Electronic Supporting Information for

Organometallic control at the nanoscale: a new, one-pot method to decorate a magnetic nanoparticle surface with noble metal atoms

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Experimental Section:

Reactants and samples preparation: All manipulations were carried out under argon atmosphere. Solids were weighed inside a glove-box (less than 1ppm O₂ and H₂O). Heptane (Aldrich, >99%) was distilled over sodium and degassed according to a freeze-pump-thaw process. Fe[N(SiMe₃)₂]₂,^[1] Rh(η^3 -C₃H₅)₃^[2] and iPr₂NH.BH₃^[3] were prepared according to literature. 2,2,6,6-Tetramethylpiperidine (TMP, +99%) was purchased from Aldrich. This amine was chosen as stabilizing agent because it does not react with the amine-borane complex or with the amino-borane one. Carbon monoxide (>99.1%) was purchased from Air Liquide.

FeRh system:

1: 640.22mg(1.7mmol) Fe[N(SiMe₃)₂]₂, 67.80mg(0.3mmol) Rh(η^3 -C₃H₅)₃ and 141.25mg (1mmol.) TMP were dissolved in 20mL degassed heptane in a Fisher Porter bottle. The green solution was frozen in a nitrogen bath and a solution of 391.08mg(3.4 mmol) of iPr₂NH.BH₃ in 20 mL of heptane was added. The reacting medium was allowed to come back to room temperature under vigorous stirring. Upon melting the precursor mixture H₂ evolution was observed accompanied by an almost instantaneous color change from the green of the Fe complex to brown and then black. Evaporation of the solvent after 12h afforded a black powder (99 mg.) which was stored in the glove-box. wt% Fe:29.2, Rh:16.3. (Fe₈₅Rh₁₅).

2: (94mg), wt% Fe: 26, and 3 (63 mg) wt% Rh: 24 were prepared in the same procedure.

CO adsorption was carried out by submitting the crude heptane solutions of the nanoparticles to a pressure of 1bar CO at room temperature. After 1 night, evaporation of the solvent afforded a black powder which was studied by IR spectroscopy. The amine ligand is totally displaced upon addition of CO, which is expected as the CO/metal surfaces bond is much stronger than the amine/metal surface one, allowing a direct comparison between the samples.

CoRh system:

87.14mg (0.23mmol) of Co[N(SiMe₃)₂]₂, 17.30mg (0.077mmol) of Rh(η^3 -C₃H₅)₃ and 43.4mg (0.30mmol) of tetramethylpiperidine were dissolved in 190mL of heptane in a Fisher Porter bottle. The green solution was frozen in a nitrogen bath and a solution of 52.9mg (0.46 mmol) of iPr₂NH.BH₃ in 10 mL of heptane was added. At this point the Fisher Porter bottle was tightly closed and the reacting medium was allowed to come back to room temperature. When the medium had completely melted, vigorous stirring induced an instantaneous colour change from green to brown and then black, simultaneously to gas evolution. Evaporation of the solvent after 15h at room temperature afforded a black powder.

Microanalysis : wt% Co 4.01%; wt% Rh 2.85%, i.e., Co₇₁Rh₂₉; mean diameter : 1.8 nm.

Techniques:

¹H NMR and ¹¹B NMR spectra were recorded respectively on a Bruker ARX 250 and a Bruker DPX 300 spectrometers.

IR spectra were recorded in transmission mode on a Perkin Elmer 1725 spectrometer. The samples were prepared as dispersions in KBr pellets.

Chemical microanalyses were performed at Antellis (www.antellis.com) by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer) after digestion of the samples in concentrated HNO₃, to determine the Fe and/or Rh content in the materials.

TEM images were recorded on a JEOL JEM1011(100kV) after drop casting a diluted solution of nanoparticles in heptane on carbon coated copper grids, at the TEMSCAN facility, Université de Toulouse. More than 200 particles were measured to draw each size histogram.

WAXS measurements:

Structural characterizations by WAXS were performed in the solid state. The fine powder was introduced into a thin walled Lindemann capillary of 1-mm diameter subsequently sealed under argon. The samples were irradiated with graphite-monochromatised molybdenum K radiation (0.071069 nm). The scattered intensity was recorded by a dedicated two-axis diffractometer. Fluorescence from iron was removed at the measurement step by filtering. Time for data collection was typically 20 hours for a set of 457 measurements collected at room temperature in the range $0^{\circ} < \theta < 65^{\circ}$ for equidistant s values [s = $4\pi(\sin\theta/\lambda)$]. Treatment of the data has been carried out according to ref. [4] to allow the analysis of the radial distribution function (RDF) of the particles.

XAS measurements at K edges:

Co, Fe and Rh absorption spectra at K edges were measured on beamline C at Hasylab in Hamburg, Germany (http://www-hasylab.desy.de/index.htm). The samples, diluted with poly-3,5-dimethylphenylene-oxide (Aldrich), were prepared as 5 mm large pellets sealed between Kapton foils to protect them from air oxidation. The dilution was adjusted to ensure optimal absorption at the edge under study. The measurements were done in transmission mode at room temperature using a double silicon monochromator set for diffraction from (111) planes for Co, Fe K-edge and (311) planes for Rh K-edge. Treatment of the data was carried out via the Athena software (http://cars9.uchicago.edu/~ravel/software/).

XAS and XMCD measurements at Rh L edges:

These measurements were performed at the ESRF ID12 beamline equipped with a EMPHU undulator (http://www.esrf.eu/UsersAndScience/Experiments/XASMS/ID12/) as reported in ref. [5]. Polarimetry measurements have shown that the circular polarization rate at Rh L_2 and L_3 edges is only 11% and 5%, respectively. Extreme care was taken to prevent the NPs oxidation prior to XMCD experiments. Samples in the form of pellets, pressed in a glove box, were mounted under argon atmosphere into special aluminum capsules covered with a 25 microns thick kapton foil. For each sample we used a separate capsule which was attached to

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a cold finger of a constant flow He cryostat. The latter was inserted in the core of a superconducting magnet providing a magnetic field of 6T. All measurements were done at a temperature ~10K which is close to the blocking temperature of the samples. XMCD signals were obtained as a direct difference of X-ray absorption near-edge structure (XANES) spectra recorded with left and right circularly polarized X-rays using total fluorescence yield detection mode, when sample is magnetized ether parallel or antiparallel to the direction of X-rays propagation. To make sure that experimental spectra are free of any experimental artifacts, we have checked that the same XMCD spectra but of opposite sign have been obtained for two directions of magnetic field. The experimental spectra were then corrected for incomplete circular polarization rate of the incoming X-rays and normalized to the edge jump equal to unity at the Rh L₃ and to 0.5 at the Rh L₂ absorption edge as in ref. [6]. To determine the values of spin and orbital contributions to the total induced magnetic moment carried by the Rh atoms in the NPs, we have used the magneto-optical sum rules analysis following the standard procedure described in ref. [7].

Data for the FeRh system (sample 1) and related references

TEM image and size histogram for:

a) Fe nanoparticles (2)



b) Rh nanoparticles (3)



XANES spectra of sample 1 recorded at Fe K-edge: before air exposure (black solid line) and after air exposure (red broken line) and Fe foil as a reference (black line plus symbols)



Full oxidation of Fe after air exposure is evidenced by the presence of the pre-edge feature and white line.

XANES spectra of sample 1 recorded at Rh K-edge: before air exposure (solid line) and after air exposure (broken line) and Rh foil as a reference (line plus symbols)



Fourier Transform of the EXAFS signal.

The intensity of the reference foil (cc Fe or fcc Rh metal foils) was divided per 10 to give a reasonably comparative picture.

This huge difference in amplitude between the references and the samples is a consequence of a much higher static disorder in the nanoparticles compared with the metal foils.

At Rh edge the Rh-Rh distances in **3** are not significantly different from the ones in the foil, which is consistent with a similar fcc environment for Rh atoms. However, in **1**, distances are much more dispersed and significantly shifted towards low values. It is however difficult to estimate the true average Rh-metal (Rh or Fe) distances in that case because of the known bias of EXAFS to favour small distances in such cases of large dispersion. The Rh-Rh distance was tentatively attributed to the right hand shoulder of the peak by comparison to the data obtained on **3**. Rh-Fe bonds would thus correspond to the max. of the peak.

At Fe edge, it is interesting to note that a similar shift of distances is also observed for both 1 and 2, which is consistent with the known polytetrahedral structure in 2 and indicates a similar structure involving both Fe and Rh atoms in 1.



RDF of the EXAFS signal for: a) 1 (solid line) and 2 (dotted line), b) 1 (solid line) and 3 (dotted line). Metal foils RDF are reported with open circles and indicated by an arrow.

IR spectra of a) 2 (Fe nanoparticles), b) 1 (Fe₈₅Rh₁₅ nanoparticles), and c) 3 (Rh nanoparticles), after exposure to 1 bar CO overnight.



NB: The amine ligand is totally displaced upon addition of CO, which is expected as the CO/metal surfaces bond is much stronger than the amine/metal surface one, allowing a direct comparison between the samples.

Data for the CoRh system (Co₃Rh₁):

TEM image and Size histogram of the CoRh nanoparticles



RDF obtained via WAXS analysis for CoRh nanoparticles, and model for a polytetrahedral packing



XAS at Rh K-edge for the CoRh nanoparticles and Rh reference foil XMCD signal at Rh L₂ edge recorded at 10K and under an applied field of 6 T



The dichroic signal observed at Rh L_2 edge clearly shows that Rh atoms are polarized. However, at Rh L_3 edge, no dichroic contribution could be measured. Consequently we cannot calculate the magnetic moment per Rh atom in this case.

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