

Electronic Supplementary Information (ESI)

## Organic carbonates as stabilizing solvents for transition-metal nanoparticles

Christian Vollmer,<sup>a</sup> Ralf Thomann<sup>b</sup> and Christoph Janiak<sup>\*a</sup>

<sup>a</sup> *Institut für Anorganische und Strukturchemie, Universität Düsseldorf, Universitätsstrasse 1, D-40225 Düsseldorf, Germany, Fax: +49 211 8112286; Tel: + 49 2118112287; E-mail: [janiak@uni-duesseldorf.de](mailto:janiak@uni-duesseldorf.de)*

<sup>b</sup> *Freiburger Materialforschungszentrum (FMF), Universität Freiburg, Stefan-Meier-Str. 21, D-79104 Freiburg, Germany.*

Email: [christian.vollmer@uni-duesseldorf.de](mailto:christian.vollmer@uni-duesseldorf.de)

Email: [ralf.thomann@fmf.uni-freiburg.de](mailto:ralf.thomann@fmf.uni-freiburg.de)

Email: [janiak@uni-duesseldorf.de](mailto:janiak@uni-duesseldorf.de)

### Experimental:

#### General

Mo(CO)<sub>6</sub>, W(CO)<sub>6</sub>, Re<sub>2</sub>(CO)<sub>10</sub>, Fe<sub>2</sub>(CO)<sub>9</sub>, Ru<sub>3</sub>(CO)<sub>12</sub>, Os<sub>3</sub>(CO)<sub>12</sub>, Co<sub>2</sub>(CO)<sub>8</sub>, Rh<sub>6</sub>(CO)<sub>16</sub> and Ir<sub>4</sub>(CO)<sub>12</sub> were obtained from STREM and Aldrich, racemic Propylene carbonate (PC) (99.7 %, H<sub>2</sub>O free), 3-mercaptopropionic acid (> 99%), cyclohexene (> 99%), 1-hexyne (> 97%) and trioctylphosphine oxide (99%) from Sigma-Aldrich.

All manipulations were done using Schlenk techniques under nitrogen since the metal carbonyls salts are hygroscopic and air sensitive. The ILs were dried at high vacuum (10<sup>-3</sup> mbar) for several days.

#### Preparation of M-NP/PC dispersion

Decomposition via microwave was carried out under argon. In a typical reaction the metal carbonyl M<sub>x</sub>(CO)<sub>y</sub> (M = Mo, W, Re, Fe, Ru, Os, Co, Rh, Ir; 3.3 mg to 10.2 mg, respectively, Table S1) was dissolved/suspended (~1 h) under an argon atmosphere at room temperature in dried and deoxygenated racemic PC (1.0 ml, 1.19 g) to give a 0.5 wt.% dispersion. For the synthesis the mixture was placed in a CEM microwave type Discover under inert argon atmosphere and the conversion was finished within 3 minutes at a power of 50 W. We used a low energy of 50 W on a vial of 10 mL filled with 1.19 g PC. Within less than 2 min of microwave radiation a temperature of 250 °C was reached.

Rh- and Ir-NPs were also prepared as 1.0 wt.% dispersion.

Rh<sub>6</sub>(CO)<sub>16</sub> decomposes at 220 °C, so it can easily be handled at room temperature under inert atmosphere.<sup>1</sup>

Literature reported decomposition temperatures are 180 °C for Mo(CO)<sub>6</sub> and W(CO)<sub>6</sub>, 177 °C for Re<sub>2</sub>(CO)<sub>10</sub>, above 100 °C for Fe<sub>2</sub>(CO)<sub>9</sub>, 155 °C for Ru<sub>3</sub>(CO)<sub>12</sub> and 224 °C for Os<sub>3</sub>(CO)<sub>12</sub>, above 100 °C for Co<sub>2</sub>(CO)<sub>8</sub>, 220 °C for Rh<sub>6</sub>(CO)<sub>16</sub> and 210 °C for Ir<sub>4</sub>(CO)<sub>12</sub>.<sup>1</sup>

**Table S1:** Microwave decomposition of metal carbonyls in PC with 50 W of power and 3 min reaction time.

Carbonyl $M_x(\text{CO})_y$	molar mass (g/mol)	mass% metal in $M_x(\text{CO})_y$	mass of $M_x(\text{CO})_y$ (mg) in PC	wt.% metal in 1.19 g (1.0 mL) PC (0.5% = 6.1 mg M)
$\text{Mo}(\text{CO})_6$	264.00	36.34	16.8	0.5
$\text{W}(\text{CO})_6$	351.90	52.24	11.5	0.5
$\text{Re}_2(\text{CO})_{10}$	652.52	57.07	10.5	0.5
$\text{Fe}_2(\text{CO})_9$	363.79	30.70	19.8	0.5
$\text{Ru}_3(\text{CO})_{12}$	639.33	47.43	12.8	0.5
$\text{Os}_3(\text{CO})_{12}$	906.81	62.93	9.8	0.5
$\text{Co}_2(\text{CO})_8$	341.94	34.47	17.5	0.5
$\text{Rh}_6(\text{CO})_{16}$	1065.62	57.94	10.5	0.5
$\text{Ir}_4(\text{CO})_{12}$	1105.00	69.58	8.8	0.5
in 0.9 g (0.75 mL) PC:				
$\text{Rh}_6(\text{CO})_{16}$	1065.62	57.94	15.5	1.0 <sup>a</sup>
$\text{Ir}_4(\text{CO})_{12}$	1105.00	69.58	12.9	1.0 <sup>a</sup>

<sup>a</sup> 1.0% = 9 mg M

#### DLS Analysis:

A Malvern Zetasizer Nano-ZS was used for the dynamic light scattering measurements working at 633 nm wavelength. Care was taken for choosing the right parameters, such as the index of refraction of the transition metals at their wavelength (Table S2).

Samples were prepared by dissolution of 0.05 or 0.1 mL of a 0.5 wt.% of the metal dispersion in acetone (99% p.a.; particle free) in a glass cuvette before measurement.

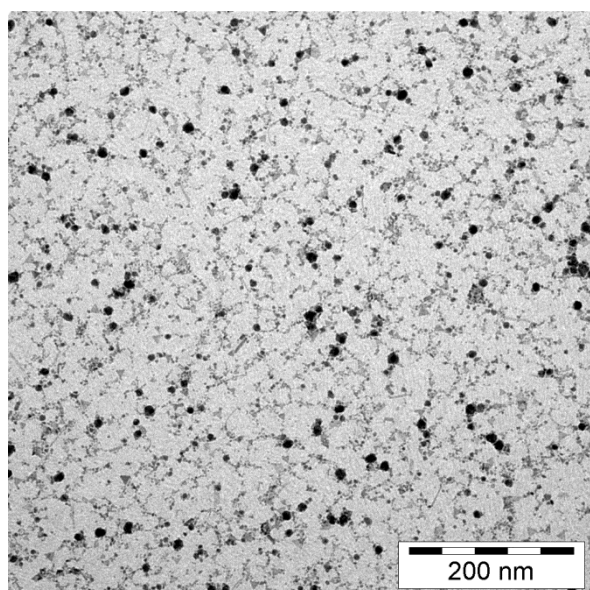
**Table S2:** Parameters for dynamic light scattering.

Element	Index of refraction	Absorption
Molybdenum	3.71	0.1
Tungsten	3.65	0.1
Rhenium	2.93	0.1
Iron	2.87	0.1
Ruthenium	4.79	0.1
Osmium	3.90	0.1
Cobalt	2.26	0.1
Rhodium	2.14	0.1
Iridium	2.53	0.1

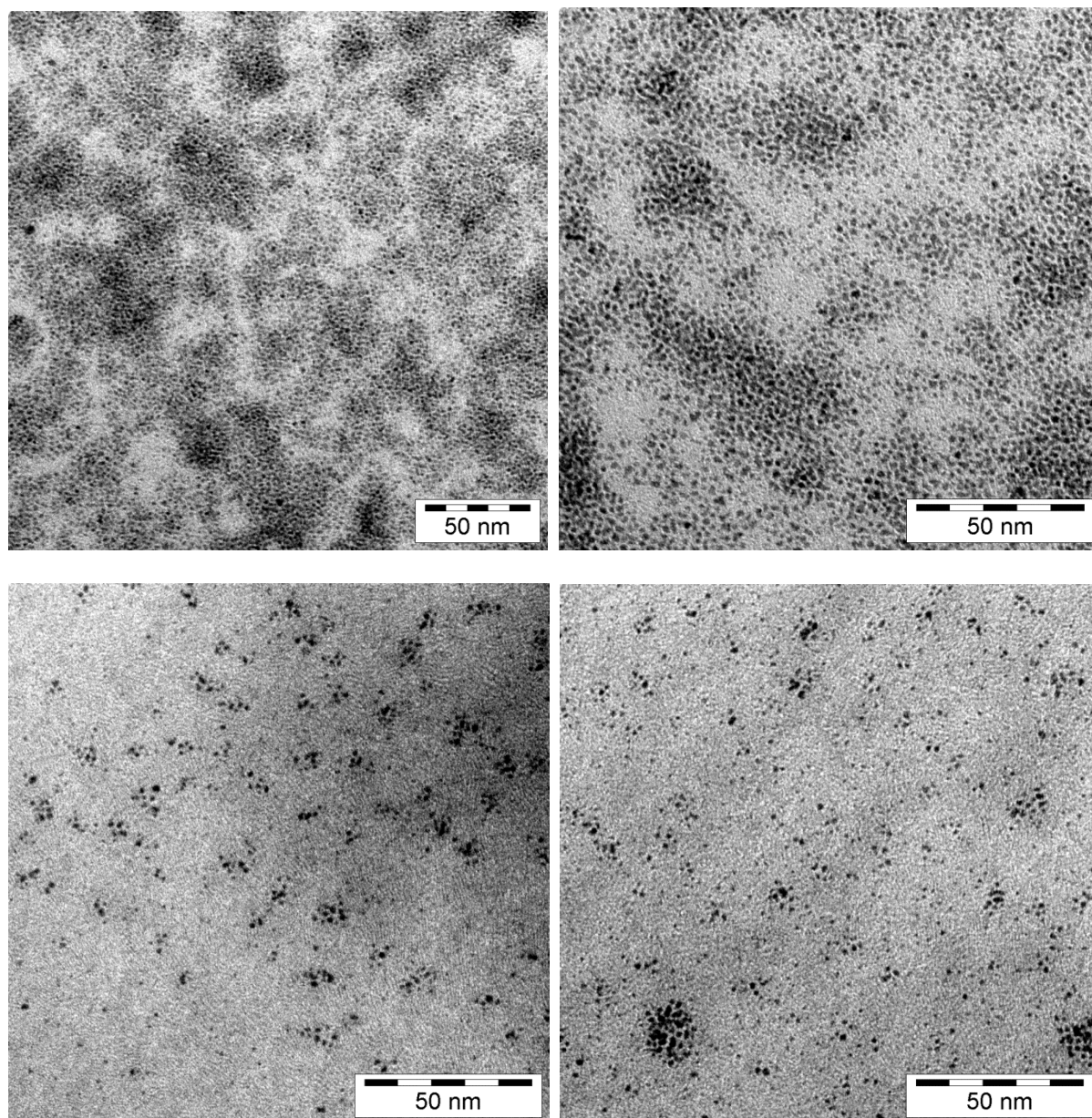
## TEM

Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) photographs were taken at room temperature from a carbon coated copper grid on a Zeiss LEO 912 transmission electron microscope operating at an accelerating voltage of 120 kV. Samples were loaded on holey, carbon coated copper grids. PC was removed by floating the grids on water for several minutes.

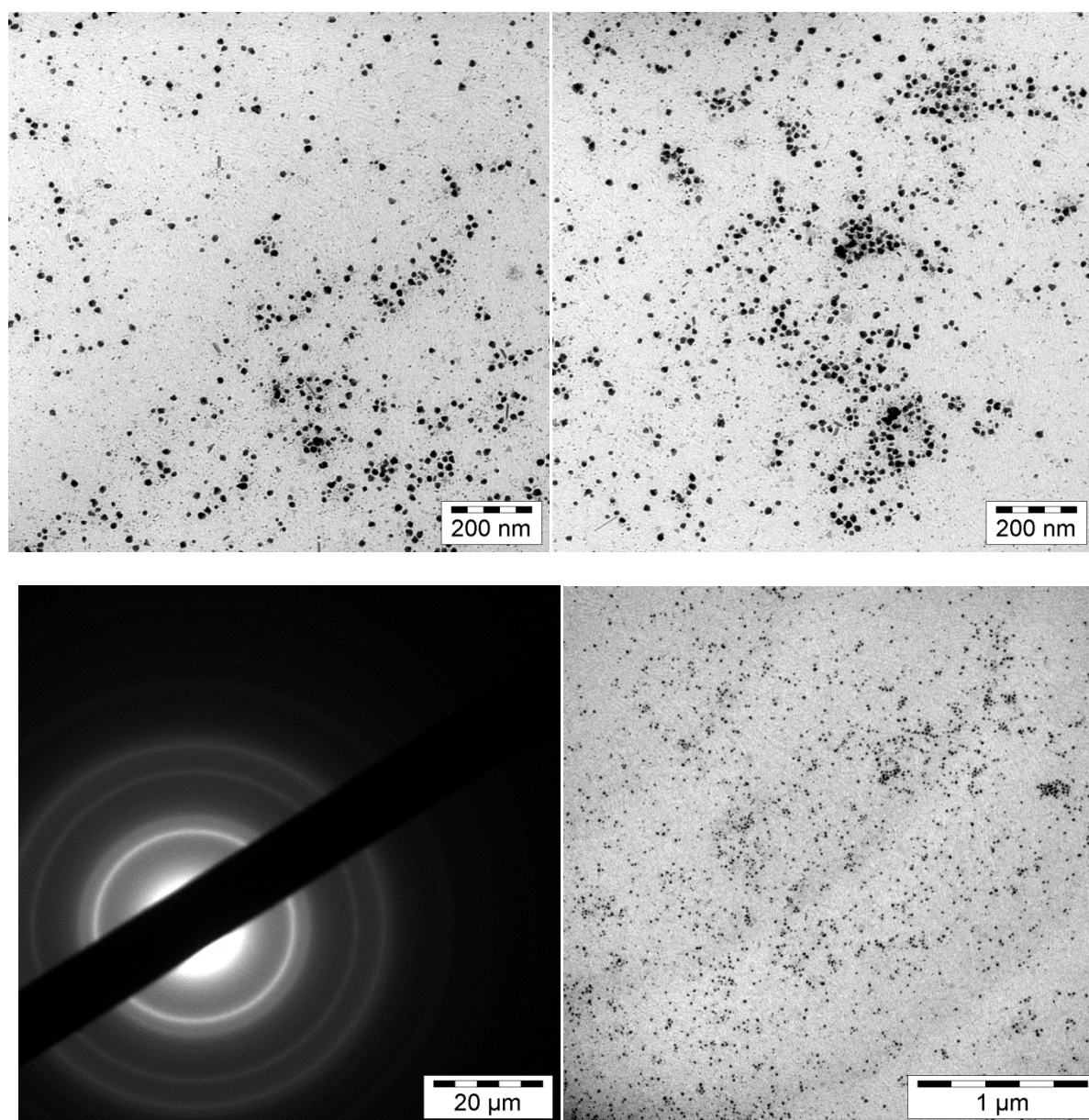
Particles diameters were measured manually using iTEM software tools for manual measurements. Completely automatic measurements, which can be easily performed for well separated particles, fail in the case of heavily clustered particles. For a better comparison of the samples also particles which would have allowed automatic detection were measured manually.



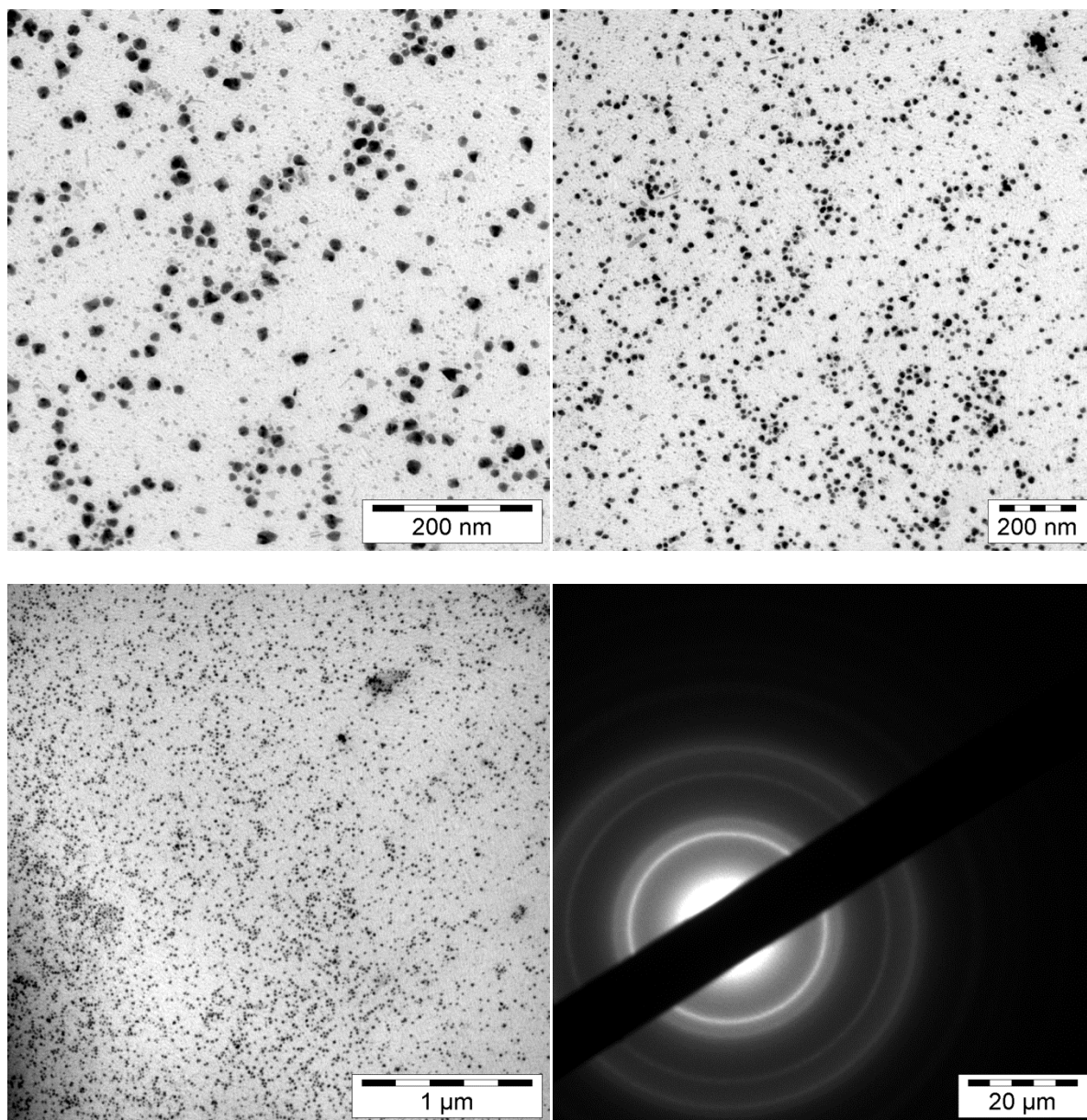
**Fig. S1** TEM of a 1.0 wt.% Rh-NP/PC dispersion (entry 9 in Table 1 in paper).



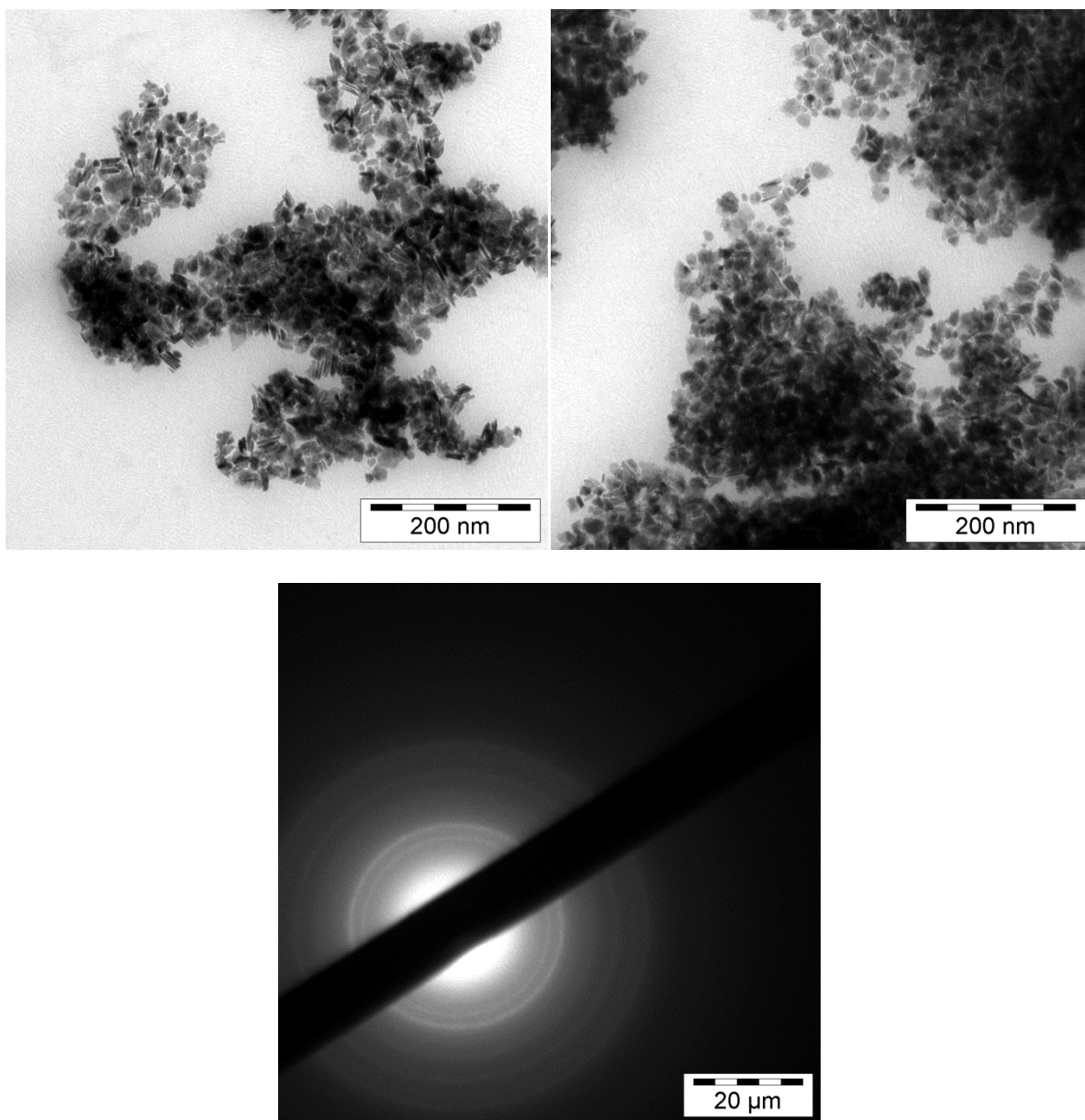
**Fig. S2** TEM of a 1.0 wt.% Ir-NP/PC dispersion (entry 11 in Table 1 in paper) – upper row: fresh sample; lower row: sample after one week.



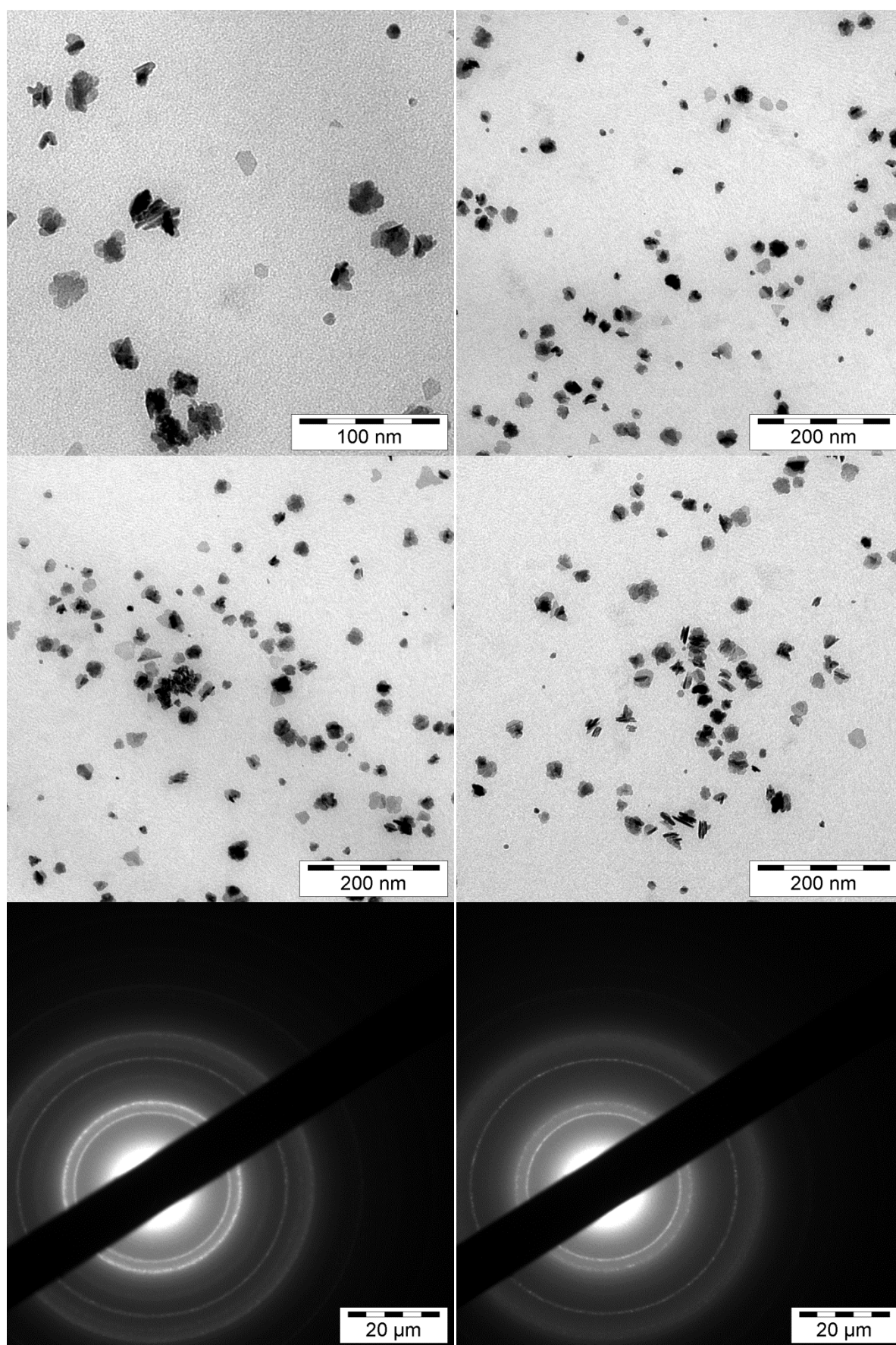
**Fig S3** TEM/SAED photographs of Rh metal nanoparticles stabilized by 3-mercaptopropionic acid from a Rh-NP/PC dispersion (0.5 wt.%).



**Fig S4** TEM/SAED photographs of Rh metal nanoparticles stabilized by trioctylphosphine oxide (TOPO) from a Rh-NP/PC dispersion (0.5 wt.%).



**Fig S5** TEM/SAED photographs of Ru metal nanoparticles stabilized by 3-mercaptopropionic acid from a Ru-NP/PC dispersion (0.5 wt.%).



**Fig S6** TEM/SAED photographs of Ru metal nanoparticles stabilized by TOPO from a Ru-NP/PC dispersion (0.5 wt.%).



### Selected area electron diffraction (SAED)

d-Spacing, intensity and hkl from STOE WinXPow version 1.10, data base, STOE & Cie GmbH, Darmstadt, Germany, 2002.

**Table S3** Diffraction rings of Ru-particles compared with IPDS database, Ru [6-663]

d-Spacing from diffraction rings [Å]	d-spacing [Å] from database	Intensity	hkl
2.10	2.0560	100	101
1.61	1.5808	25	102
not seen	1.3530	25	110
1.26	1.2189	25	103
1.15	1.1299	20	201

**Table S4** Diffraction rings of Rh-particles compared with IPDS database, Rh [5-685]

d-Spacing from diffraction rings [Å]	d-spacing [Å] from database	Intensity	hkl
2.23	2.1960	100	111
1.94	1.9020	50	200
1.39	1.3450	26	220
1.17	1.1468	33	311
not seen	1.0979	11	222
not seen	0.9508	7	400
0.89	0.8724	20	331

**Table S5** Diffraction rings of Ir-particles compared with IPDS database, Ir [6-598]

d-Spacing from diffraction rings [Å]	d-spacing [Å] from database	Intensity	hkl
2.25	2.2170	100	111
1.95	1.9197	50	200
1.38	1.3575	40	220
1.20	1.1574	45	311

In the SAED pictures the ring diameters were measured manually using the scale bar in the picture and the d-spacing was then calculated with a TEM specific constant of 79.5 according to: d-spacing (in Å) = 79.5 / diffraction ring diameter (in µm).

## Catalysis:

### General:

An autoclave with a glass inlay was used. The hydrogenation reactions were carried out in the glass inlay.

The autoclave was conditioned by evacuation and re-filling with nitrogen. All autoclave loading was carried out under nitrogen. Stirring rate was 850 rpm. The H<sub>2</sub> uptake over time was monitored with a Büchi pressflow gas controller (bpc). After quantitative or near quantitative conversion was reached (adjudged by the H<sub>2</sub> consumption) the reactor was depressurized, the volatile organic components were condensed under vacuum into a clean cold trap. The Rh-NPs/ PC dispersion is left behind in the glass inlay of the autoclave and was re-used by adding fresh substrate.

The cyclohexene or benzene to cyclohexane conversion was verified by gas chromatographic (GC) analysis of the product (Perkin Elmer 8500 HSB 6, equipped with a DB-5 film capillary column, 60 m · 0.32 mm, film thickness 25 µm, oven temperature 40 °C, N<sub>2</sub> carrier flow 120 L/min and a flame ionization detector, FID, 250 °C detector temperature).

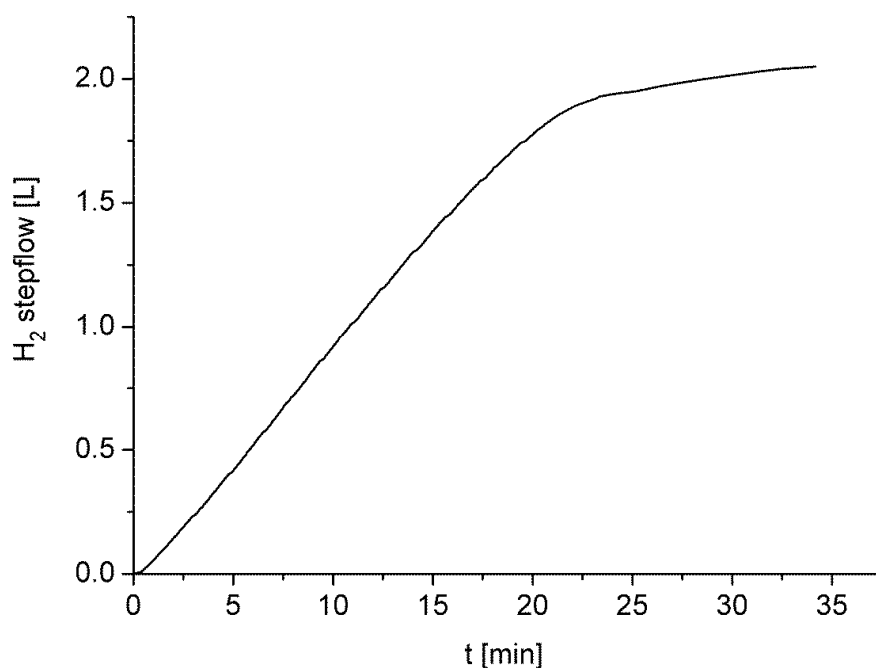
The cyclohexene to cyclohexane and 1-hexyne to hexane conversion was analyzed by putting a drop of the mixture into a GC sample vial with 1 ml of water. Addition of water as a non-electrolyte can enlarge the activity coefficient of organic components, thereby increase their detection sensitivity through the increase in peak area. The FID does not detect water.<sup>2</sup>

### Conditions for cyclohexene hydrogenation:

Cyclohexene 10 mL, 0.89 mol (density 0.811 g/ml,  $M = 82.14$  g/mol); Rh metal (9 mg,  $8.8 \times 10^{-5}$  mol); 25-95 °C, 4-10 bar H<sub>2</sub>.

### Conditions for 1-hexyne hydrogenation:

1-hexyne (1.0 mL, 1.8 mmol (density 0.72 g/ml,  $M = 82.11$  g/mol); Rh metal (9 mg,  $8.8 \times 10^{-5}$  mol); 25 °C, 10 bar H<sub>2</sub>.



**Fig. S7** H<sub>2</sub> uptake (in liter) over time for entry 2 in Table 2: Hydrogenation of cyclohexene (10 ml, 0.1 mol) to cyclohexane with a 0.75 mL of a 1 wt.% Rh-NP/PC dispersion and molar cyclohexene/metal ratio of 88000 at 90 °C, 4 bar H<sub>2</sub> pressure (cf. Table 2). An H<sub>2</sub> uptake of 2.24 L (0.1 mol H<sub>2</sub>, ideal gas behavior) corresponds to 100% conversion.

Table S6 and S7 summarize cyclohexene and 1-hexyne, respectively, hydrogenation activities of related M-NPs (in ILs and on supports) from the literature.

**Table S6** Catalyst activities of M-NPs in the cyclohexene to cyclohexane hydrogenation

Metal-NP system	H <sub>2</sub> pressure	Conversion [%]	Activity [mol product × (mol Rh) <sup>-1</sup> × h <sup>-1</sup> ] (TOF [h <sup>-1</sup> ])	Ref.
Ru / BMImBF <sub>4</sub>	10 bar	95	522	7
Ru / BMImBF <sub>4</sub>	4 bar	> 99	388	3
Ru, solventless	4 atm	> 99	1000	4
Ru / BMImBF <sub>4</sub>	4 atm	> 99	100	4
Ru / BMImPF <sub>6</sub>	4 atm	> 99	62	4
Ru / graphene	4 bar	> 99	1570	5
Rh/PC	4 bar	95	1875	This work
Rh / PTFE	4 bar	> 99	32800	6
(2.1±0.5 Rh-NPs)				
Rh / BMImBF <sub>4</sub>	10 bar	95	884	7
Rh / graphene	4 bar	> 99	360	5
(2.8±0.5 nm Rh-NPs)				
Rh / attapulgite	30 bar	> 99	2700	8
(3 nm Rh-NPs)				
Rh / silica-coated magnetite NPs	6 atm	> 99	7600	9
(3-5 nm Rh-NPs)				
Pd / Polyglycerol	40.52	no conv. given	1190	10
Pt / BMImPF <sub>6</sub>	4 atm	> 99	156	11
Pt, solventless	4 atm	> 99	833	11
Pt / acetone	4 atm	> 99	833	11
Pt / SiO <sub>2</sub>	1 bar	no conv. given	890	12
Pt / SiO <sub>2</sub>	10 torr cyclohexene, 200 torr H <sub>2</sub>	no conv. given	12960	13

**Table S7** Catalyst activities of M-NPs in the 1-hexyne to hexane hydrogenation.

Metal-NP system	H <sub>2</sub> pressure	Conversion [%]	Activity [mol product × (mol Rh) <sup>-1</sup> × h <sup>-1</sup> ] (TOF [h <sup>-1</sup> ])	Ref.
Rh/PC	4 bar	88	51	This work
Pt <sub>2</sub> (P <sub>2</sub> O <sub>5</sub> H <sub>2</sub> ) <sub>4</sub> <sup>4-</sup>	20.7 atm	not given	not given	14
1 % Pd/Al <sub>2</sub> O <sub>3</sub>	1 atm	50	22680, TOF = 6.3 s <sup>-1</sup>	15
5 % Pd/Al <sub>2</sub> O <sub>3</sub>	1 atm	50	11520, TOF = 3.2 s <sup>-1</sup>	15

- 1 A. F. Hollemann and N. Wiberg, *Lehrbuch der anorganischen Chemie*, **102** ed, de Gruyter, Berlin, 2007, p. 1781-1782.
- 2 H. Hachenberg, K. Beringer, *Die Headspace-Gaschromatographie als Analysen- und Meßmethode*, Vieweg, Braunschweig/Wiesbaden, Germany, 1996, pp. 32–35.
- 3 L. M. Rossi, G. Machado, P. F. P. Fichtner, S. R. Teixeira and J. Dupont, *Catal. Lett.*, 2004, **92**, 149–155.
- 4 E. T. Silveira, A. P. Umpierre, L. M. Rossi, G. Machado, J. Morais, I. L. R. Baumvol, S. R. Teixeira, P. F. P. Fichtner and J. Dupont, *Chem. Eur. J.*, 2004, **10**, 3734-3740.
- 5 D. Marquardt, C. Vollmer, R. Thomann, P. Steurer, R. Mülhaupt, E. Redel and C. Janiak, *Carbon*, 2011, **49** 1326-1332.

- 
- 6 C. Vollmer, M. Schröder, Y. Thomann, R. Thomann and C. Janiak, *Appl. Catal. A*, 2012, **425-426**, 178-183. <http://dx.doi.org/10.1016/j.apcata.2012.03.017>
  - 7 C. Vollmer, E. Redel, K. Abu-Shandi, R. Thomann, H. Manyar, C. Hardacre and C. Janiak, *Chem. – Eur. J.*, 2010, **16**, 3849-3858.
  - 8 S. Miao, Z. Liu, Z. Zhang, B. Han, Z. Miao, K. Ding and G. An, *J. Phys. Chem. C*, 2007, **111**, 2185-2190.
  - 9 M. J. Jacinto, P. K. Kiyohara, S. H. Masunaga, R. F. Jardim and L. M. Rossi, *Applied Catalysis A: General*, 2008, **338**, 52–57.
  - 10 R. Sablong, U. Schlotterbeck, D. Vogt and S. Mecking, *Adv. Synth Catal.*, 2003, **345**, 333-336.
  - 11 C. W. Scheeren, G. Machado, J. Dupont, P. F. P. Fichtner and S. G. Texeira, *Inorg. Chem.*, 2003, **42**, 4738-4742.
  - 12 L. Armelao, D. B. D. Amico, R. Braglia, F. Calderazzo, F. Garbassi, G. Marra and A. Merigo, *Dalton Trans.*, 2009, 5559-5566.
  - 13 R. M. Rioux, B. B. Hsu, M. E. Grass, H. Song and G. A. Somorjai, *Catal Lett.*, 2008, **126**, 10-19.
  - 14 J. Lin and C.U. Pittman, *J. Orgmet. Chem.* 1996, **512**, 69-78.
  - 15 J. A. Anderson, J. Mellor and R. P. K. Wells, *J. Catal.* 2009, **261**, 208-216.