Electronic Supplementary Material (ESI) for Nanoscale Advances.

SUPPORTING INFORMATION

1. Experimental procedures

2. TEM images of Rh nanoparticles obtained under various conditions.

1. Experimental procedures

Materials and methods. All manipulations were performed with Schlenk-line techniques under an inert atmosphere of dry argon. Solvents were dried by standard procedures and distilled under argon prior to use. 4,4'-Azobis(4-cyanopentanoic acid) (ACPA, >98%, Fluka), diethylene glycol dimethacrylate (DEGDMA, 95%, Sigma-Aldrich), 4-(diphenylphosphino)styrene (DPPS, 97%, Sigma-Aldrich), triphenylphosphine (PPh_3 or TPP, 98.5%, Fluka), chloro(1,5-cyclooctadiene)rhodium(I) dimer ($[RhCl(COD)]_2$, min. 40.8% Rh, ACROS Organics), 1,3,5-trioxane (>99%, Sigma-Aldrich), acetophenone (99%, Sigma-Aldrich), *n*-decane (99%, Alfa Aesar), *n*-dodecane (99%, Sigma-Aldrich), 1-nonanol (>99%, TCI) and poly(ethylene oxide) dimethyl ether (PEOMA, Mn = 950 g mol^{-1}, Sigma-Aldrich) were used as received. Styrene (St, 99%, Acros) was distilled under reduced pressure prior to use. Latexes of the CCM particles with a neutral shell and TPP functions in the hydrophobic core, R_0-$(MAA_{0.5}$-*co*-$PEOMA_{0.5})_{30}$-*b*-$(S_{1-x}$-co-$DPPS_x)_{300}$-*b*-$(S_{0.9}$-*co*-$DEGDMA_{0.1})_{140}$-SC(S)SPr (**CCM-N-x**, x = 0.05 or 0.1)[1] and with a cationic shell, R_0-$(4VPMe^+I^-)_{140}$-*b*-S_{50}-*b*-$(S_{1-x}$-*co*-$DPPS_x)_{300}$-*b*-$(S_{0.9}$-*co*-$DEGDMA_{0.1})_{140}$-SC(S)SPr (**CCM-C-x**, x = 0.05, 0.1 or 0.2)[2] were prepared as previously described. The macroRAFT agent R_0-$(4VPMe^+I^-)_{140}$-*b*-S_{50}-SC(S)SPr·34(DMF) (yellow powder, molar mass = 40073 g mol^{-1}) was synthesized in three steps from 4-cyano-4-thiothiopropylsulfanyl pentanoic acid (CTPPA, or R_0-SC(S)SPr with R_0 = $-C(CH_3)(CN)CH_2CH_2COOH$),[3-4] vinyl pyridine, styrene and methyl iodide as previously described.[5] The deionized water was obtained from a Purelab Classic UV system (Elga Lab-Water). The metal complexation reactions to generate the various [RhCl(COD)(TPP@CCM)] samples were carried out as described previously.[1-2] Freeze-drying was carried out with a LABCONCO Freezone 4.5 Plus instrument.

Characterization Techniques. The morphological analyses of the copolymer nano-objects were performed by transmission electron microscopy (TEM) at the Centre de Microcaractérisation Raimond Castaing (Toulouse, France) with a JEOL JEM 1400 transmission electron microscope working at 120 kV. Diluted latex samples were dropped on a formvar/carbon-coated copper grid and dried under vacuum for 24 hours. The CCM and NG particle diameters were estimated using the ImageJ software. The gas-chromatography (GC) analyses of residual substrate and products in the organic layer after catalysis were conducted with a Shimadzu GC 2014 chromatograph equipped with a SLB 5ms capillary column (30 m×0.32 mm; 0.23 μm film thickness) for the styrene hydrogenation experiments and with a Hewlett Packard 4890A chromatograph equipped with a SPB 20 capillary column (30 m×0.32 mm; 0.25 μm film thickness) for the acetophenone hydrogenation experiments. Both GC instruments were coupled to a flame ionization detector (FID) and used helium as carrier gas. The peak assignments were assisted by a separate GC/MS analysis.

General procedure for the synthesis of rhodium nanoparticles from the [RhCl(COD)(TPP@CCM)] latexes. In a vial containing a magnetic stirrer under argon was added 0.4 mL of the desired [RhCl(COD)(TPP@CCM)] latex (see above), 0.5 mL of degassed toluene and an excess of triethylamine (ca. 5-10 equiv. per metal). The vial was placed into an autoclave, which was then charged with 20 bar of dihydrogen. The autoclave was placed in a thermostatic oil bath at the desired temperature (see Results and Discussion) and stirred at 1200 rpm. After 20h, the vial was taken out of the autoclave under argon. The resulting black latex was allowed to decant until yielding a neat phase separation (ca. 5-7 min for **CCM-N**, < 3 min for **CCM-C**) and then the upper toluene was removed by pipette, leaving a latex of toluene-swollen

CCM particles containing the metallic nanoparticles. The products were characterized by TEM (see Results and Discussion).

Synthesis of rhodium nanoparticles in a homogeneous phase with PEOMA stabilisation. In a vial containing 10 mg of PEOMA (10.5 μmol, 210 μmol of EO units) was added a solution of $[RhCl(COD)]_2$ (either 5.2 mg, 10.5 μmol, or 1.3 mg, 2.6 μmol) in 0.5 mL of degassed toluene, to yield an EO/Rh ratio of 10:1 or 40:1, respectively. The vial was placed into the autoclave, which was then sealed, charged with 20 bar of H_2 and placed in an oil bath at 60°C with magnetic stirring at 1200 rmp for 20 h.

Synthesis of rhodium nanoparticles in a homogeneous phase with PPh_3 stabilisation. In a vial containing 23.6 mg of tryphenylphosphine (0.09 mmol) was added a solution of $[RhCl(COD)]_2$ (either 22.19 mg, 0.045 mmol, or 5.4 mg, 0.011 mmol) in 0.5 mL of degassed toluene, to yield a P/Rh ratio of 1:1 or 4:1, respectively. The vial was placed into the autoclave, which was then sealed, charged with 20 bar of H_2 and placed in an oil bath at the set temperature, with magnetic stirring at 1200 rpm for 20 h.

General procedure for the aqueous biphasic catalytic hydrogenation of acetophenone and styrene. In a vial containing the desired RhNP@CCM latex prepared as described above, the desired amount of a substrate/toluene mixture (see Results and Discussion) was layered on top. Decane or dodecane (internal standard) was then added to the organic layer (substrate/internal standard molar ratio = ca. 4). The vial was then placed inside an autoclave, which was subsequently charged with dihydrogen (20 bar), placed in a thermostatic oil bath and stirred at 1200 rpm. At the set reaction time, the stirring was stopped, the autoclave was vented and the vial was taken out under argon and allowed to decant until a neat phase separation was obtained (ca. 15 min with

CCM-N, < 3 min with **CCM-C**). After phase separation, the latex was extracted with diethyl ether (5×0.3 mL). The combined organic phases were used for the GC analysis.

General procedure for the aqueous biphasic catalytic hydrogenation of 1-octene. The [RhCl(COD)(TPP@**CCM-C**)] and RhNP@**CCM-C** latexes were prepared as described above. These latexes were freeze-dried for 2 days at -87°C and 0.04 mbar, then dispersed again in distilled water to yield the same concentration as for the starting latex. For each catalytic experiment, a 0.4 mL sample of latex was introduced in a vial, layered with the desired amount of 1-octene (see table 4) containing the decane internal standard (plus 1-nonanol is desired, see table 4), and finally placed in the autoclave, which was pressurized with H_2 and stirred for 3 hours in a 25°C thermostatic bath. The autoclave was then vented and the vial was taken out under argon and allowed to decant until a neat phase separation was obtained (< 3 min). After phase separation, the latex was extracted with diethyl ether (5×0.3 mL). The combined organic phases were used for the GC analysis.

General procedure for homogeneous catalytic hydrogenations with nanoparticles stabilized by PEOMA or PPh_3. To the vial containing the PEOMA- or PPh_3-stabilized rhodium nanoparticles were added the desired amounts of styrene, 1-nonanol and the *n*-decane internal standard (see Results and Discussion). The vial was then placed inside an autoclave, which was sealed, charged with 20 bar dihydrogen and placed in a thermostatic oil bath with magnetic stirring at 1200 rpm. At the set reaction time, the stirring was stopped, the autoclave was vented and the vial was taken out under argon to allow the nanoparticles to decant. A solution aliquot was withdrawn and diluted with diethyl ether for the GC analysis.

Procedure used for the latex separation, recovery and recycling

At the set reaction time, the stirring was stopped, the autoclave was vented and the vial was taken out under argon and allowed to decant until a neat phase separation was obtained (< 3 min with **CCM-C**). After phase separation, the latex was extracted with 0.3 mL diethyl ether or 0.3 mL toluene. Being 5 min stirring and 5 min decantation, the organic solution was withdrawn. The washing was repeated for 5 times under argon. The combined organic phases were used for the GC analysis. For the recycling experiments, a fresh substrate solution (same amounts as in the initial run) was added to the same vial, followed by reaction and product separation according to the same protocol. To regenerate NPs, 0.5 mL toluene and 5 equiv. per metal triethylamine were added into the vial. The vial was placed into an autoclave charged with 20 bar of dihydrogen. The autoclave was placed in a thermostatic oil bath at the desired temperature (80°C or 90°C) and stirred at 1200 rpm for 20 h or 2 h.

2. TEM images of Rh nanoparticles obtained under various conditions

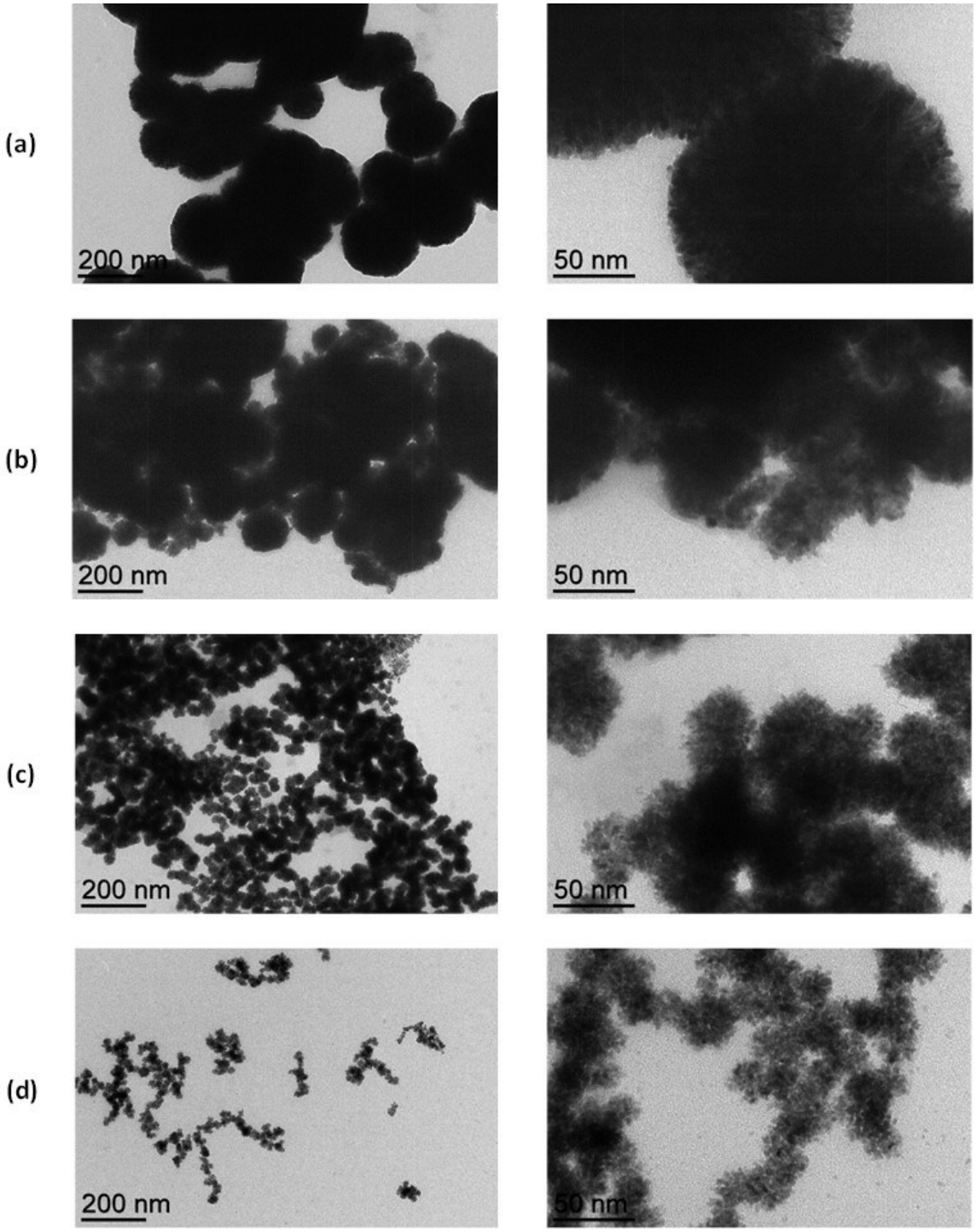

Figure S1. TEM images of the Rh NPs obtained from a toluene solution of $[RhCl(COD)]_2$ in the presence of PEOMA ((a) and (b) or **macroRAFT-N** ((c) and (d)), H_2 (20 bar) and NEt_3 (10 equiv per Rh) at 60°C. (a) and (c): PEOMA/Rh = 0.5:1. (b) and (d): PEOMA/Rh = 2:1.

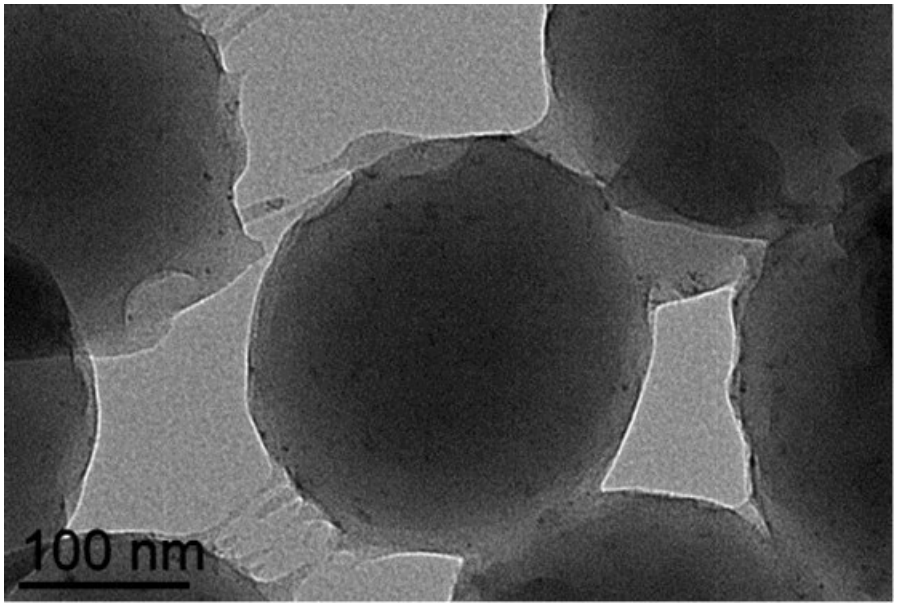

Figure S2. TEM image of the Rh NP@(**CCM-N-0.1**) obtained from a 25% loaded latex (P/Rh = 4) without added base at 90°C for 20 h.

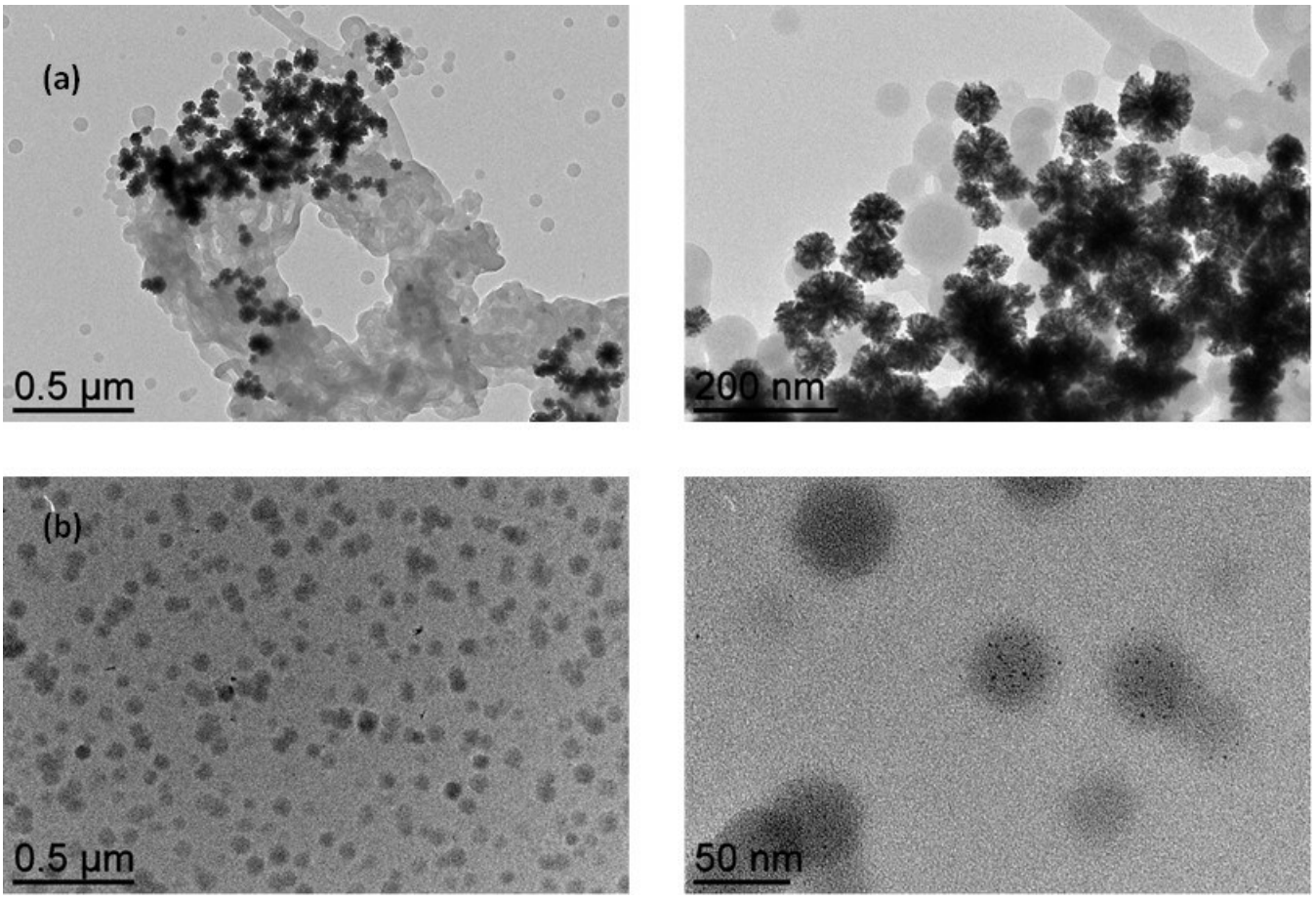

Figure S3. TEM images of the **CCM-N-0.2** polymer latex after loading with $[RhCl(COD)]_2$ and reduction with H_2 (20 bar) in the presence of NEt_3 (5 equiv. per Rh) for 20 h. (a) P/Rh = 1, 25°C. (b) P/Rh = 4, 60°C.

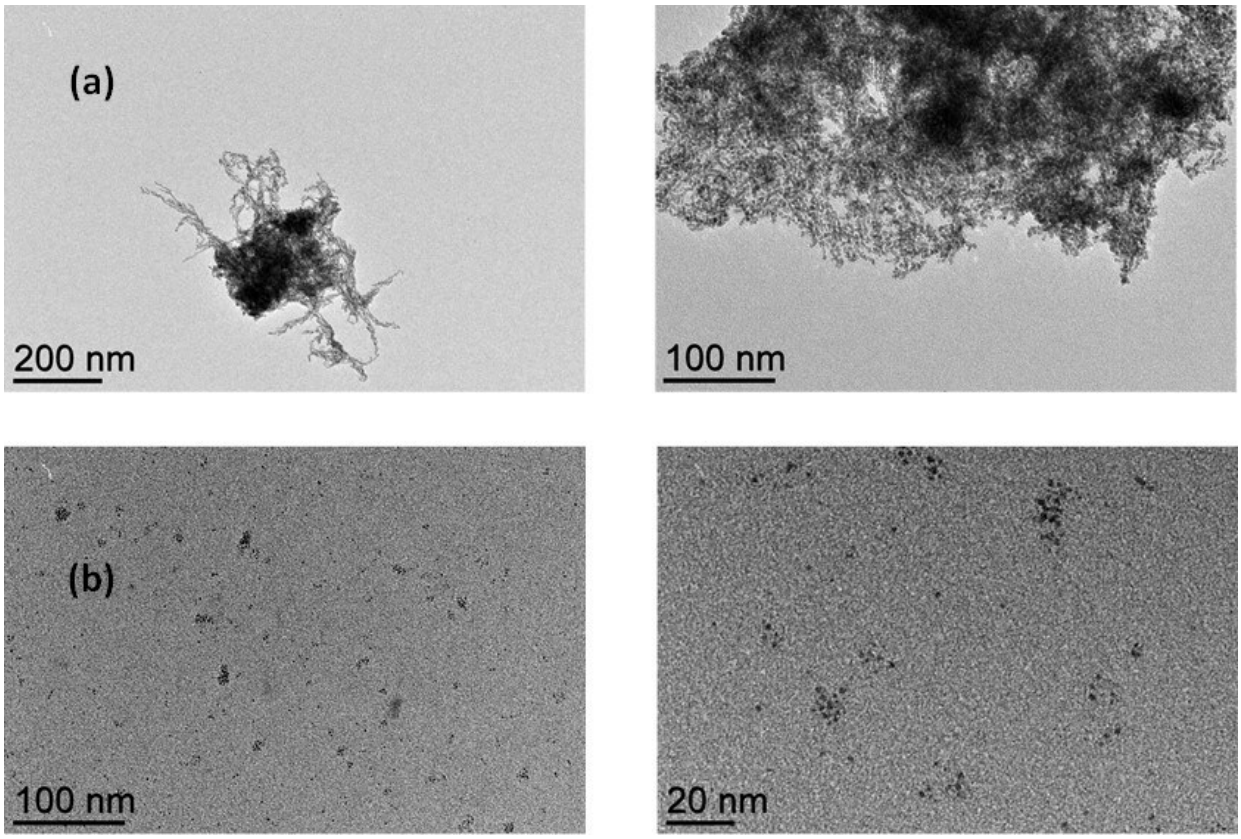

Figure S4. TEM images of the Rh NPs obtained from a toluene solution of $[RhCl(COD)]_2$ in the presence of PPh_3, H_2 (20 bar) and NEt_3 (5 equiv per Rh). (a) P/Rh = 1:1, T = 25°C. (b) P/Rh = 4:1, 60°C.

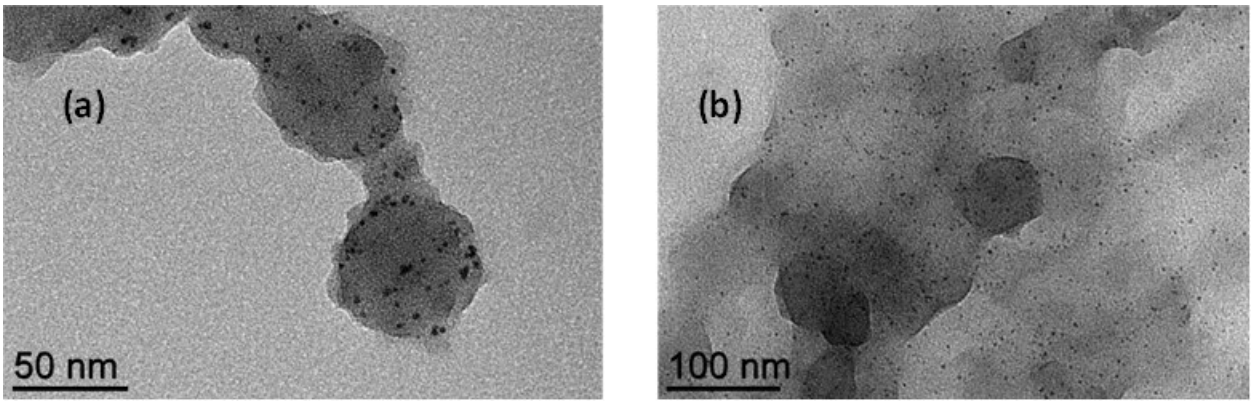

Figure S5. TEM images of Rh NP@(**CCM-C 0.1**) obtained with P/Rh = 1:1 and reduction with H_2 (20 bar) at 25°C for 20 h with different NEt_3/Rh ratios: (a) 0; (b) 1 (an image corresponding to NEt_3/Rh = 5 is available in Figure 3 (a)).

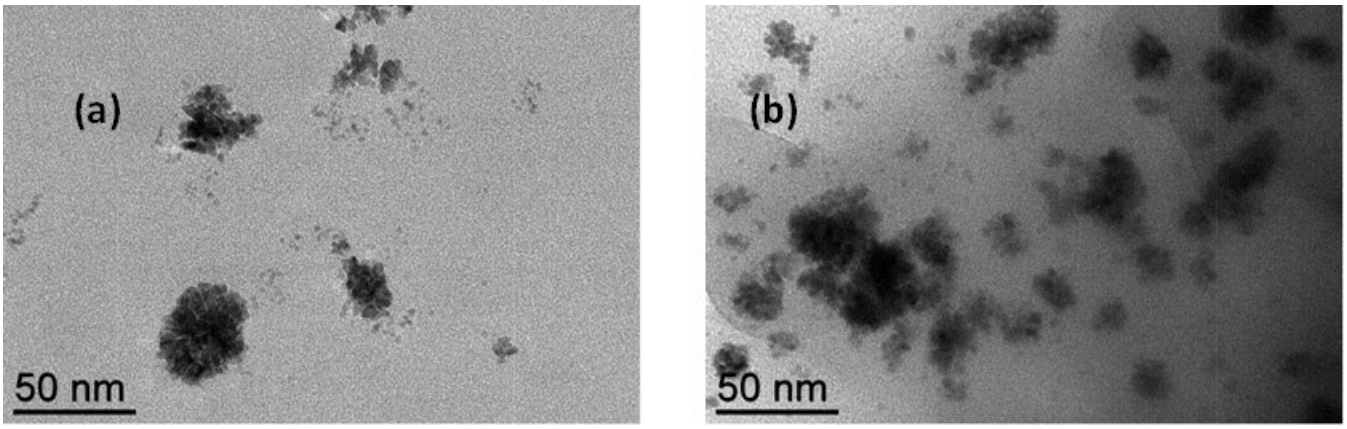

Figure S6. TEM images of Rh NP@(**macroRAFT-C**) obtained by $[RhCl(COD)]_2$ reduction with H_2 (20 bar) at 60°C in methanol in the presence of NEt_3 (10 equiv. per Rh) for 20 h. (a) $4VPMe^+I^-$/Rh = 4.7 (equivalent to the experiment with **CCM-C 0.1** at P/Rh = 1). (b) $4VPMe^+I^-$/Rh = 18.8 (equivalent to the experiment with **CCM-C 0.1** at P/Rh = 4).

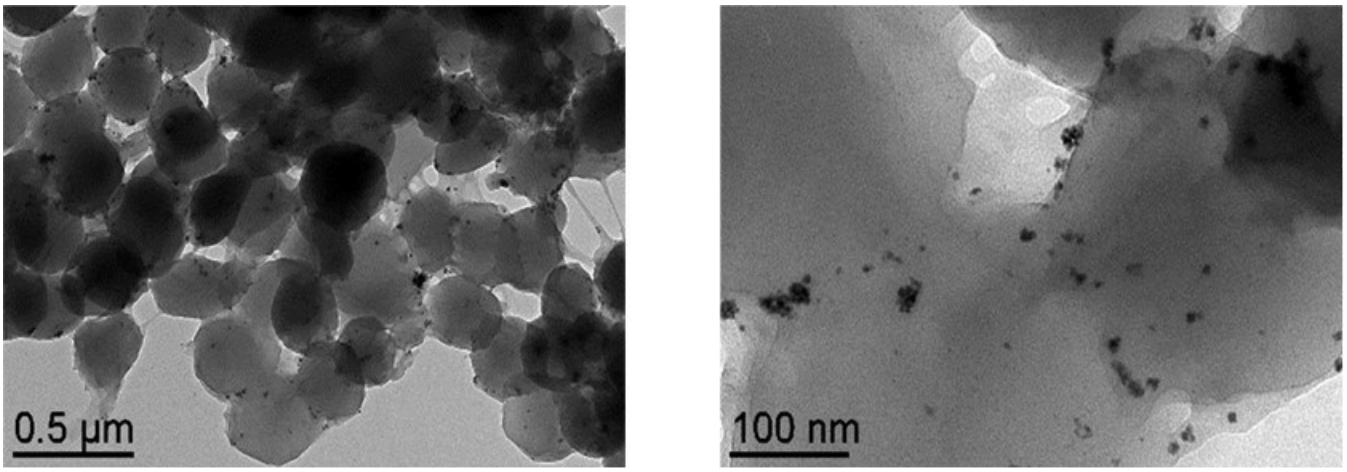

Figure S7. TEM images of the RhNP@**CCM-N-0.1** (P/Rh = 4) latex after the catalytic run of entry 27 (Table 2).

1. Zhang, X.; Cardozo, A. F.; Chen, S.; Zhang, W.; Julcour, C.; Lansalot, M.; Blanco, J.-F.; Gayet, F.; Delmas, H.; Charleux, B.; Manoury, E.; D'Agosto, F.; Poli, R., *Chem. Eur. J.* **2014,** 20 (47), 15505–15517.
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3. Xu, X.; Smith, A. E.; Kirkland, S. E.; McCormick, C. L., *Macromolecules* **2008,** 41 (22), 8429-8435.
4. Boursier, T.; Chaduc, I.; Rieger, J.; D'Agosto, F.; Lansalot, M.; Charleux, B., *Polym. Chem.* **2011,** 2 (2), 355-362.
5. Wang, H.; Vendrame, L.; Fliedel, C.; Chen, S.; Gayet, F.; Manoury, E.; Zhang, X.; Lansalot, M.; D'Agosto, F.; Poli, R., *Macromolecules* **2020,** 53 2198-2208.