | 2.6                         | Ru  | 0.12                             | 0.04                                  | 0.02                                  |
|         |           | Pt                          |     | 0.03                             | 0.05                                  | 0.06                                  |
|         |           | Au                          |     | 0.02                             | 0.09                                  | 0.03                                  |

\(^a\)Metal loading calculated from incorporation yield determined by ICP analysis of metals in the solid samples.

\(^b\)Calculated values are bulk molar ratios based on the experimental metal loadings. The amount of metal taken into consideration for the calculations corresponds to the amount incorporated on the support. The amount of C taken into consideration corresponds to the amount of support used by considering that it is only constituted of carbon.
**Figure S1:** Positive SIMS spectrum of cluster 4 incorporated on CNF–PPh₂ (before thermal treatment).
Figure S2: TEM images of cluster \([\text{Ru}_6\text{C(CO)}_{16}(\text{Au}\{\text{PPh}_3\})_2]\) (5) after thermal treatment: (a) on CNF-PPh\(_2\), (b) on MWNT-PPh\(_2\). TEM images of cluster 6 to 8 on MWNT-PPh\(_2\) after thermal treatment: (c) \([\text{Ru}_5\text{Au}_2\text{C(CO)}_{14}(\text{PPh}_3)_2]\) (6), (d) \([\text{Ru}_4\text{Au}_2\text{C(CO)}_{12}(\text{PPh}_3)_2]\) (7) and (e) \([\text{Ru}_5\text{PtAu}_2\text{C(CO)}_{15}(\text{PPh}_3)_2]\) (8). EDXS analysis of the large particles for cluster 5 on CNF-PPh\(_2\) (f).
Physicochemical methods of characterization

The experimental strategies were in general very similar to our previous, related, studies [J. Mater. Chem., 2013, 1, 2050-2063; Catal. Today, 2014, 235, 112-126]. Infrared spectra of the clusters were recorded in dichloromethane solution on a Bruker Equinox 55 spectrometer with a solution cell from Perkin Elmer.

The elemental analyses (C, H, N) were performed by the Analytical Chemistry service of University College London.

XPS analyses were performed on a Kratos Axis Ultra spectrometer (Kratos Analytical – Manchester – UK) equipped with a monochromatized aluminum X-ray source (powered at 10 mA and 15 kV). The sample powders were pressed into small stainless steel troughs mounted on a multi specimen holder. The pressure in the analysis chamber was about 10\(^{-6}\) Pa. The angle between the normal to the sample surface and the direction of photoelectrons collection was about 0°. Analyses were performed in the hybrid lens mode, the resulting analyzed area being 700 × 300 µm. The pass energy was set at 160 eV for the survey scan and 40 eV for narrow scans. In the latter conditions, the full width at half maximum (FWHM) of the Ag 3d\(_{5/2}\) peak of a standard silver sample was about 0.9 eV. Charge stabilization was achieved by using the Kratos Axis device. The following sequence of spectra was recorded: survey spectrum, C 1s, O 1s, N 1s, Cl 2p, S 2p, P 2p, Pt 4f (or Au 4f) and C 1s again to check for charge stability and the absence of degradation of the sample during the analyses. The C–(C,H) component of the C1s carbon peak has been fixed at 284.8 eV to set the binding energy scale. Spectra were decomposed with the CasaXPS program (Casa Software Ltd., UK) with a Gaussian/Lorentzian (70/30) product function and after subtraction of a linear baseline. Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters, experimental sensitivity factors and transmission factors provided by the manufacturer. The constraints used for decomposition of p, d and f doublets are summarized in Table S4, with the FWHM ratio being equal to 1 in all cases. Given the overlap of the C 1s and Ru 3d\(_{5/2}\) peaks, these constraints were particularly important in order to quantify ruthenium. The following method was
used: a Gaussian/Lorentzian (85/15) was placed at the position of the Ru 3d\(_{5/2}\) peak, which is visible on the right-hand side (lower binding energy) of the C 1s peak. The contribution of the Ru 3d\(_{5/2}\) peak to subtract from the carbon component was calculated by reference to the Ru 3d\(_{5/2}\) peak by placing another Lorentzian/Gaussian (85/15) at 4.17 eV toward higher binding energy, and imposing an area ratio equal to 0.667. Because of this problem of overlap, the experimental error on the Ru surface atomic concentration is high and therefore the Ru/C surface ratios have to be taken with caution.

**Table S4:** Constraints for XPS results treatment.

| Analytical peaks | Area ratio | Δ(B−A) (eV) |
|------------------|------------|-------------|
|                  | A          | B/A         |              |
| Cl 2p\(_{3/2}\)  | Cl 2p\(_{1/2}\) | 0.500      | 1.6          |
| S 2p\(_{3/2}\)   | S 2p\(_{1/2}\)  | 0.500      | 1.18         |
| P 2p\(_{3/2}\)   | P 2p\(_{1/2}\)  | 0.500      | 0.84         |
| Ru 3d\(_{5/2}\)  | Ru 3d\(_{3/2}\)  | 0.667      | 4.17         |
| Pt 4f\(_{7/2}\)  | Pt 4f\(_{5/2}\)  | 0.750      | 3.33         |
| Au 4f\(_{7/2}\)  | Au 4f\(_{5/2}\)  | 0.750      | 3.67         |

Atomic emission measurements (ICP-AES) of platinum, gold and ruthenium were carried out on a ICAP6500 spectrophotometer from Thermo Scientific.

TOF-SIMS measurements were performed with an IONTOF V spectrometer. The sample was bombarded with pulsed Bi\(_3^+\) ions (30 keV). The analyzed area used in this work was a square of 500 × 500 µm and the data acquisition time was 60 s. On insulating samples (such as the pure clusters), charge effects were compensated by means of an interlaced pulsed electron flood gun (\(E_k = 20\) eV). With these parameters, the primary ion dose density was lower than \(10^{11}\) Bi\(^+/\)cm\(^2\). The powders were pressed with a spatula onto a double-sided silver adhesive sheet.
TGA analyses of the clusters were recorded on a SDT 2960 simultaneous DSC-TGA instrument from TA Instruments. These analyses were carried out with a heating ramp of 10 °C/min under N₂ flow (100 mL/min) with the samples placed into alumina containers.

Low magnification Transmission Electron Microscopy (TEM) images were obtained with a LEO 922 OMEGA energy filter TEM operated at 200 kV. The sample is prepared by suspending the solid samples in hexane which is then sonicated for 1 min. One drop of supernatant was then deposited on a holey carbon film supported on a copper grid, before being dried at room temperature overnight under vacuum prior to imaging.

High resolution TEM (HRTEM) studies were carried out by dispersing the sample powder in ethanol. The diluted suspension went through ultrasonic treatment for approximately 10 min to obtain a better dispersion, before being dropped onto a holey carbon film on a copper TEM grid. Aberration corrected HRTEM, high resolution high angle annular dark field scanning transmission electron microscopy (HAADF-STEM) and energy dispersive X-ray spectroscopy (STEM-EDX) experiments were carried out on a FEI Titan 50-80 “cube” microscope fitted with an aberration-corrector for the imaging lens and another for the probe forming lens as well as a monochromator and EDX detector, operated at 120kV in order to minimize knock-on damage to the supporting CNTs and CNFs. The monochromator was excited to extend the information limit down to approximately 1Å. HAADF-STEM was performed using a convergence semi-angle of 21.5 mrad.
Catalysis

i. Catalyst preparation

In a first step, the ruthenium-based precursors (2), (4), (6), (8) or (9) (5 wt % of Ru after ligands removal) and 850 mg of phosphine or ammonium functionalized nanofibers were introduced together in a 100 mL Schlenk flask with 1:1 mixture of toluene/dichloromethane (total volume = 80 mL). Then, the suspension was stirred at room temperature for 5 days in the dark under N$_2$ atmosphere. Finally, the solid was filtered out, washed with dichloromethane and dried at room temperature under vacuum. In the second step, the solid sample was pre-activated. It was placed into porcelain combustion boats and heated under N$_2$ stream at selected temperature during 1 h in a tubular oven. In the third step, the activated sample was reintroduced in a 100 mL Schlenk flask. Cesium oxalate was added to the solid (ratio 1:1 with respect to ruthenium, which was determined by ICP after activation under N$_2$) in a mixture of methanol/air-free water (9:1, total volume = 30 mL). The suspension was stirred at room temperature for 1 hour under N$_2$ atmosphere and then the solvent was evacuated in vacuo. The solid was dried overnight. The final activation was realized after charging the catalysts in the microreactor (400 °C, 4 h, under H$_2$). Table S5 summarizes the experimental conditions used for ruthenium-based catalysts synthesis.
Table S5: Experimental conditions used for the incorporation of ruthenium-based clusters on various supports.

| Precursor | Precursor quantity (mg) | Support | Temperature of pre-activation |
|-----------|-------------------------|---------|-----------------------------|
| [Ru₅C(CO)₁₅] (2) = Cat1 | 79 | CNF-PPh₂ | 300 °C |
| [Ru₅PtC(CO)₁₄(COD)] (4) = Cat2 | 102 | CNF-PPh₂ | 300 °C |
| [Ru₃C(CO)₁₄(Au{PPh₃})₂] (6) = Cat3 | 154 | CNF-PPh₂ | 350 °C |
| [Ru₅PtC(CO)₁₄(Au{PPh₃})₂] (8) = Cat4 | 172 | CNF-PPh₂ | 350 °C |
| (PPN)[Ru₅Co(CO)₁₃] (9) = Cat5 | 177 | CNF-NMe₃⁺ | 400 °C |

ii. Catalyst testing

The catalytic tests were realized in a lab plant constructed for ammonia synthesis as presented in Figure S3. Two laboratory lines, N₂ and H₂ lines, were used with regulatory valves, to feed reagents. The flow rates were regulated with needle valves and were measured with a bubble flowmeter placed at the end of the plant. H₂ and N₂ from their lines went through a mixer where they were mixed together in the stoichiometric ratio (3:1) before going in the reactor. There, in the presence of a catalyst and at the controlled temperature, they reacted and then went through a series of gas collectors, the first two filled with a 0.1 mol/L solution of HCl and the last one with distilled water and a few drops of phenolphthalein as indicator to visualize any possible passage of NH₃. After this, the exit gas went into an aspirating nose connected to the global suction system. The ammonia produced was obtained by titration of liquid collected in the first two traps with NaOH 0.1 mol/L and phenolphthalein as indicator.

Reaction Conditions:
- Charge: 0.5 g of catalyst
- Pressure: atmospheric
- Temperature: from 250 to 400 °C
- H₂/N₂ (molar ratio) = 3:1
- Global Flow Rate: 40 mL/min at STP conditions
Figure S3: Laboratory plant for ammonia synthesis.
## Ammonia synthesis: results

Table S6. Results in ammonia synthesis for Cs-promoted Ru\textsubscript{5}/CNF-PPh\textsubscript{2} (Cat1)

|                        | 225°C | 250°C | 275°C | 300°C |
|------------------------|-------|-------|-------|-------|
| Time of test (h)       | 7     | 7     | 7     | 7     |
| Weight of catalyst (g) | 0.5042| 0.5042| 0.5042| 0.5042|
| Total moles of NH\textsubscript{3} produced | 0.0036| 0.0026| 0.0033| 0.0023|
| Moles/h of NH\textsubscript{3} produced | 0.0005| 0.0004| 0.0005| 0.0003|
| mmol/h*g cata          | 1.0115| 0.7367| 0.9251| 0.6446|
| Nitrogen feed (moles/h)| 0.0268| 0.0268| 0.0268| 0.0268|
| Hydrogen feed (moles/h)| 0.0803| 0.0803| 0.0803| 0.0803|
| Degree of conversion   | 0.0095| 0.0069| 0.0087| 0.0060|
| NH\textsubscript{3} production (%) | 0.4786| 0.3481| 0.4375| 0.3044|
Table S7. Results in ammonia synthesis for Cs-promoted Ru₅Pt/CNF-PPh₂ (Cat2)

|                          | 325°C | 350°C | 375°C | 400°C |
|--------------------------|-------|-------|-------|-------|
| Time of test (h)         | 6     | 6     | 6     | 6     |
| Weight of catalyst (g)   | 0.5506| 0.5506| 0.5506| 0.5506|
| Total moles of NH₃ produced | 0.0025| 0.0026| 0.0025| 0.0024|
| Moles/h of NH₃ produced  | 0.0004| 0.0004| 0.0004| 0.0004|
| mmol/h*g cata            | 0.7416| 0.7870| 0.7416| 0.7113|
| Nitrogen feed (moles/h)  | 0.0268| 0.0268| 0.0268| 0.0268|
| Hydrogen feed (moles/h)  | 0.0803| 0.0803| 0.0803| 0.0803|
| Degree of conversion     | 0.0076| 0.0081| 0.0076| 0.0073|
| NH₃ production (%)       | 0.3828| 0.4063| 0.3828| 0.3671|
Table S8. Results in ammonia synthesis for Cs-promoted Ru$_5$Au$_2$/CNF-PPh$_2$ (Cat3)

|                          | 350°C | 375°C | 400°C |
|--------------------------|-------|-------|-------|
| Time of test (h)         | 5     | 5     | 5     |
| Weight of catalyst (g)   | 0.5072| 0.5072| 0.5072|
| Total moles of NH$_3$ produced | 0.0009| 0.0011| 0.0006|
| Moles/h of NH$_3$ produced | 0.0002| 0.0002| 0.0001|
| mmol/h*g cata            | 0.3687| 0.4383| 0.2354|
| Nitrogen feed (moles/h)  | 0.0268| 0.0268| 0.0268|
| Hydrogen feed (moles/h)  | 0.0803| 0.0803| 0.0803|
| Degree of conversion     | 0.0035| 0.0042| 0.0022|
| NH$_3$ production (%)     | 0.1749| 0.2083| 0.1116|
Table S9. Results in ammonia synthesis for Cs-promoted Ru₅PtAu₂/CNF-PPh₂ (Cat4)

|                      | 300°C | 350°C | 375°C | 400°C |
|----------------------|-------|-------|-------|-------|
| Time of test (h)     | 5     | 5     | 5     | 5     |
| Weight of catalyst (g)| 0.4980| 0.4980| 0.4980| 0.4980|
| Total moles of NH₃ produced | 0.0005| 0.0006| 0.0007| 0.0005|
| Moles/h of NH₃ produced | 0.0001| 0.0001| 0.0001| 0.0001|
| mmol/h*g cata        | 0.2108| 0.2490| 0.2811| 0.1867|
| Nitrogen feed (moles/h) | 0.0268| 0.0268| 0.0268| 0.0268|
| Hydrogen feed (moles/h) | 0.0803| 0.0803| 0.0803| 0.0803|
| Degree of conversion  | 0.0020| 0.0023| 0.0026| 0.0017|
| NH₃ production (%)    | 0.0982| 0.1159| 0.1309| 0.0869|
Table S10. Results in ammonia synthesis for Cs-promoted Ru$_3$Co/CNF-NMe$_3^+$ (Cat5)

|                          | 300°C | 350°C | 375°C |
|--------------------------|-------|-------|-------|
| Time of test (h)         | 5     | 5     | 5     |
| Weight of catalyst (g)   | 0.4962| 0.4962| 0.4962|
| Total moles of NH$_3$ produced | 0.0024| 0.0004| 0     |
| Moles/h of NH$_3$ produced | 0.0005| 0.0001| 0     |
| mmol/h*g cata            | 0.9472| 0.1532| 0     |
| Nitrogen feed (moles/h)  | 0.0268| 0.0268| 0.0268|
| Hydrogen feed (moles/h)  | 0.0803| 0.0803| 0.0803|
| Degree of conversion     | 0.0088| 0.0014| 0     |
| NH$_3$ production (%)     | 0.4409| 0.0710| 0     |
**Figure S4:** TEM images of Cata 1 (Ru₅/CNF-PPh₂) after test.