Material synthesis in ionic liquids – with a focus on metal nanoparticles

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Symposium
“Material Synthesis in Ionic Liquids and Interfacial Processes“
13/04/2016-15/04/2016
Goslar

Ionic liquids (ILs)

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Definition:

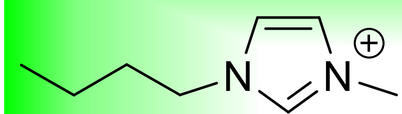
"Ionic liquids are ionic compounds (salts) which are liquid below 100 °C."

Building blocks:

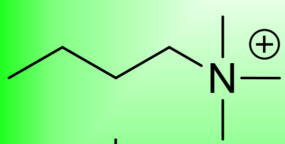
weakly-coordinating cation — weakly-coordinating anion

Examples

Cations:



$BMIm^+$
1-n-Butyl-3-Methyl-Imidazolium



$BtMA^+$
n-Butyl-tri-Methyl-Ammonium

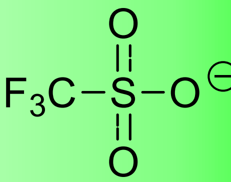
- ionic charge
- high polarity
- high dielectric constant
- supramolecular network

Anions:

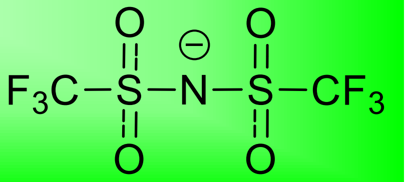
BF_4^-

PF_6^-

OTf^- =



NTf_2^- =



see also: Dupont & Scholten, *Chem. Soc. Rev*. **2010**, *39*, 1780.

Material synthesis in ionic liquids

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what you often read (for example):

- ionic liquids are unique alternatives to traditional aqueous or organic solvents;

- preparation of (advanced functional) materials in ILs is very promising;

- benefits of using ILs in materials synthesis;

ionothermal synthesis

because of ILs':
- excellent solvating properties,

- negligible vapor pressure,

- high thermal stability,

- wide liquidus range,

- ability to dissolve a variety of materials.

Further reading:
J. Łuczak, M. Paszkiewicz, A. Krukowska, A. Malankowska, A. Zaleska-Medyns, Ionic liquids for nano- and microstructures preparation.
Part 1: Properties and multifunctional role,
Part 2: Application in synthesis,
Adv. Coll. Inferfac. Sci. 2016, 230, 13-28;
Adv. Coll. Inferfac. Sci. 2016, 227, 1-52.

Material synthesis in ionic liquids

ionothermal synthesis is often combined with

- **"nano"** (including systems > 100 nm);

- use of **microwave heating**

Ionic liquids (ILs)
- and microwave heating

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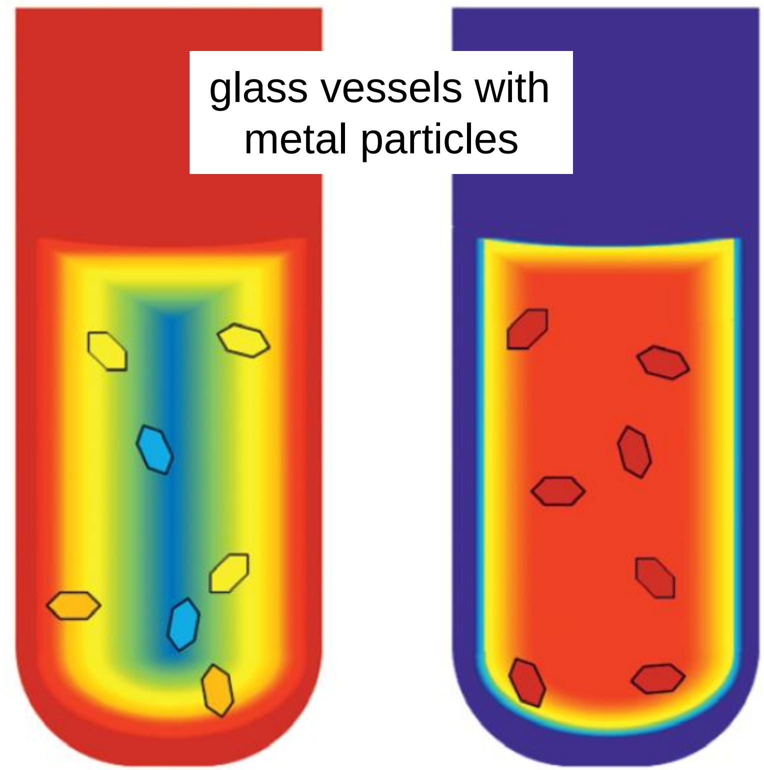
excellent absorption efficiency of ILs for microwave energy

- microwave heating is extremely rapid ("simple" and "energy saving")
- microwave radiation can interact directly with the reaction components



temperature profile

conventional heating   µ-wave heating

M. F. Groh, M. Heise, M. Kaiser, M. Ruck, *Nachr. Chemie* **2013**, *61*, 26-29.

Material synthesis in ionic liquids

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ionothermal synthesis is often combined with
- "nano" (including systems > 100 nm);

- use of microwave heating;

- synthesis of **new "phases"** inaccessible in conventional solvents or otherwise "standard" conditions;

- **morphology control** by ILs;
-- "the role of ILs in ionothermal syntheses can be templating, cotemplating, and no templating"; (R.E. Morris, *Chem. Commun*. **2009**, 2990.)

- ILs / ionothermal methods are employed in
-- the synthesis of zeolites, metal-organic frameworks, metal nanoparticles, metal nanorods, metal oxide NPs, semiconductors, polynuclear metal complexes, microporous and mesoporous carbon and graphene, ...
-- electrochemical synthesis of nanomaterials (cf. work of *Endres*)

Further reading:
Z. Li et al., Ionic liquids for synthesis of inorganic nanomaterials, *Curr. Opinion Sol. State Mater. Sci.* **2008**, 12, 1-8.
X. Duan et al., The art of using ionic liquids in the synthesis of inorganic nanomaterials, *CrystEngComm* **2014**, 16, 2550-2559.

Material synthesis in ionic liquids

noted less often:

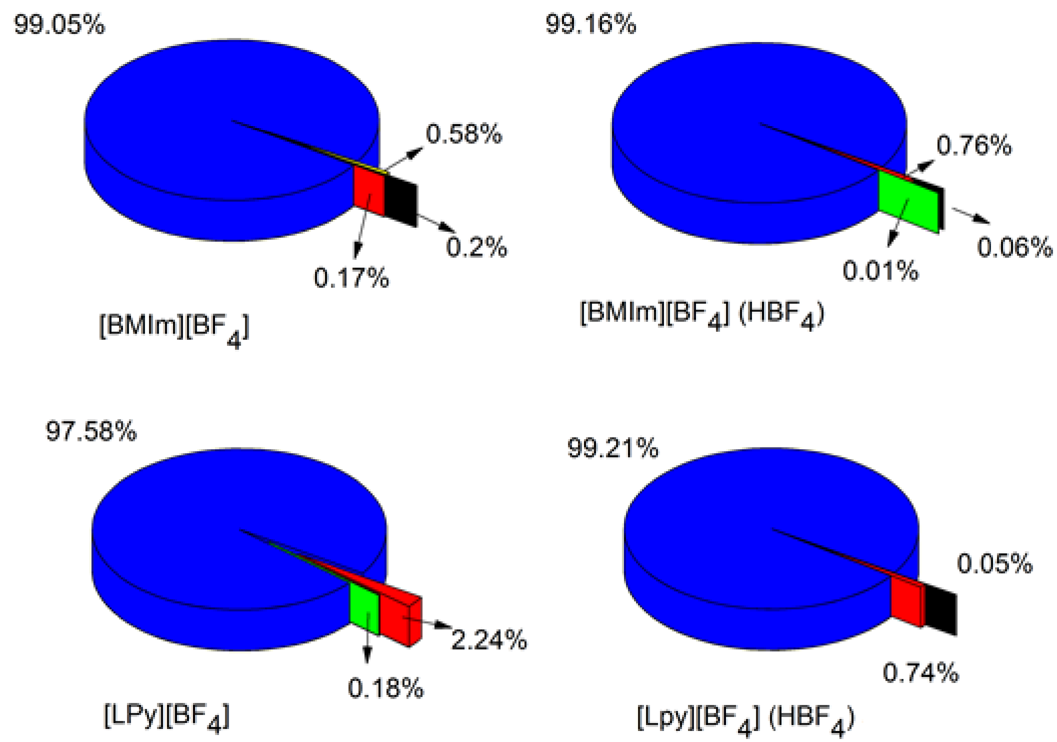
- problem of IL purity,

- IL hydrolysis and decomposition

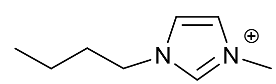
Ionic liquids (ILs)
- halide analysis

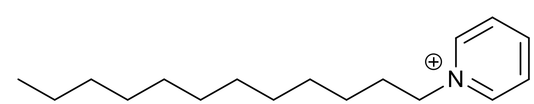
Dionex ICS-1100

+ headspace-KFT for water content



bromide, chloride, fluoride, BF_4

$[BMIm]^+$ = 

$[Lpy]^+$ = 

Material synthesis in ionic liquids

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Examples:

- ZnO micro-pyramids

- CdSe nanoparticles

- metal nanoparticles
-- Pt
-- CuZn
-- NiGa
-- RuSn

- metal nanoparticles deposited on "graphene"

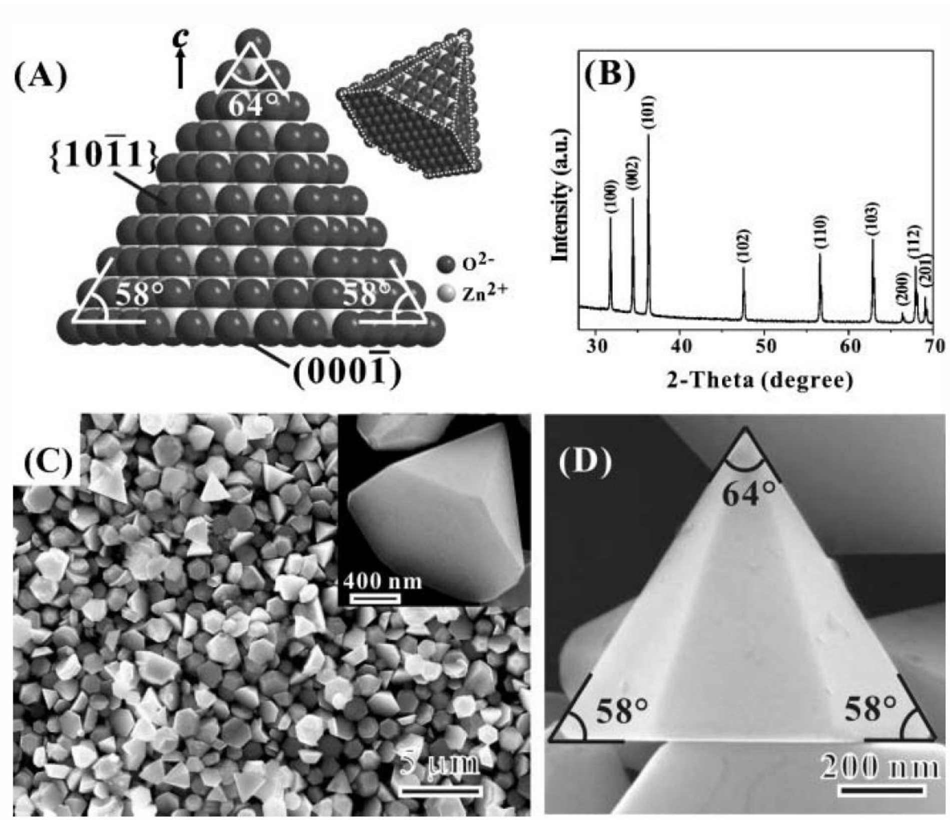
See also:
F. Endres,
Ionic Liquids: Solvents for the Electro-deposition of Metals and Semiconductors,
ChemPhysChem **2002**, 3, 144-154.

A. Panniello et al.
Semiconductor nanocrystals dispersed in imidazolium-based ionic liquids: a spectroscopic and morphological investigation,
J. Nanopart. Res. **2013**, 15, 1567

ZnO micro-pyramids

IL: oleic acid+ ethylenediamine

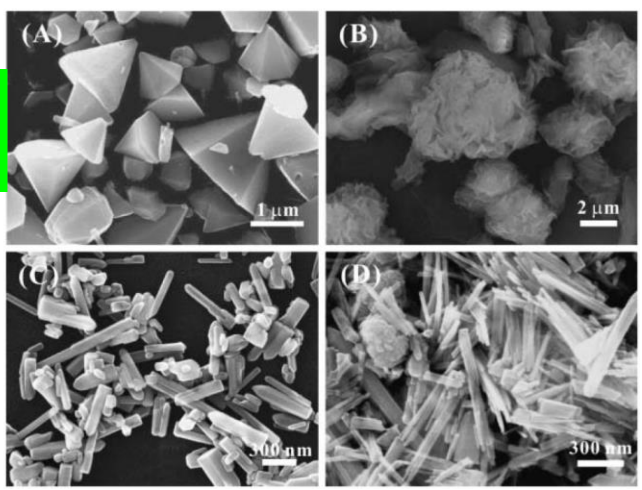
$Zn(O_2CCH_3)_2$ ⟶ (286 °C, 1 h)



for comparison:

OA +en

OA

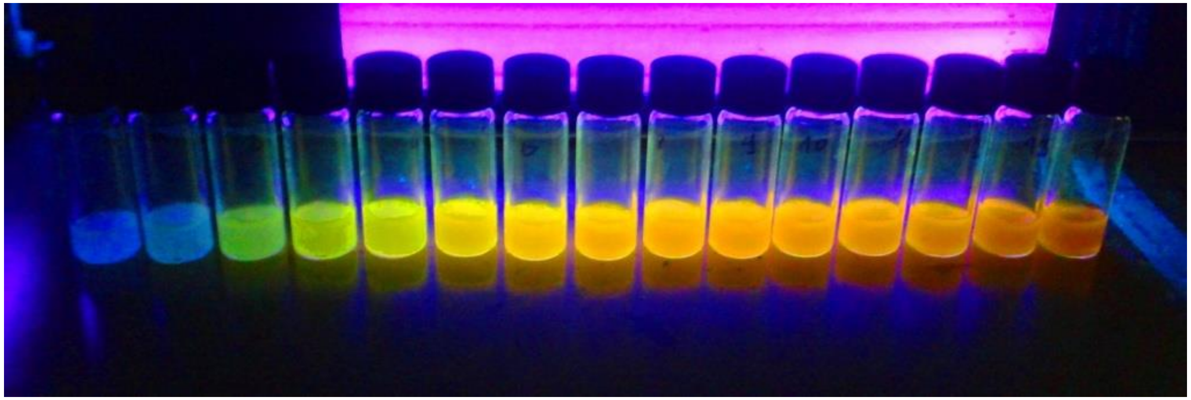


TOA

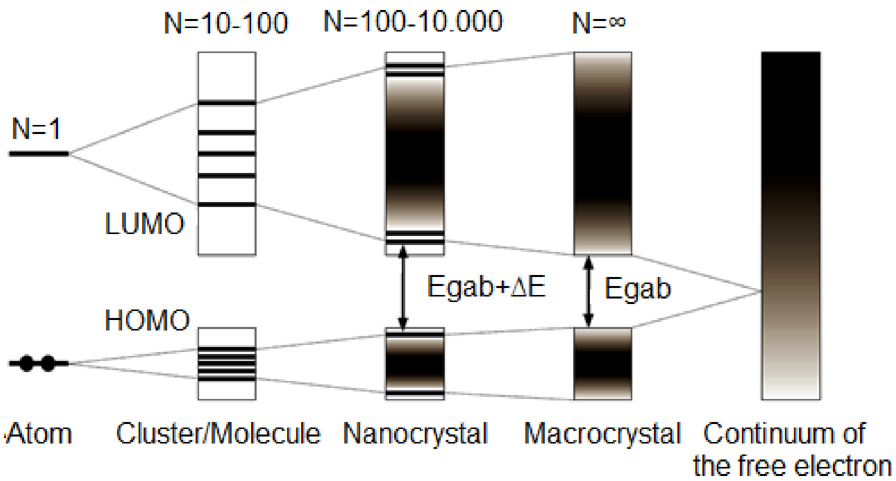
air

X. Zhou, Z.-X. Xie, Z.-Y. Jiang, Q. Kuang, et al. *Chem. Commun.* **2005**, 5572–5574

CdSe nanoparticles



- Novel properties - electron tunneling, size quantization of energy levels
- Discrete electronic energy levels below 7.6 nm (particle in the box)
- Hypsochromic shift of the absorption due to quantum confinement



M.L. Landry, T.E. Morrell, T.K. Karagounis, C.-H. Hsia, C.Y. Wang, *J. Chem. Ed.* **2014**, *91*, 274−279.

Synthetic methods to metal chalcogenides

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- Colloidal solution methods
- **High temperature injection methods**
- Solvothermal/hydrothermal processes
- Synthesis from elemental precursors
- Pulse plasma assisted synthesis
- Sonochemical processes
- Reflux condensation methods
- Microwave assisted synthesis
- Ionic liquid assisted methods

→

Possible advantages:
Variety of IL media,
Variety of precursors,
No stabilizing agents necessary

P.K. Bajpai, S. Yadav, A. Tiwari, H.S. Virk, *Solid State Phenomena* **2015**, 222, 187.

K. Klauke, B. Hahn, K. Schütte, J. Barthel, C. Janiak, *Nano-Structures & Nano-Objects* **2015**, 1, 24-31.

A. Guleria, A.K. Singh, M.C. Rath, S.K. Sarkar, S. Adhikari, *Dalton Trans.* **2014**, 43, 11843.

MSe-NPs in [BMIm][BF_4]: dual-source precursor in fluorous IL

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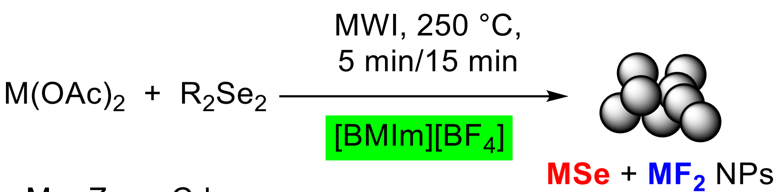
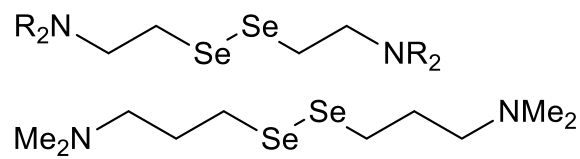
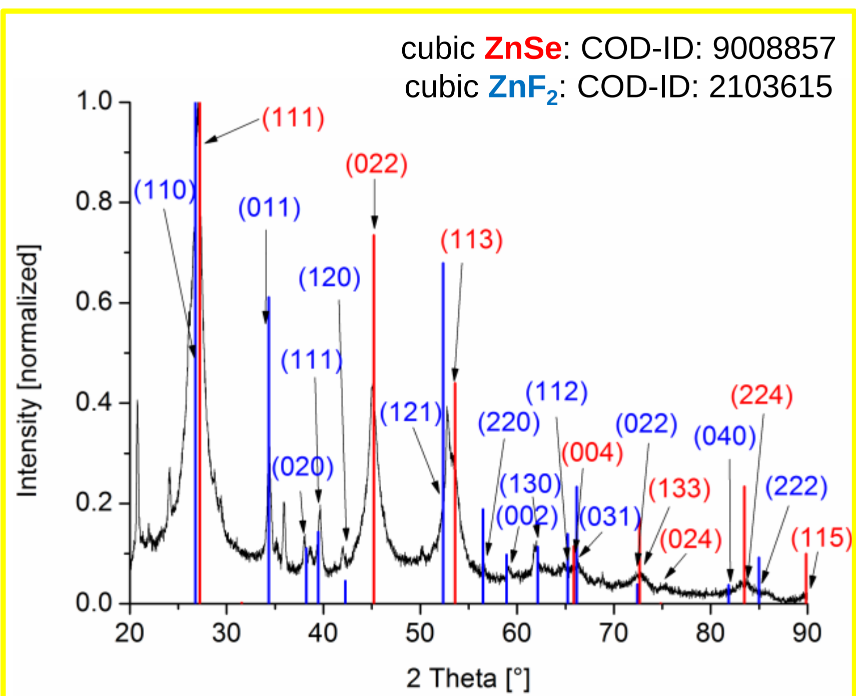


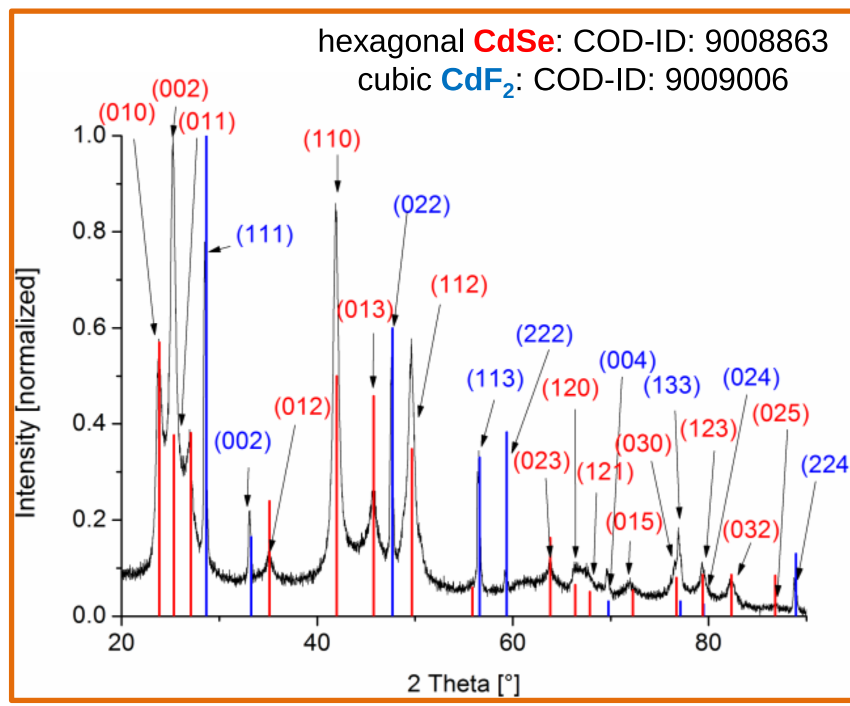
M = Zn or Cd

R_2Se_2 (diselenides):



R = Me, Et





K. Klauke, B. Hahn, K. Schütte, J. Barthel, C. Janiak, *Nano-Structures & Nano-Objects* **2015**, 1, 24-31.

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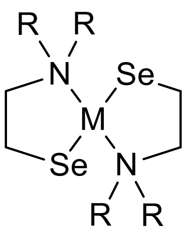
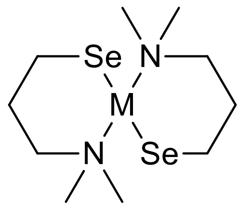
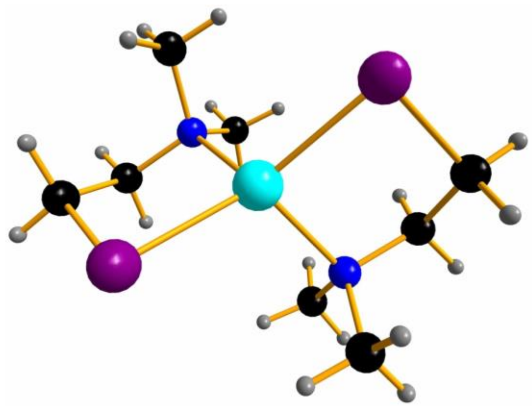


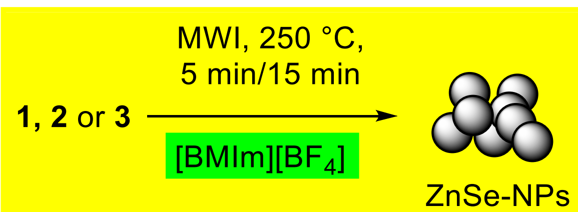
M/R	Me	Et
Zn	**1**	**2**
Cd	**4**	**5**



M	
Zn	**3**
Cd	**6**

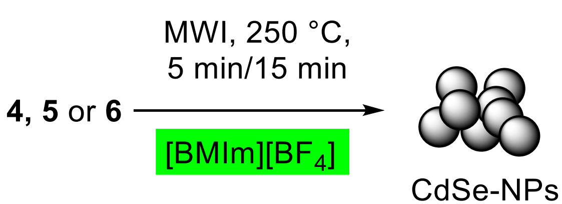


V. K. Jain *et al.*; *Polyhedron* **2006**, 25, 2383–2391

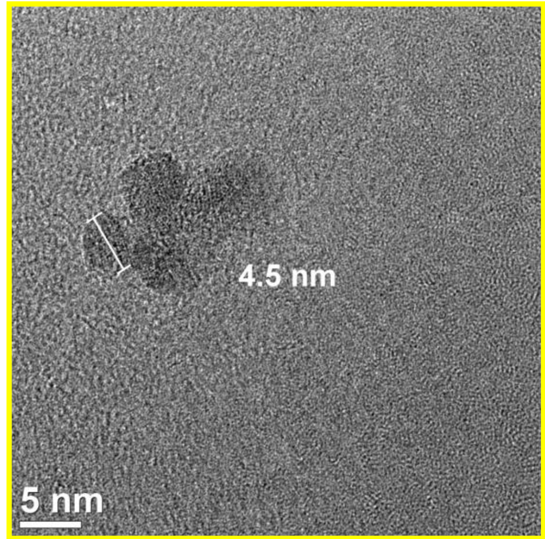


4 – 7 nm

no ZnF_2



10 – 19 nm



see poster P12 of K. Klauke

K. Klauke, B. Hahn, K. Schütte, J. Barthel, C. Janiak, *Nano-Structures & Nano-Objects* **2015**, 1, 24-31.

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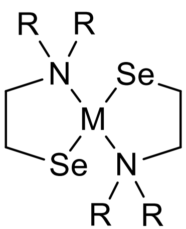

M/R	Me	Et
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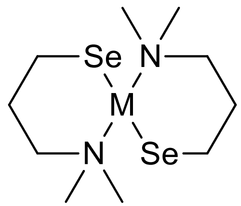
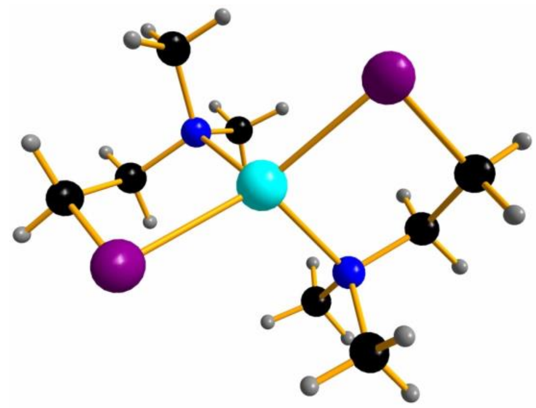
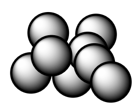


M	
Zn	**3**
Cd	**6**



V. K. Jain *et al.*; *Polyhedron* **2006**, 25, 2383–2391

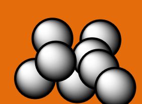
1, 2 or **3** —MWI, 250 °C, 5 min/15 min; [BMIm][BF_4]→



ZnSe-NPs

4 – 7 nm

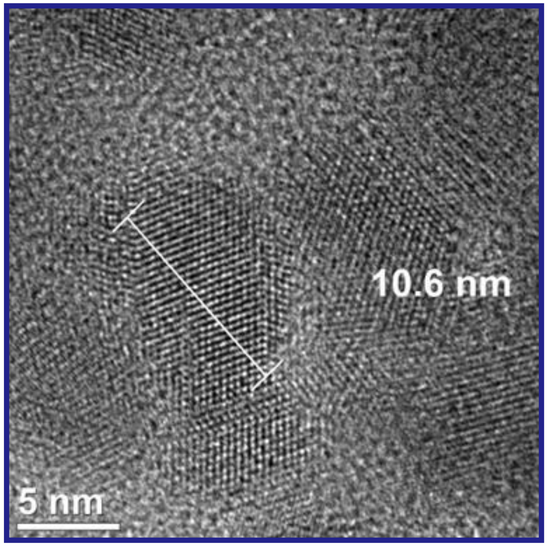
4, 5 or **6** —MWI, 250 °C, 5 min/15 min; [BMIm][BF_4]→



CdSe-NPs

10 – 19 nm

no CdF_2



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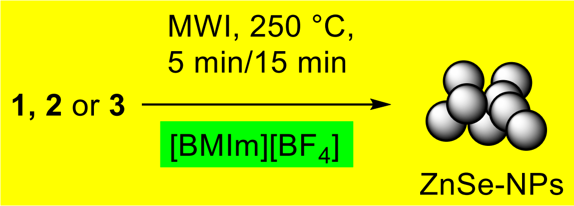

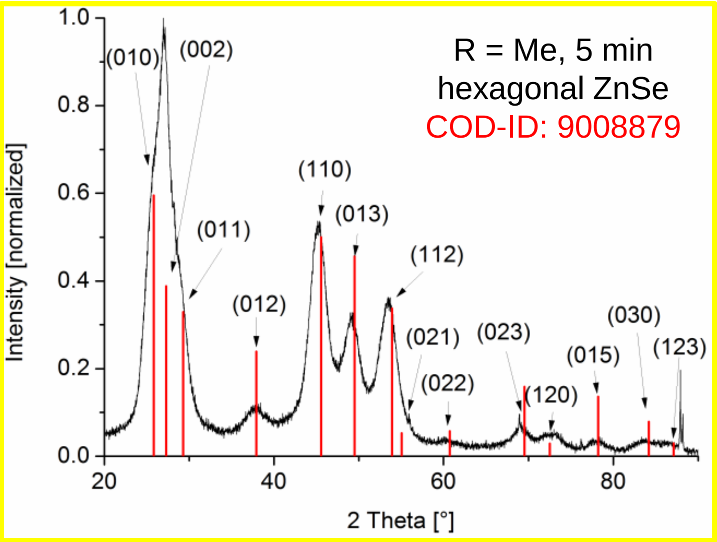

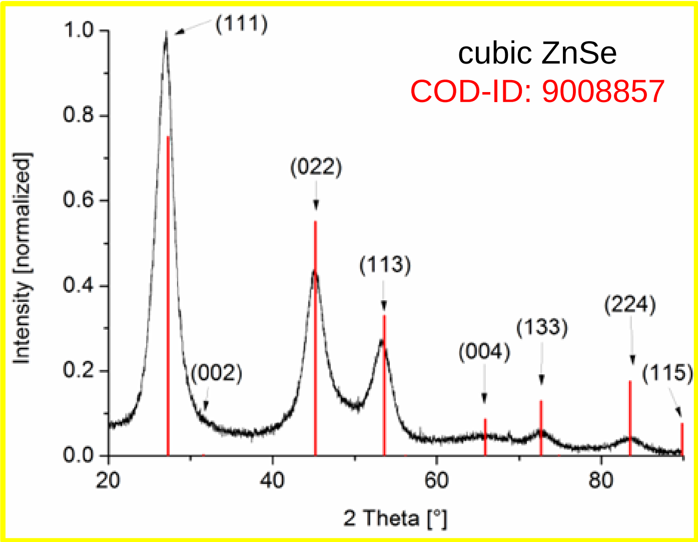

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Examples:

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- CdSe nanoparticles

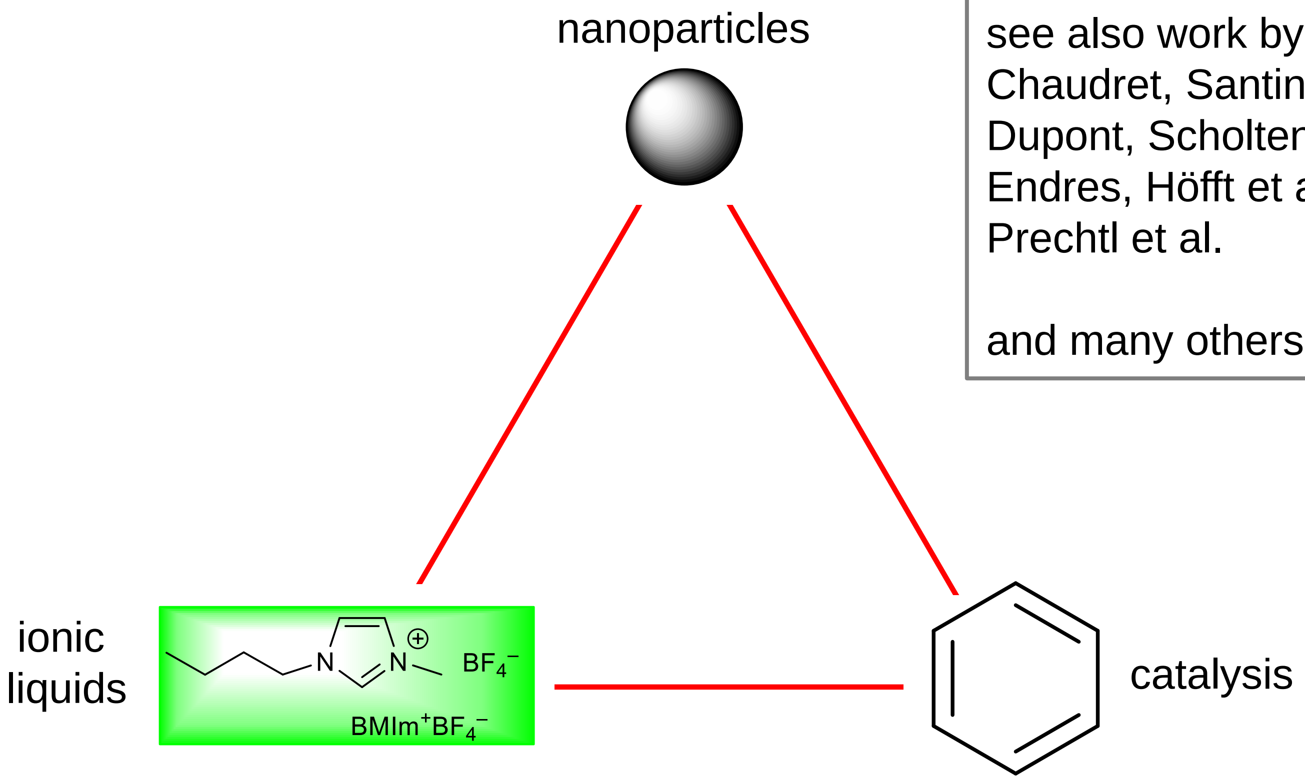
- metal nanoparticles
  - -- Pt
  - -- CuZn
  - -- NiGa
  - -- RuSn

- metal nanoparticles deposited on "graphene"

M-NPs in ILs:
see also work by
Chaudret, Santini, Philippot et al.
Dupont, Scholten et al.
Endres, Höfft et al.
Prechtl et al.

and many others

Scope



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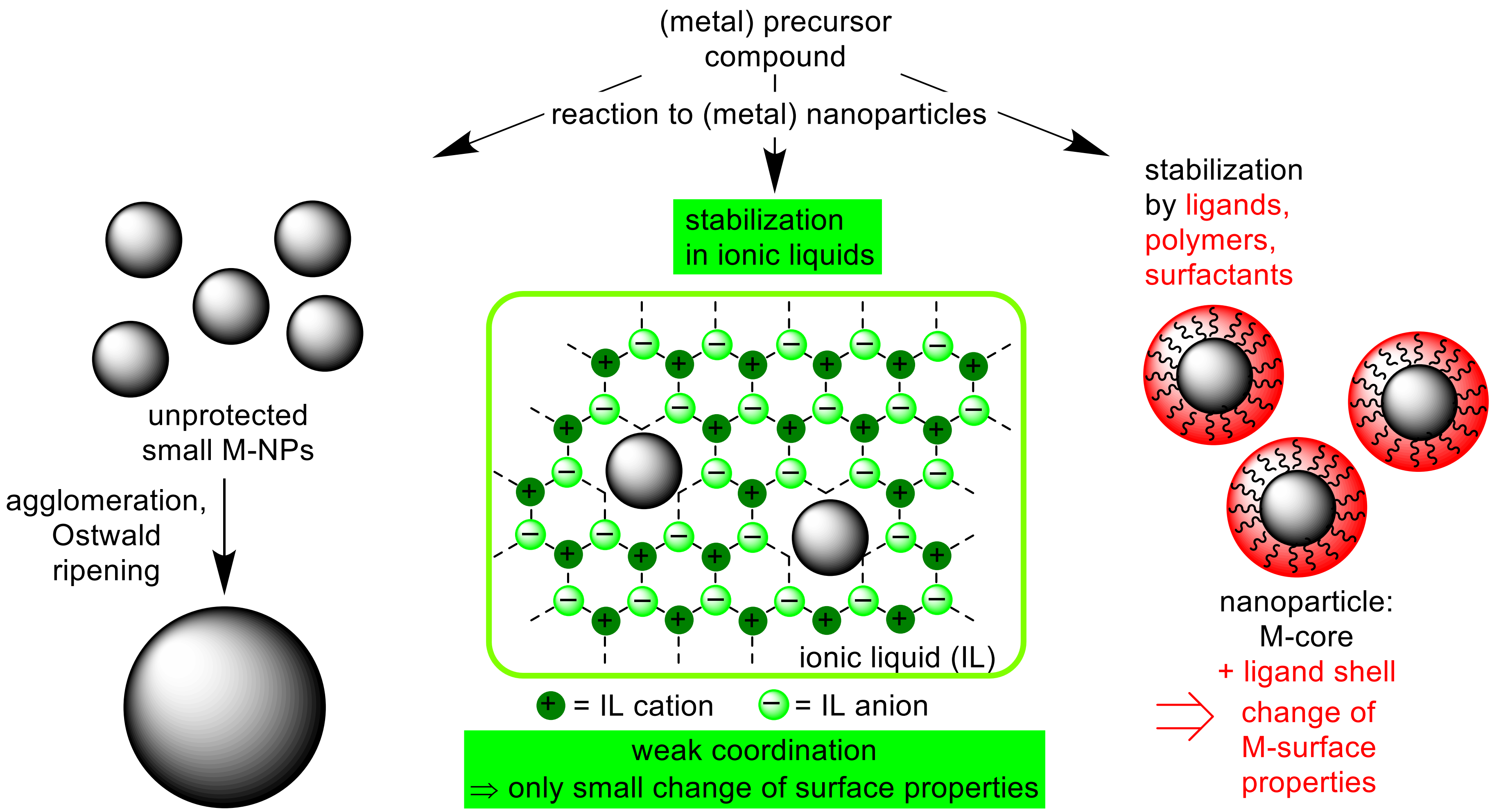
and many others

Further reading:

J.D. Scholten, B.C. Leal, J. Dupont, Transition Metal Nanoparticle Catalysis in Ionic Liquids, *ACS Catalysis* **2012**, 2, 184−200.

V.I. Pârvulescu, C. Hardacre, Catalysis in Ionic Liquids, *Chem. Rev.* **2007**, 107, 2615-2665.

Stabilization of (metal) nanoparticles



Coord. Chem. Rev. **2011**, *255*, 2039.
Review: *Z. Naturforsch. B*, **2013**, *68*, 1059.

"Ligand-free" metal nanoparticles in ionic liquids

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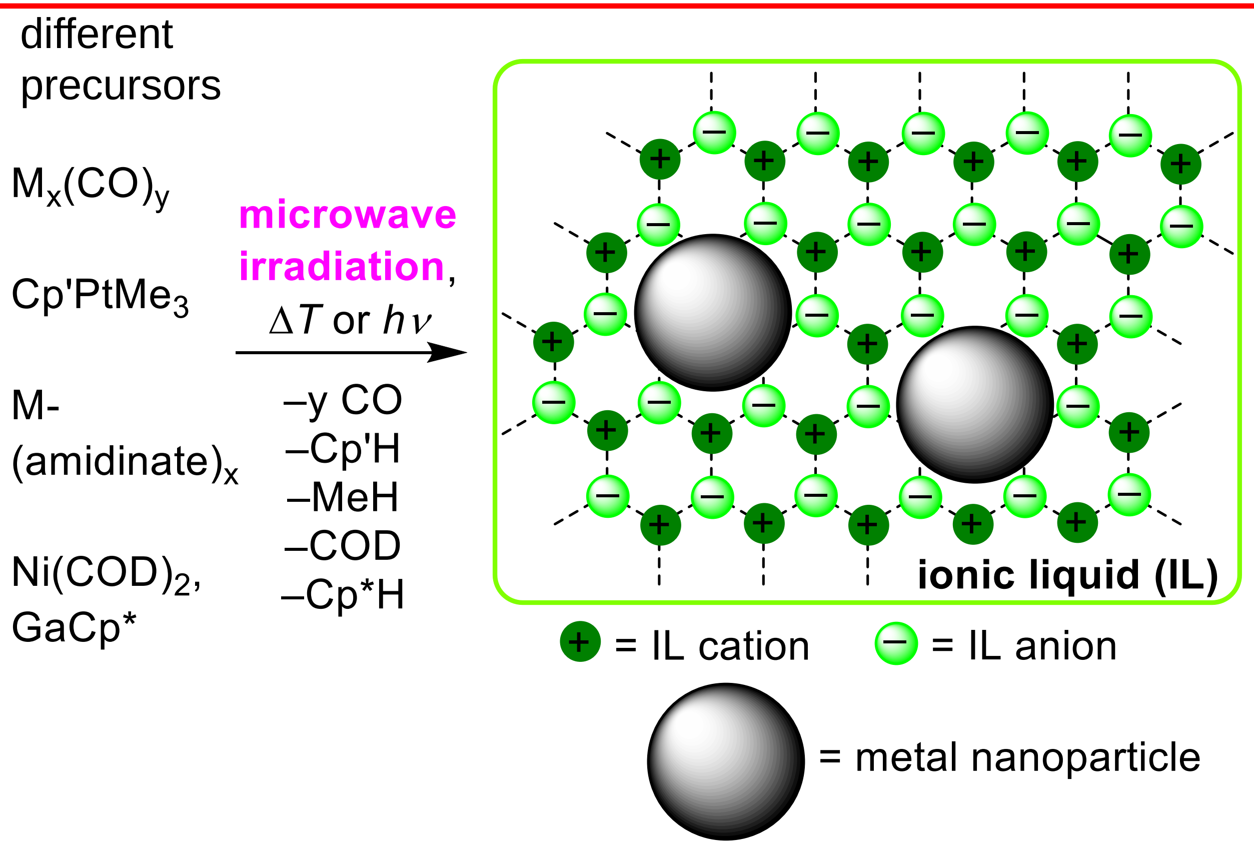
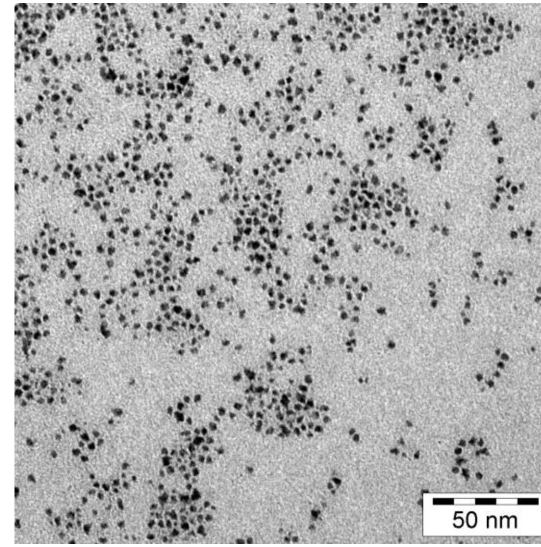


no stabilizing capping ligands necessary!

Example:



Re-NPs, Ø 2.4(9) nm from $Re_2(CO)_{10}$

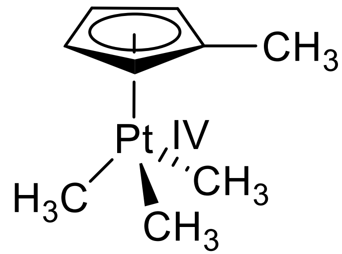
Chem. Commun. **2008**, 1789.
Organometallics **2008**, *27*, 1976.
J. Organomet. Chem. **2009**, *694*, 1069.
Chem. Eur. J. **2010**, *16*, 3849.
Dalton Trans. **2011**, *40*, 8290.
Coord. Chem. Rev. **2011**, *255*, 2039.

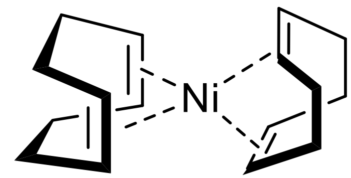
Review: *Z. Naturforsch. B*, **2013**, *68*, 1059.
Ionic Liquids (ILs) in Organometallic Catalysis / Topics in Organometallic Chemistry, Springer, **2015**

Organometallic precursors for metal nanoparticles

Examples:

$M_x(CO)_y$





$Ni(COD)_2$

GaCp*

Organometallic precursors
- considered early on but less developed – need to prepare sensitive organometallics

possible advantages:
- clean and low-temperature thermolysis or photolysis

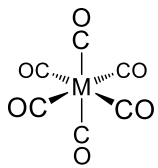
- labile M–C bond with low dissociation energy

- M–C + H_2 gives M–C bond hydrogenolysis → M–H + H–C
→ M + H_2

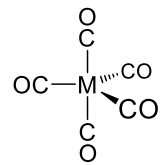
= "soft wet-chemical synthesis" of metal nanoparticles
for size, shape and composition control

Further reading; review: C. Amiens, B. Chaudret, D. Ciuculescu-Pradines, V. Collière, K. Fajerwerg, P. Fau, M. Kahn, A. Maisonnat, K. Soulanticac, K. Philippot, *New J. Chem.* **2013**, *37*, 3374-3401.

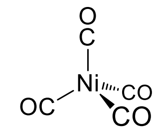
$M_x(CO)_y$ precursors



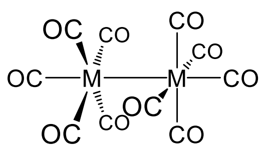
M = V, Cr, Mo, W



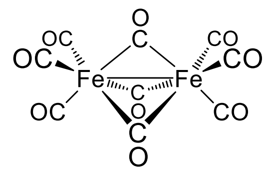
M = Fe, Ru, Os



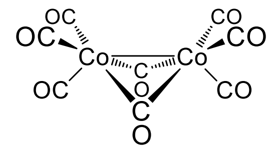
$Ni(CO)_4$



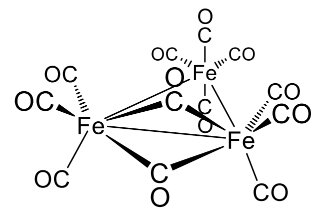
M = Mn, Tc, Re



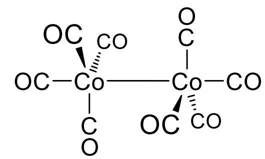
$Fe_2(CO)_9$



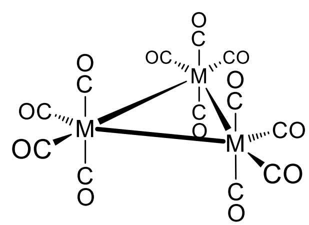
$Co_2(CO)_8$ solid state



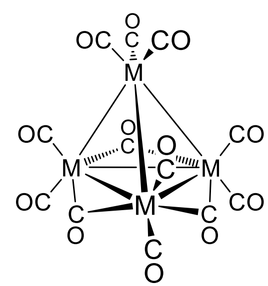
$Fe_3(CO)_{12}$



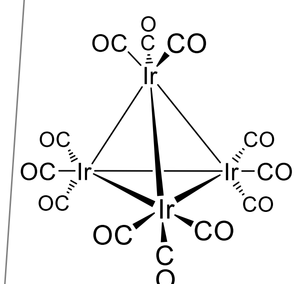
$Co_2(CO)_8$ gas phase



$M_3(CO)_{12}$, M = Ru, Os

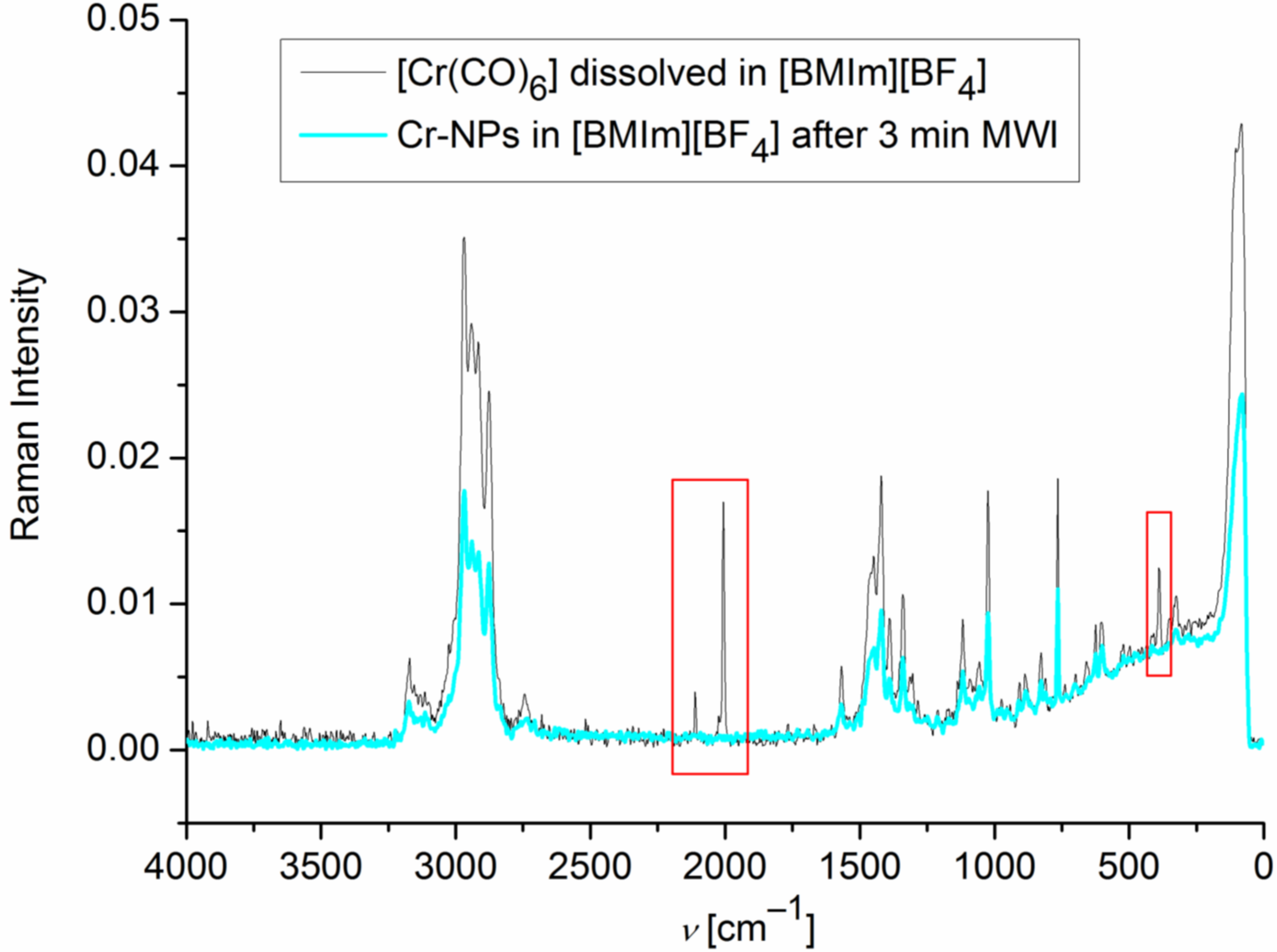


$M_4(CO)_{12}$, M = Co, Rh



$Ir_4(CO)_{12}$

absence of CO by Raman-FT spectroscopy:



Chem. Eur. J. **2010**, *16*, 3849.

Ionic liquids for the synthesis of metal nanoparticles
- $M_x(CO)_y$ precursors

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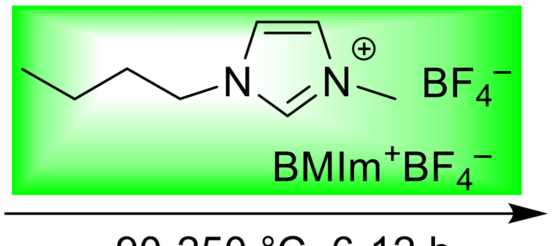
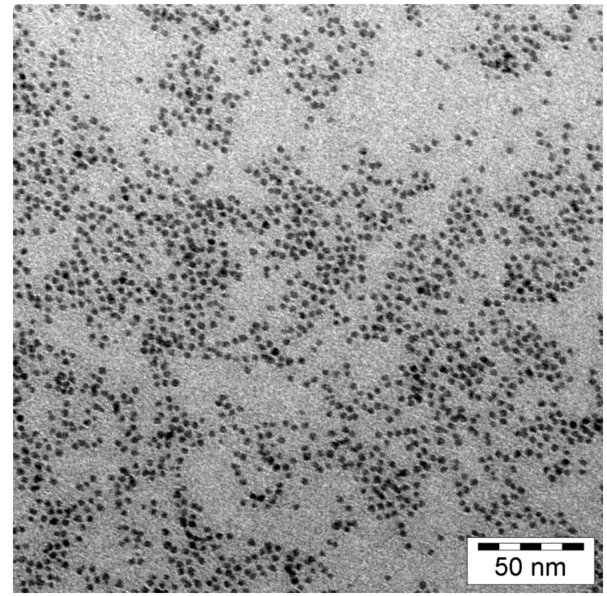
reaction and stabilizing medium:

$Fe_2(CO)_9$
or
$Ru_3(CO)_{12}$
or
$Os_3(CO)_{12}$



90-250 °C, 6-12 h
UV-hν, 15 min
or MWI, 3 min
–9 or 12 CO

M-nanoparticles
M = Fe, Ru, Os
∅ 1.5-2.5 nm

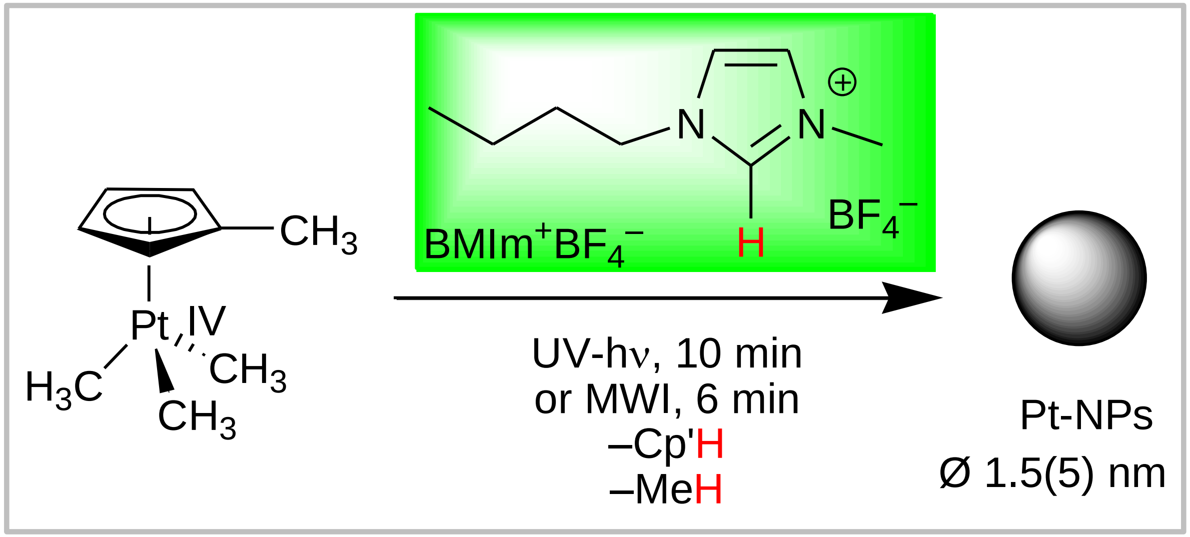


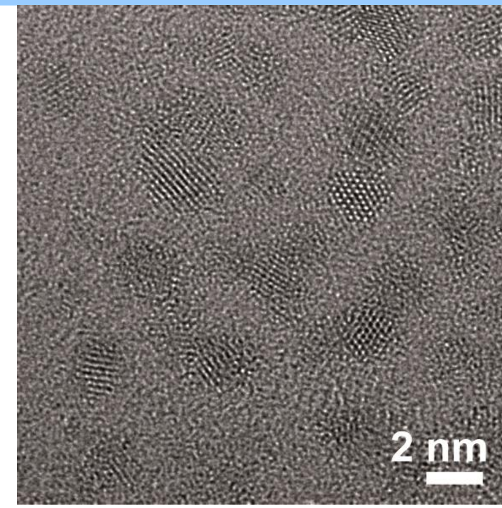
Ru-NPs
Ø 1.6(4) nm

Ru, Rh, Ir-NP/IL dispersions are active hydrogenation catalysts for olefins and aromatics

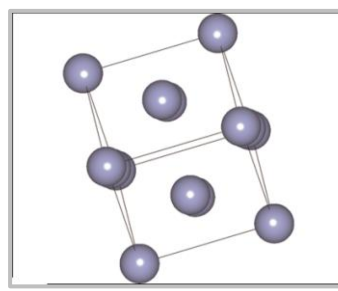
Cr, Mo, W: *Chem. Commun.* **2008**, 1789-1791.
Fe, Ru, Os: *Organometallics* **2008**, *27*, 1976-1978.
Co, Rh, Ir: *J. Organomet. Chem.* **2009**, *694*, 1069-1075.
Ru, Rh, Ir et al.: *Chem. Eur. J.* **2010**, *16*, 3849-3858.

Ionic liquids for the synthesis of metal nanoparticles - e.g. Pt-nanoparticles

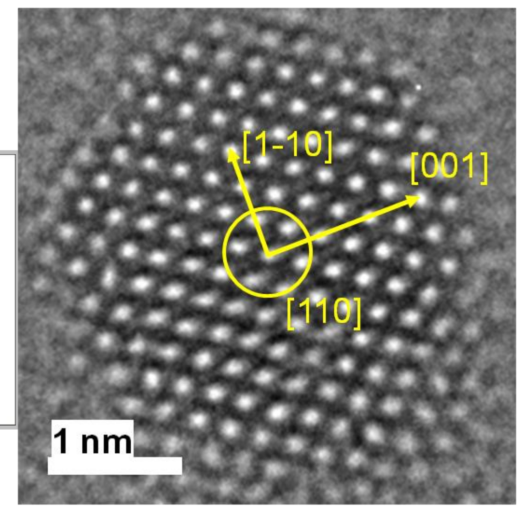




- longterm (>10 months) stable dispersions



fcc lattice



Pt-NP/IL dispersions
active hydrosilylation catalysts

CrystEngComm **2012**, *14*, 7607-7615.

Pt-nanoparticles as hydrosilylation catalyst

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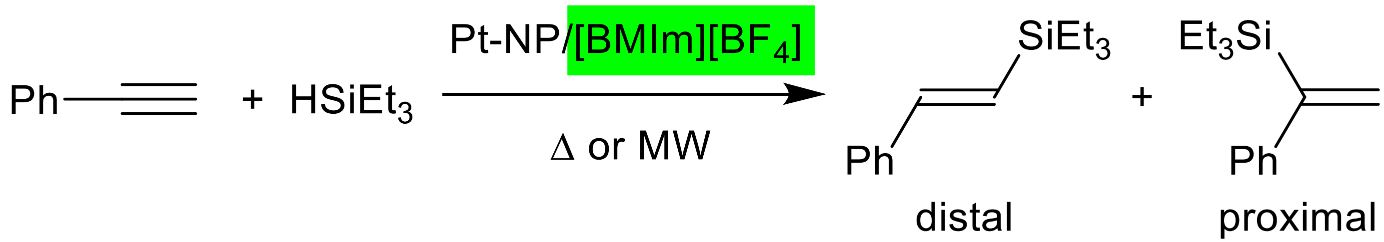
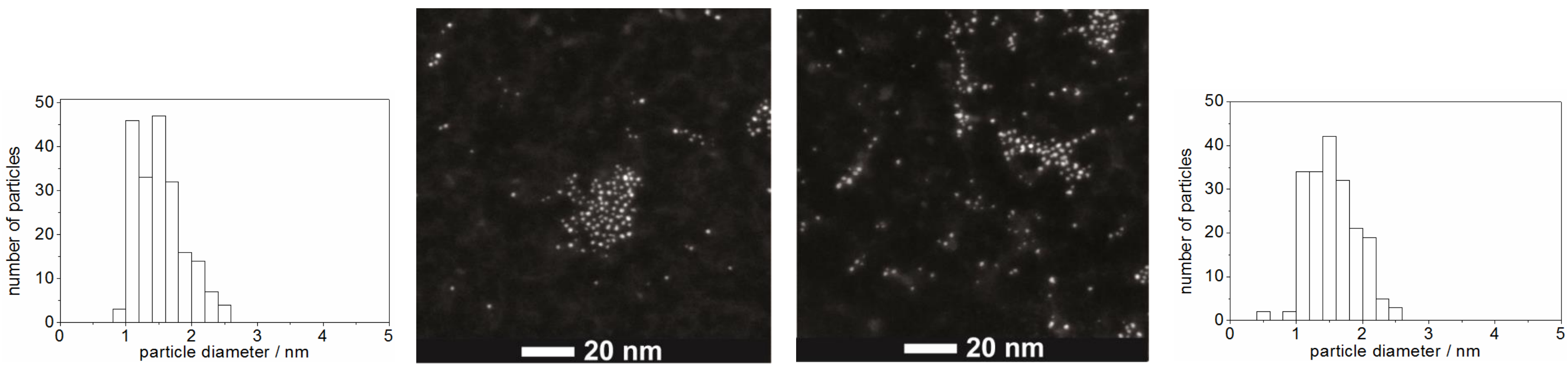


1.4-4 : 1

up to TOF 96000 h^{-1} at 0.0125 mol% Pt and quantitative conversion

Pt-NPs unchanged after catalysis:

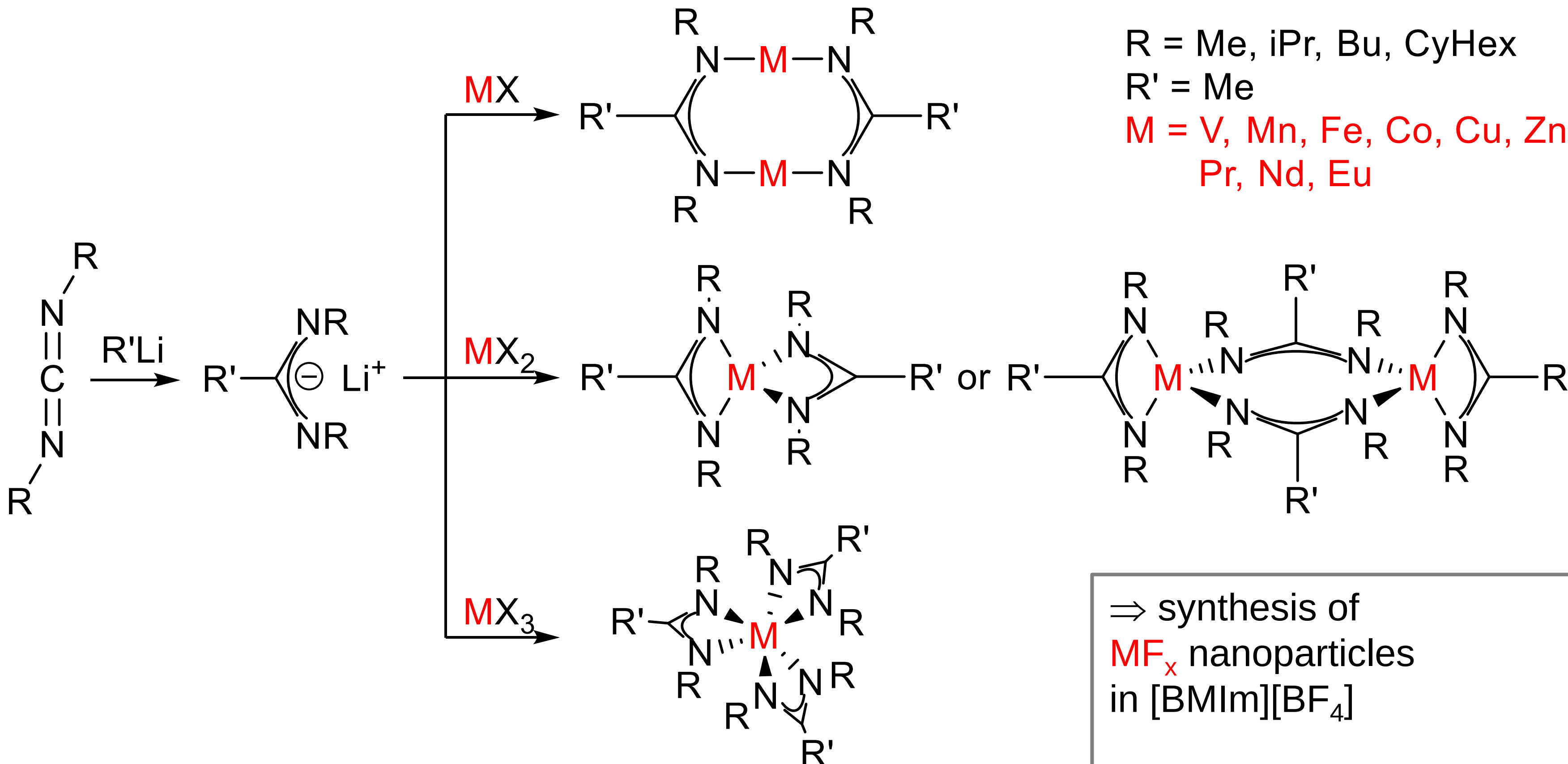


Ø 1.5±0.4 nm

Ø 1.6±0.4 nm

CrystEngComm **2012**, *14*, 7607-7615.

Metal-organic precursors for metal nanoparticles
- metal amidinates



R = Me, iPr, Bu, CyHex
R' = Me
M = V, Mn, Fe, Co, Cu, Zn, Pr, Nd, Eu

⇒ synthesis of MF_x nanoparticles in $[BMIm][BF_4]$

interest in electrochemical analysis

B. S. Lim, A. Rahtu, J.-S. Park, R. G. Gordon, *Inorg. Chem.* **2003**, *42*, 7951-7958.

Bimetallic nanoparticles
- CuZn and Cu_3Zn nanobrass

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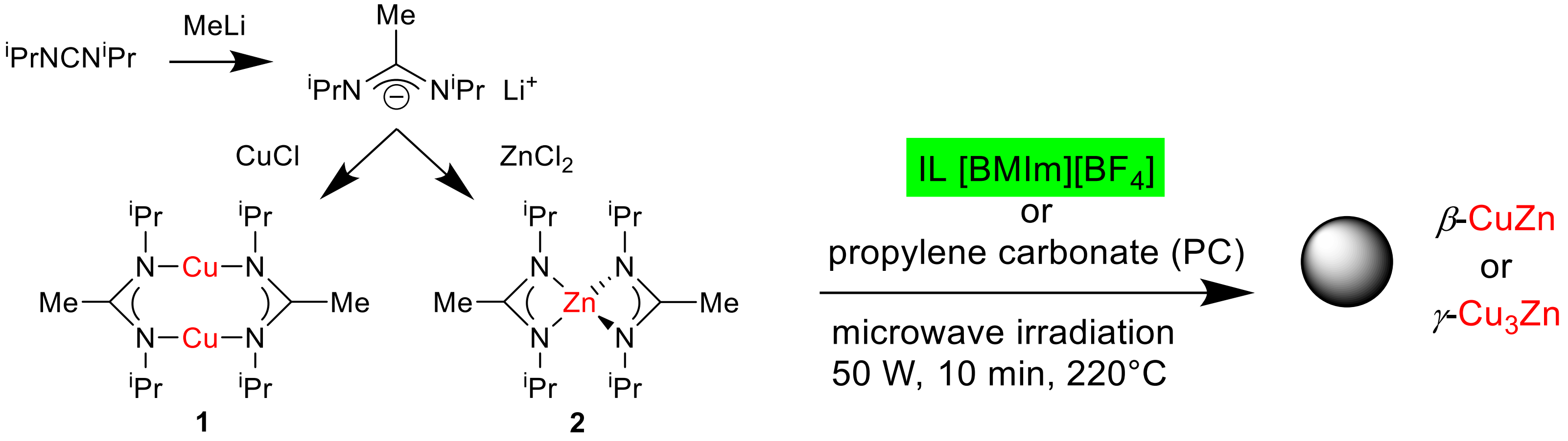
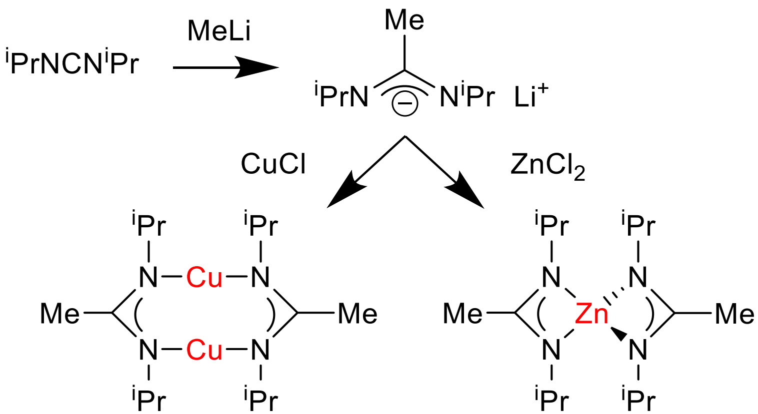
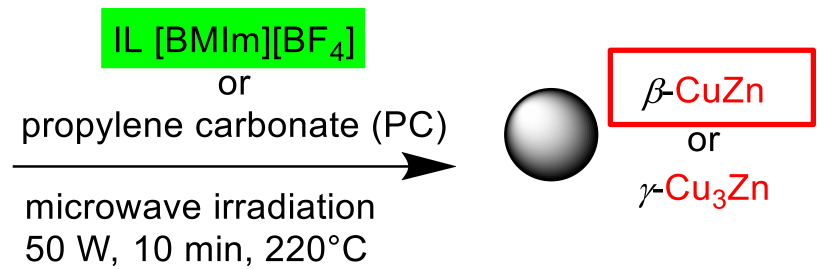


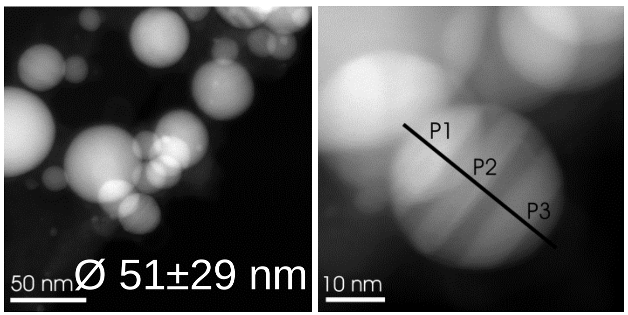
Nanoscale **2014**, *6*, 3116-3126.

Bimetallic nanoparticles
- CuZn and Cu_3Zn nanobrass

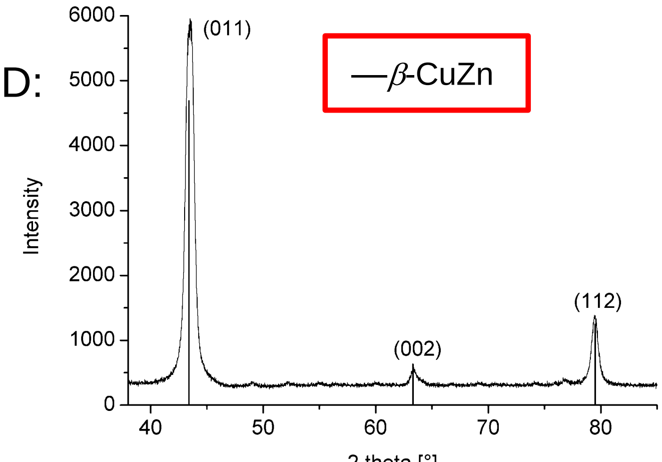




STEM (with EDX):

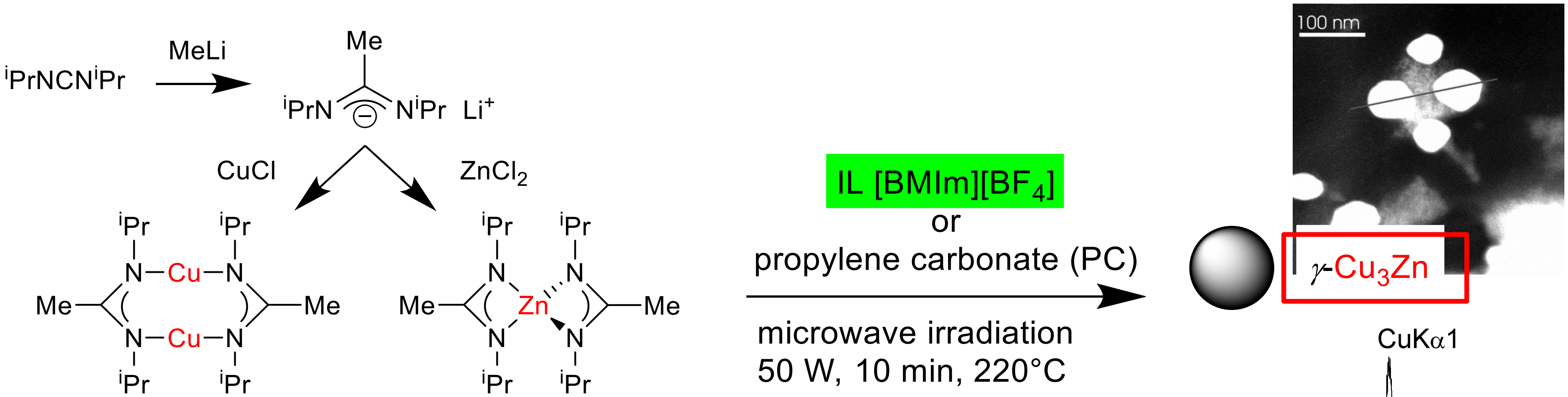


PXRD:

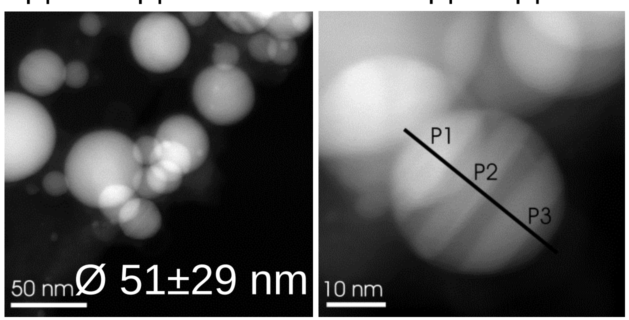


Nanoscale **2014**, *6*, 3116-3126.

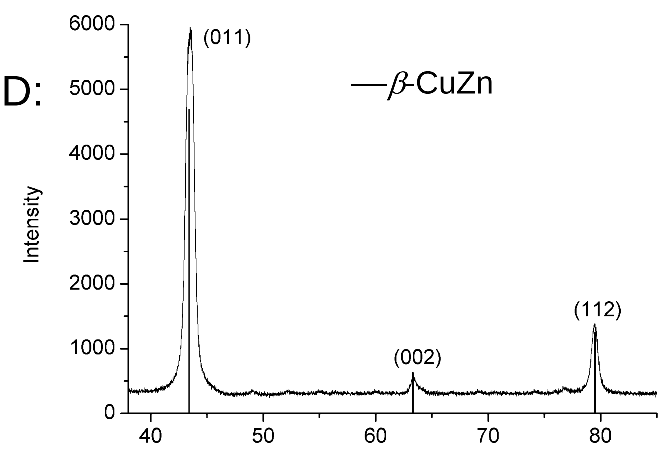
Bimetallic nanoparticles
- CuZn and Cu_3Zn nanobrass



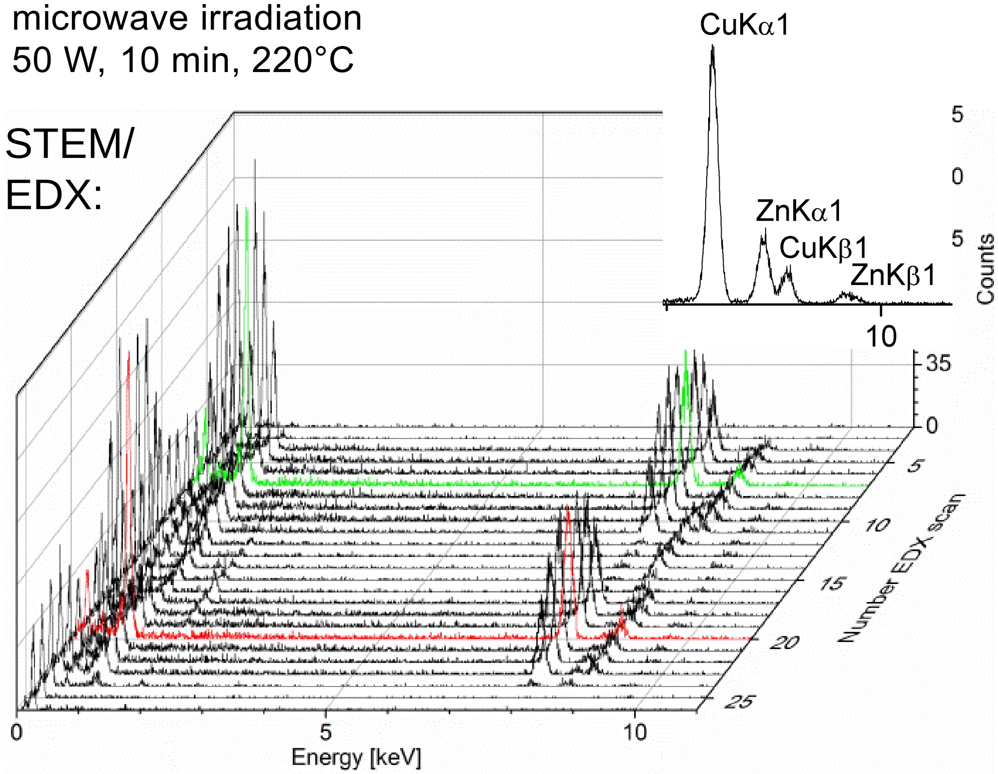
STEM (with EDX):



PXRD:



STEM/ EDX:



Nanoscale **2014**, *6*, 3116-3126.

Bimetallic alloy nanoparticles
- CuZn and Cu_3Zn nanobrass

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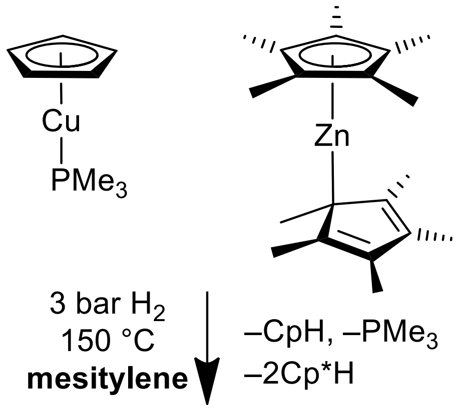
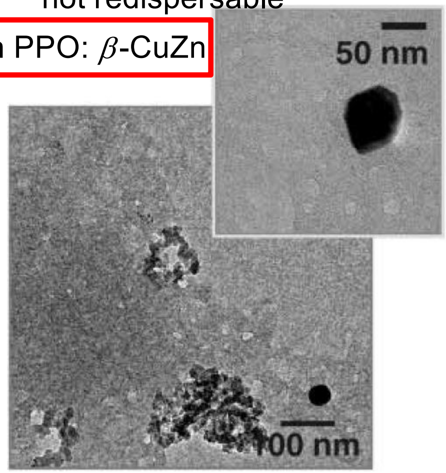
non-IL



β-CuZn↓ agglomerate, not redispersable

with PPO: β-CuZn



catalytically inactive

Fischer et. al., *J. Mater. Chem.* **2006**, *16*, 2420.

NP analysis: (S)TEM, local-resolution EDX, SAED, PXRD, EXAFS, DLS

Bimetallic alloy nanoparticles
- CuZn and Cu_3Zn nanobrass

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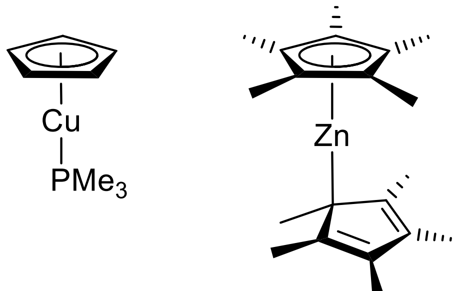
non-IL

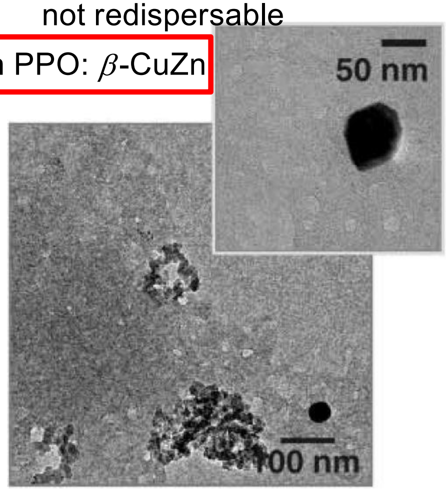


3 bar H_2
150 °C
mesitylene

–CpH, –PMe_3
–2Cp*H

β-CuZn↓ agglomerate,
not redispersable

with PPO: β-CuZn



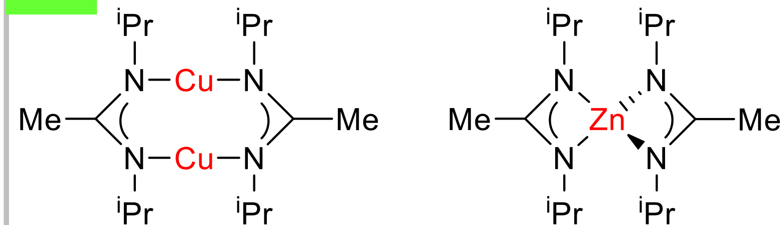
catalytically inactive

Fischer et. al., *J. Mater. Chem.* **2006**, *16*, 2420.

versus

NP analysis:
(S)TEM,
local-resolution EDX,
SAED,
PXRD,
EXAFS,
DLS

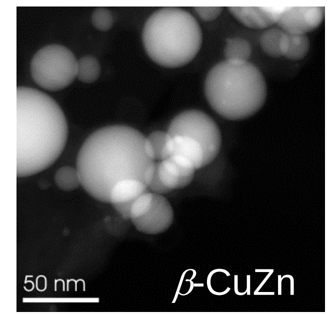
IL



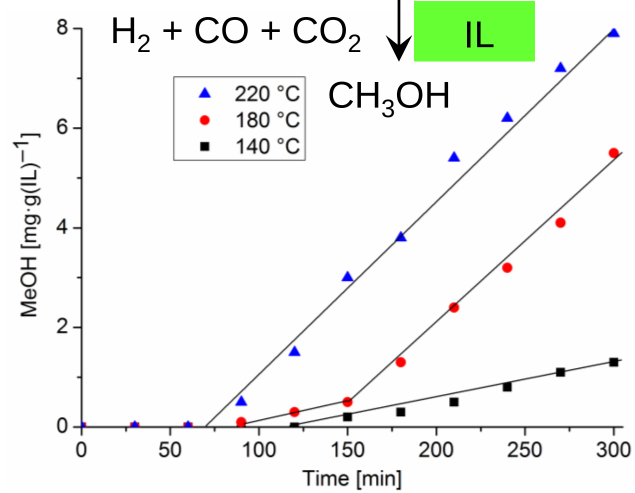
microwave irradiation
50 W, 10 min, 220°C
$[BMIm][BF_4]$

β-CuZn
γ-Cu_3Zn

catalytically active



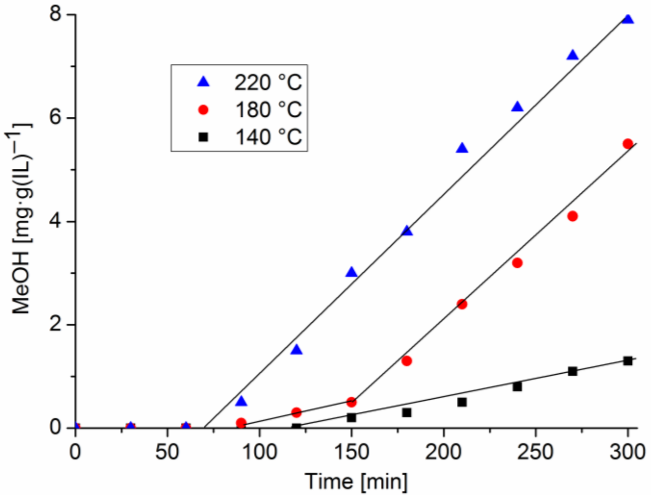
$H_2 + CO + CO_2$ → IL
CH_3OH



Fischer, Janiak et al. *Nanoscale* **2014**, *6*, 3116.

Bimetallic nanoparticles
- "CuZn" for MeOH catalysis

CH_3OH formation:



Nanoscale **2014**, *6*, 3116-3126.

Bimetallic nanoparticles
- “CuZn” after MeOH catalysis

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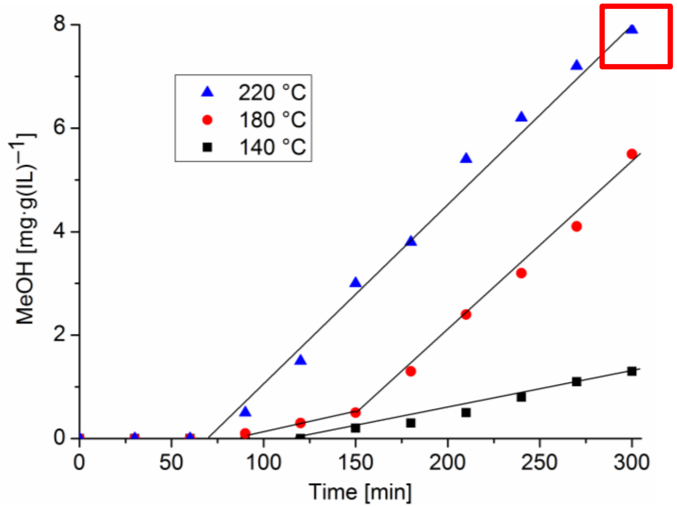
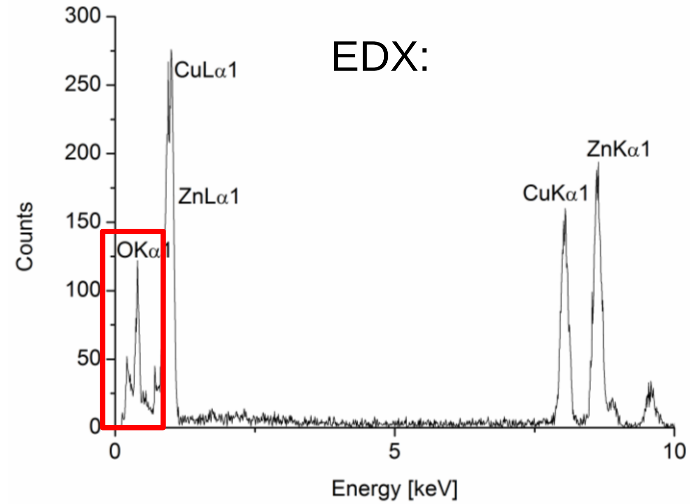
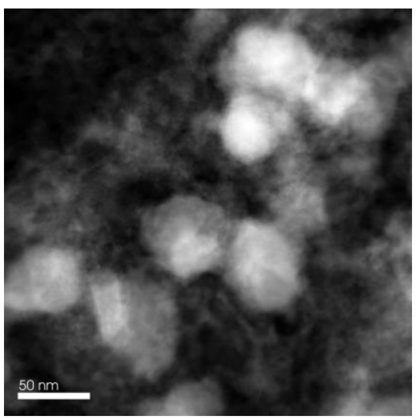
CH_3OH formation:



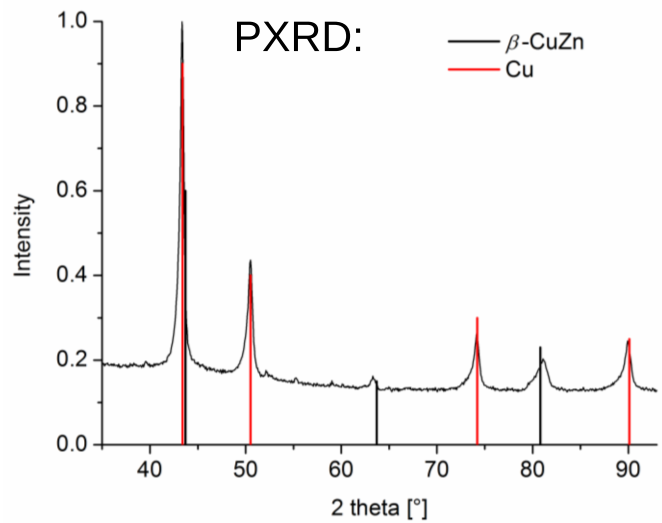
EDX:



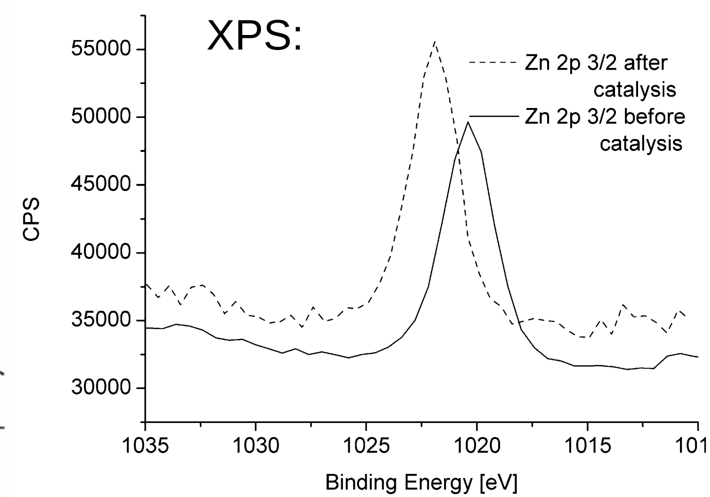
STEM:



PXRD:



XPS:



Conclusion: β-CuZn ⟶ Cu/ZnO
(+β-CuZn)

Nanoscale **2014**, *6*, 3116-3126.

Bimetallic nanoparticles
- NiGa and Ni_3Ga

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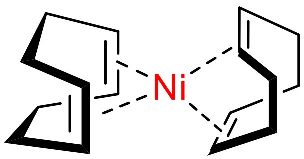
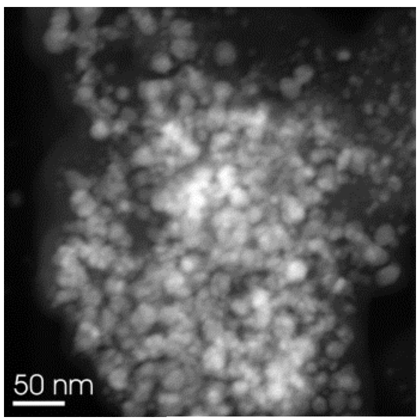
a  + b GaCp* → NiGa or Ni_3Ga

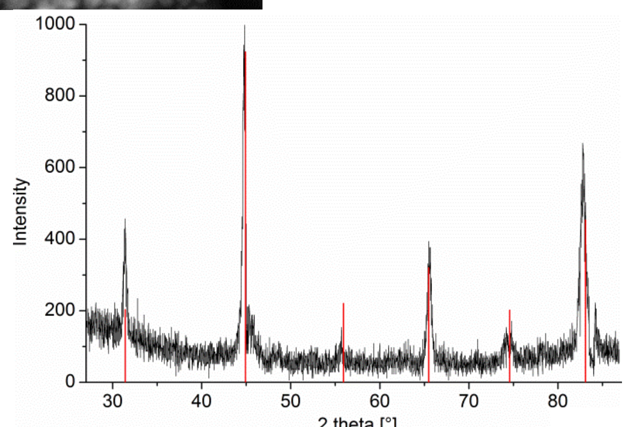
[BMIm][BF_4]
microwave irradiation
50 W, 10 min
(to 220°C)

–COD, –(Cp*)

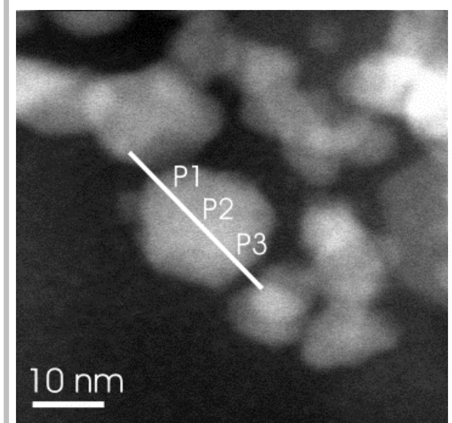
NiGa



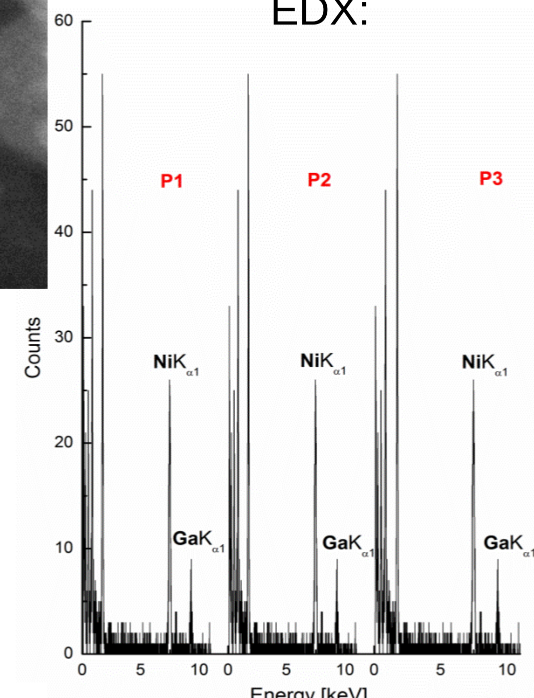
PXRD:



Ni_3Ga

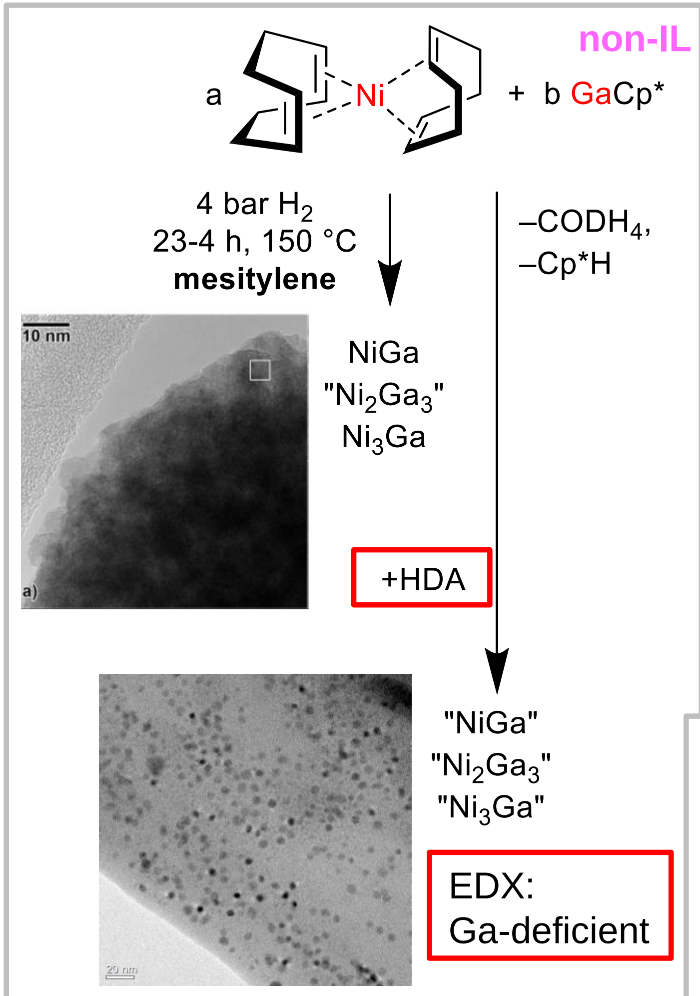


EDX:



Nanoscale **2014**, *6*, 5532-5544.

Bimetallic alloy nanoparticles
- NiGa and Ni_3Ga



NP analysis:
(S)TEM,
local-resolution EDX,
PXRD,
DLS

Fischer, Janiak et al., *Nanoscale* **2014**, *6*, 5532-5544.

Bimetallic alloy nanoparticles
- NiGa and Ni_3Ga

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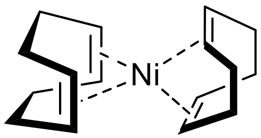
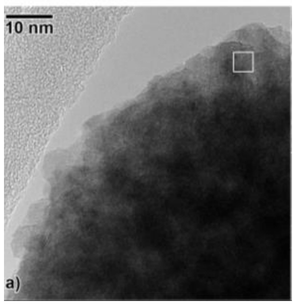
non-IL versus IL

non-IL

a  + b GaCp*

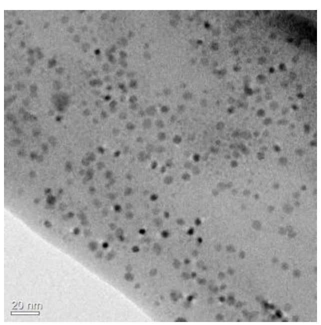
4 bar H_2
23-4 h, 150 °C
mesitylene

$-CODH_4$,
$-Cp^*H$



NiGa
"Ni_2Ga_3"
Ni_3Ga

+HDA

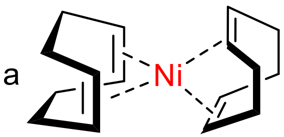


"NiGa"
"Ni_2Ga_3"
"Ni_3Ga"

EDX:
Ga-deficient

NP analysis:
(S)TEM,
local-reso-
lution EDX,
PXRD,
DLS

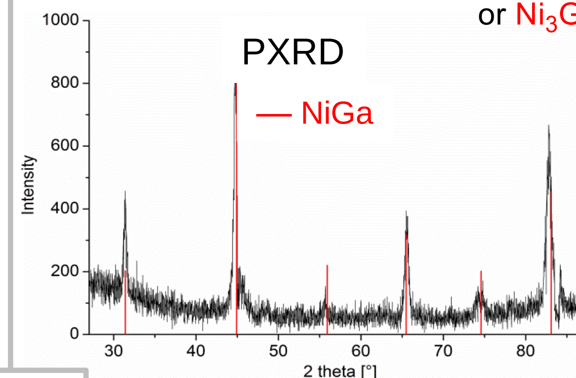
IL

a  + b GaCp*

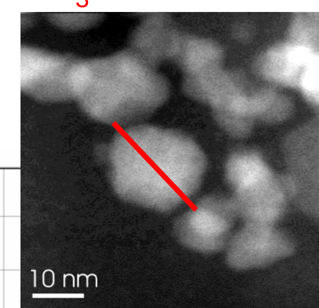
microwave irradiation
50 W, 10 min, 220°C
[BMIm][BF_4]

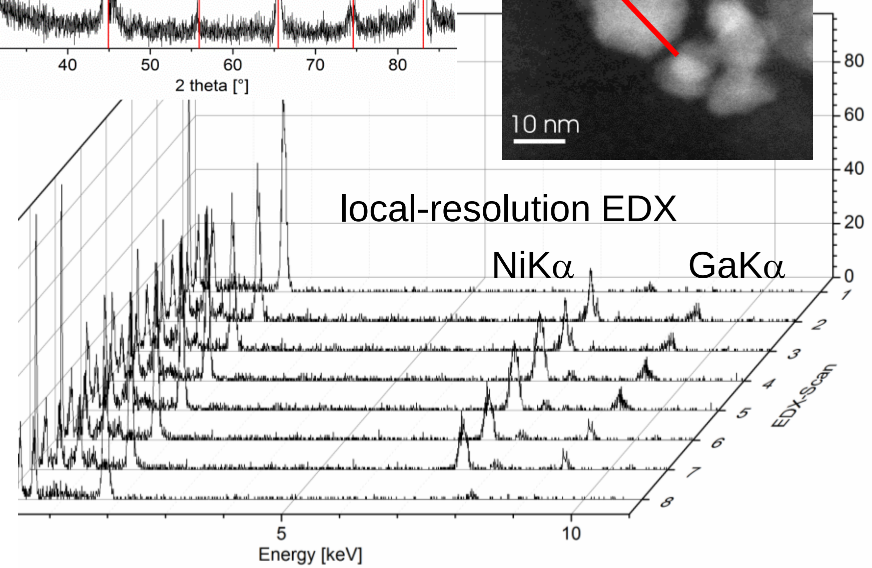
–COD,
–(Cp*)

NiGa
or Ni_3Ga



Ni_3Ga:





Fischer, Janiak et al., *Nanoscale* **2014**, *6*, 5532-5544.

NiGa/ionic liquid
- catalytic semihydrogenation of alkynes

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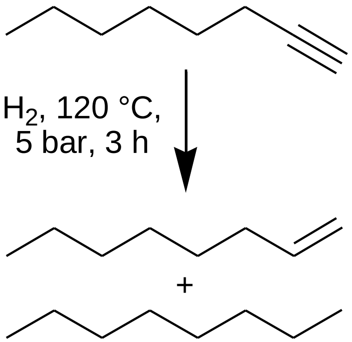
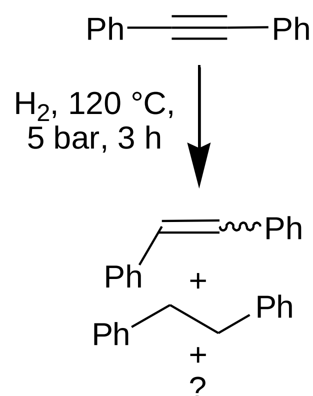


	Ni-NP /[BMIm][BF_4]	NiGa-NP /[BMIm][BF_4]
Conversion:	96%	87-89%
Selectivity:	3%	93-94%
	97%	6-7%

see poster P6 of I. Simon

Can Hume-Rothery phases replace noble-metal catalysts?

Fischer, Janiak et al., *Nanoscale* **2014**, *6*, 5532-5544.



	Ni-NP /[BMIm][BF_4]	NiGa-NP /[BMIm][BF_4]
Conversion:	89%	82-90%
Selectivity:	8%	84-87%
	78%	10-11%
	15%	4%

Normally semihydrogenation requires noble metals:
Pd: Conley, Mitsudome, Antonietti **2013**,
Pt: Attard, **2013**
Ru: Niu, **2013**
Rh: Ruck, Armbrüster, **2012**
Au: Yamamoto, **2012**

Semihydrogenation with PdGa, Pd_2Ga, Pd_3Ga_7 see Armbrüster et al., *J. Phys. Chem. C* **2011**, *115*, 1368; *JACS* **2010**, *132*, 14745; **2011**, *133*, 9112;
with Fe_4Al_{13} see Armbrüster, Schlögl, Grin et al. *Nat. Mater.* **2012**, *11*, 690.

NiGa/ionic liquid
- catalytic semihydrogenation of alkynes

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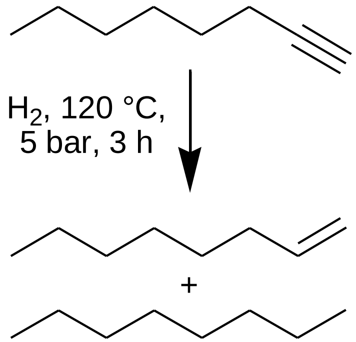


	Ni-NP /[BMIm][BF_4]	NiGa-NP /[BMIm][BF_4]
Conversion:	96%	87-89%
Selectivity:	3%	93-94%
	97%	6-7%

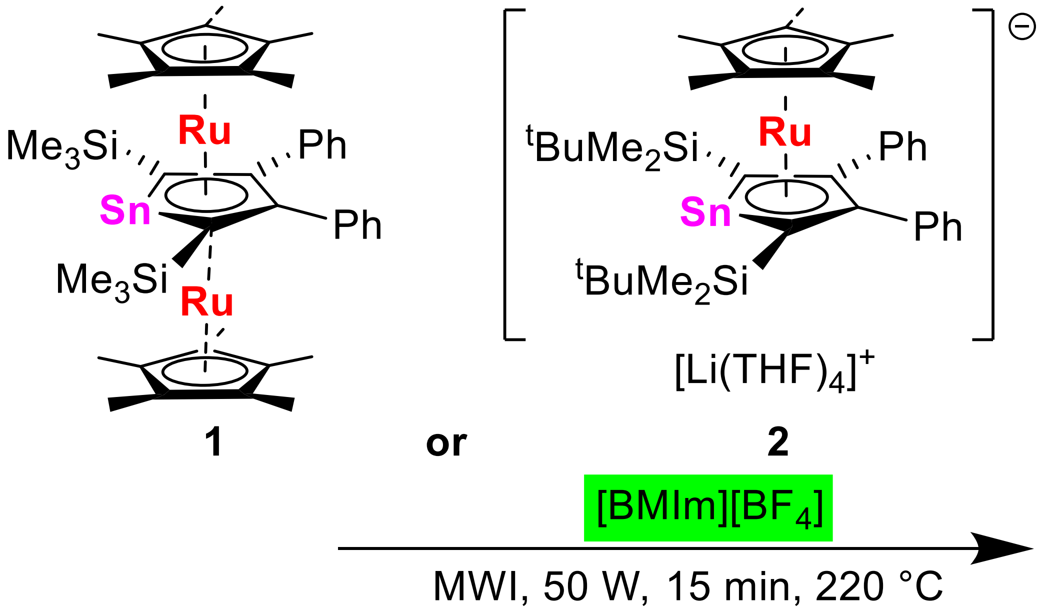
Can Hume-Rothery phases replace noble-metal catalysts?

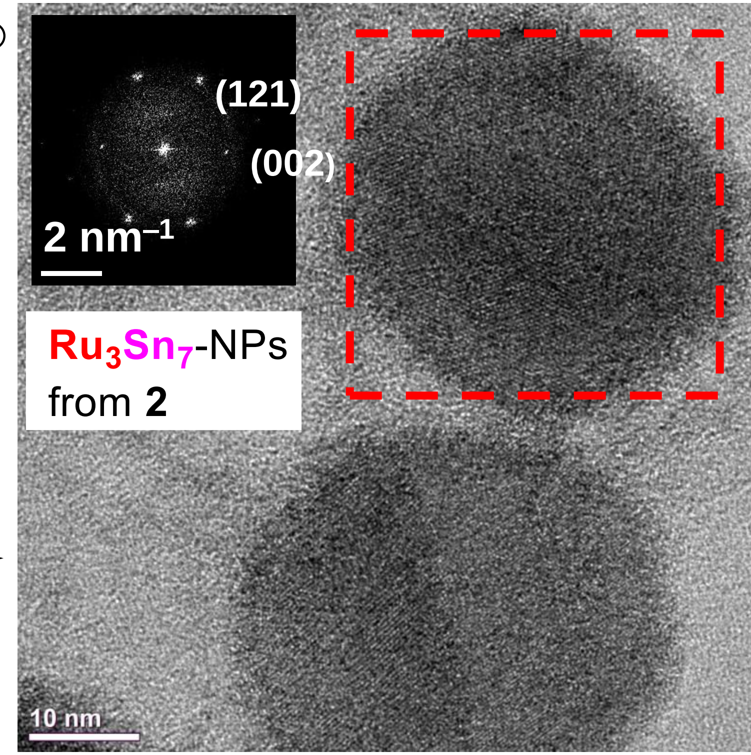
Fischer, Janiak et al., *Nanoscale* **2014**, *6*, 5532-5544.

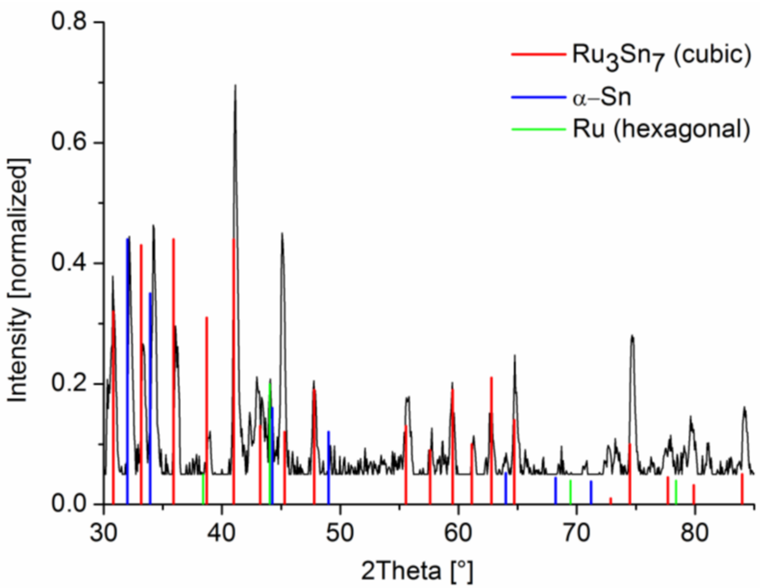
Normally semihydrogenation requires noble metals.

metal classification											T_2 + B = Hume-Rothery			
T_1		**T_2**									**B**			
Li	Be													
Na	Mg											(Al)		
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi

Bimetallic alloy nanoparticles
- "Ru_2Sn" and Ru_3Sn_7







with Masaichi Saito

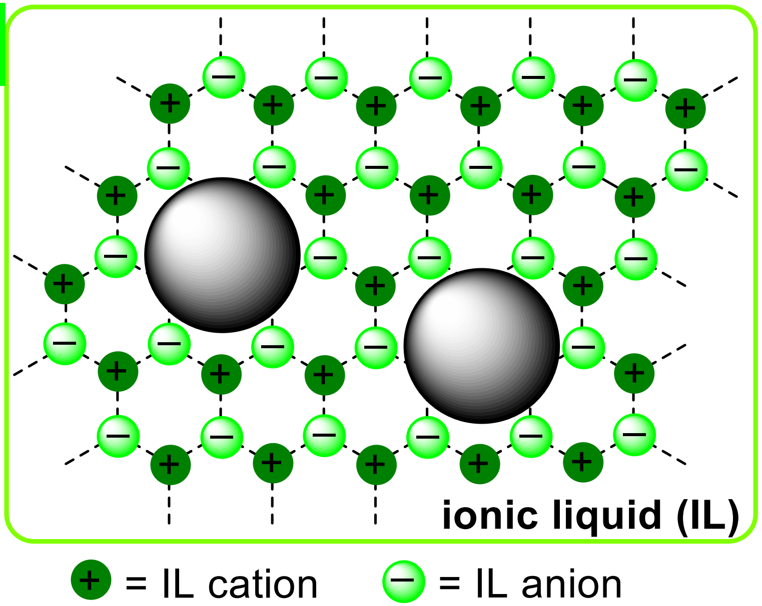
J. Organomet. Chem. **2016**, in press.

Stabilization of metal nanoparticles
from IL-dispersion onto surfaces

stabilization in ionic liquids

metal pre-cursor compound

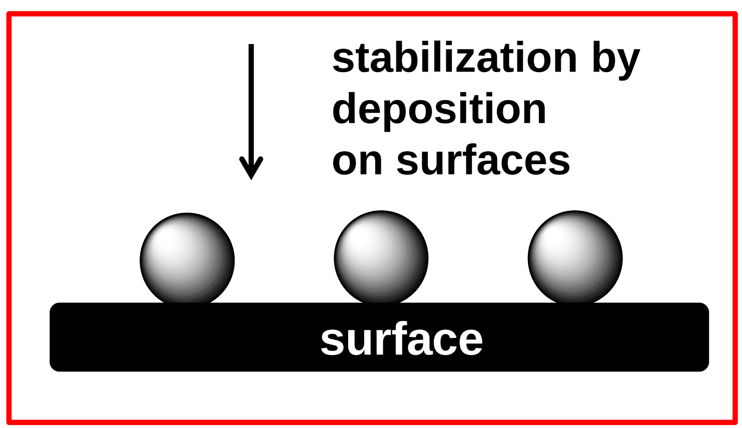
microwave irradiation



No stabilizing capping ligands necessary!

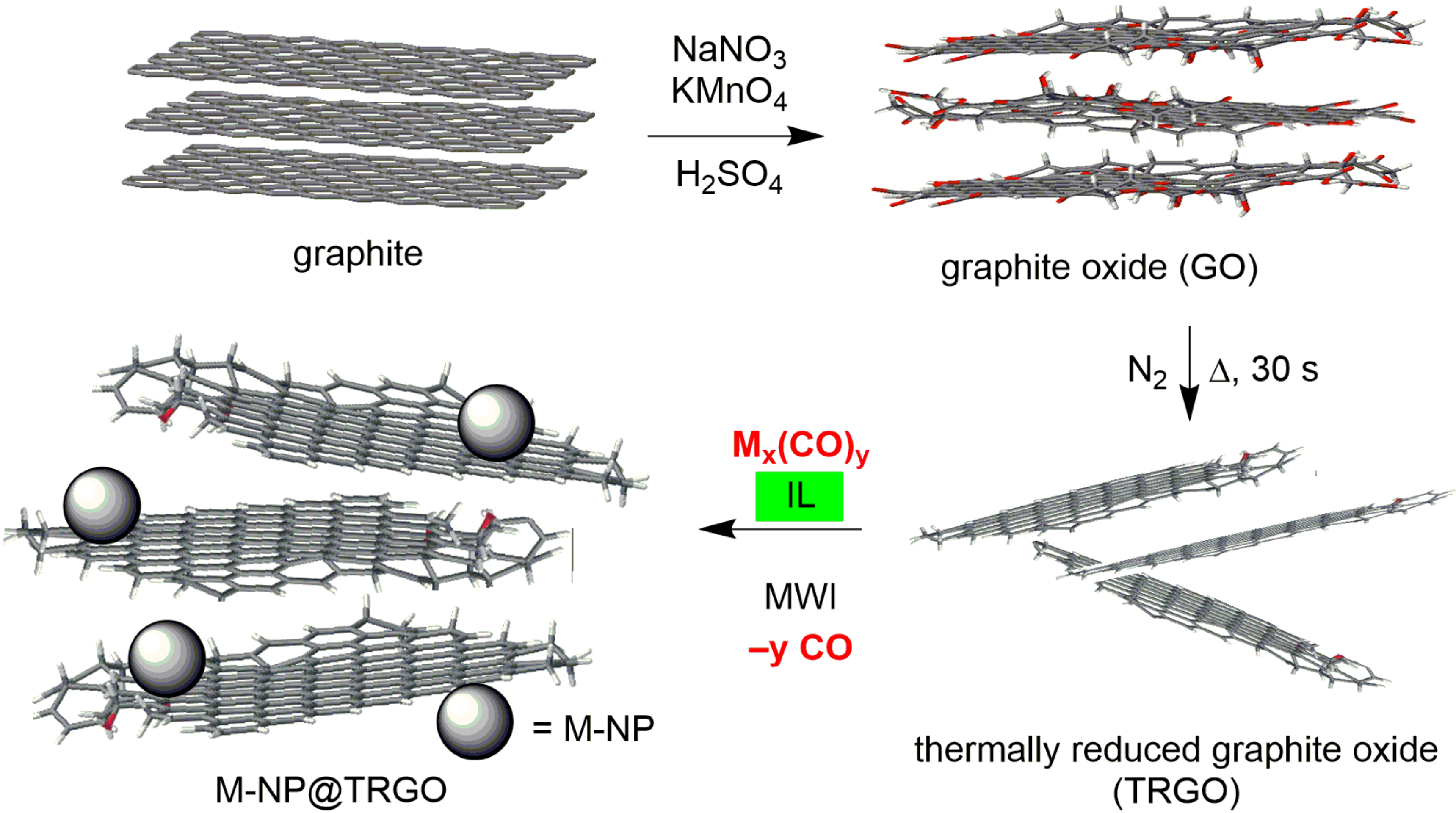
weak coordination
⇒ only small change of surface properties

Chem. Eur. J. **2009**, *15*, 10047.
Angew. Chem. Int. Ed. **2011**, *50*, 9735.
Coord. Chem. Rev. **2011**, *255*, 2039.
Carbon **2011**, *49*, 1326.
Appl. Catal. A **2012**, *425-426*, 178.
Review: *Z. Naturforsch. B*, **2013**, *68*, 1059.
Carbon **2014**, *66*, 285.
Nanoscale **2014**, *6*, 3116.
Nanoscale **2014**, *6*, 5532.



Thermally reduced graphite oxide (TRGO) as nanoparticle support

HEINRICH HEINE UNIVERSITÄT DÜSSELDORF



Graphite oxide, GO: Brodie, *Liebigs Ann. Chem.* **1860**, *114*, 6.
Hummers, Offeman, *J. Am. Chem. Soc*. **1958**, *80*, 1339.
Boehm, *Z. Anorg. Allg. Chem.* **1967**, *353*, 236.

Stabilization of metal nanoparticles on graphene networks

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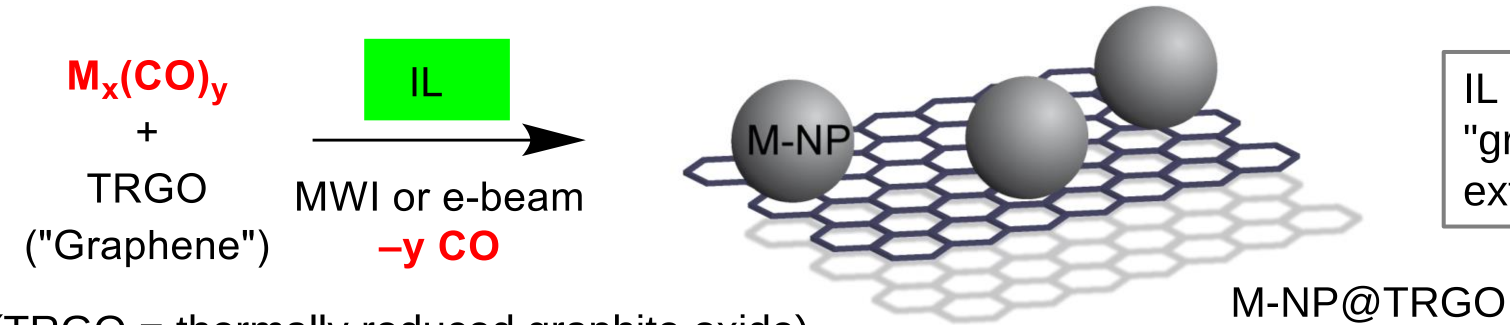
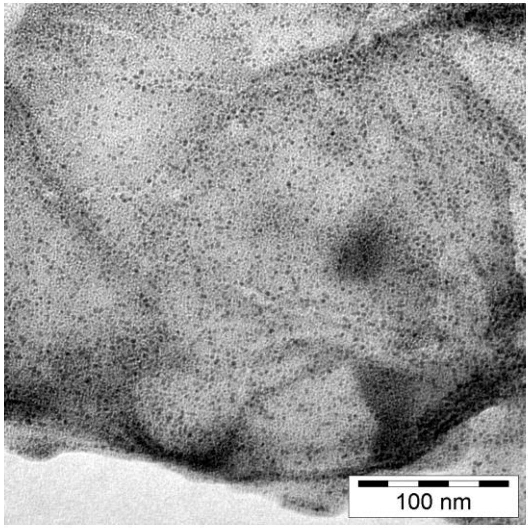
UNIVERSITÄT DÜSSELDORF

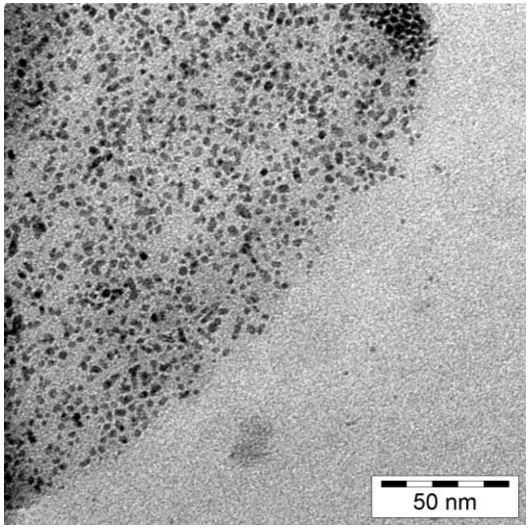


IL also for "graphene" exfoliation

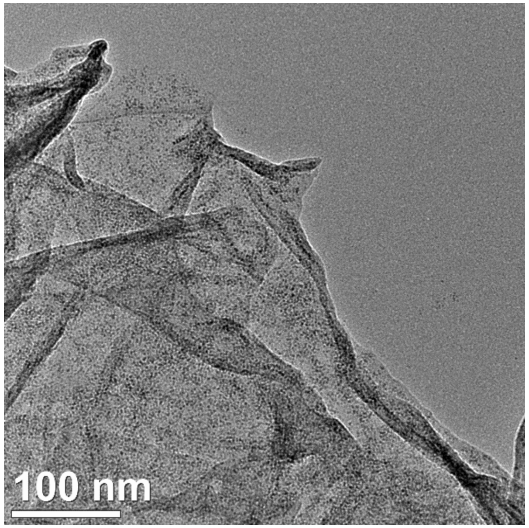
(TRGO = thermally reduced graphite oxide)



Ru-NP@TRGO
2.2 (±0.4) nm



Rh-NP@TRGO
2.8 (±0.5) nm



Ir-NP@TRGO
3.6 (±1.0) nm

Marquardt, D., Vollmer, C., Thomann, R., Steurer, P., Mülhaupt, R., Redel, E., Janiak, C., *Carbon* **2011**, 49, 1326-1332.
Marcos-Esteban, R., Schütte, K., Brandt, P., Marquardt, D., Meyer, H., Beckert, F., Mülhaupt, R., Kölling, H., Janiak, C., *Nano-Structures & Nano-Objects* **2015**, *2*, 11-18.

Metal-NPs@TRGO-SH synthesis in ILs

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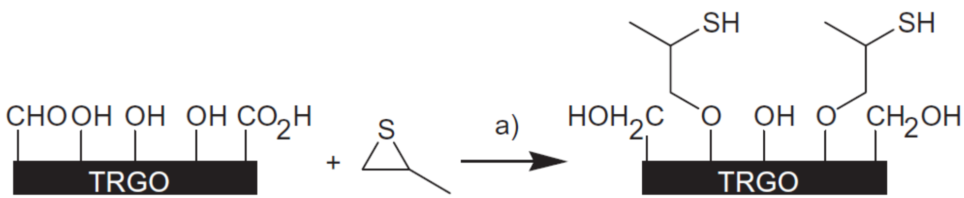
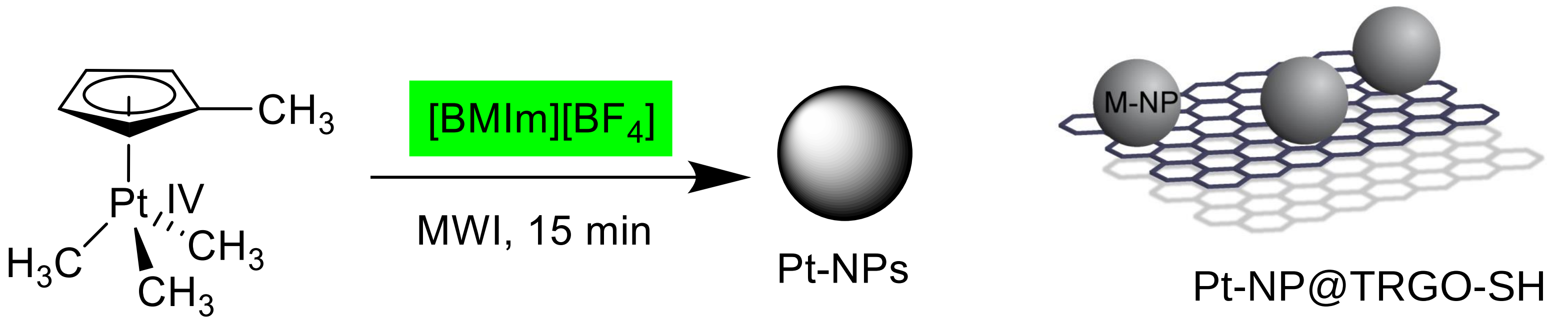
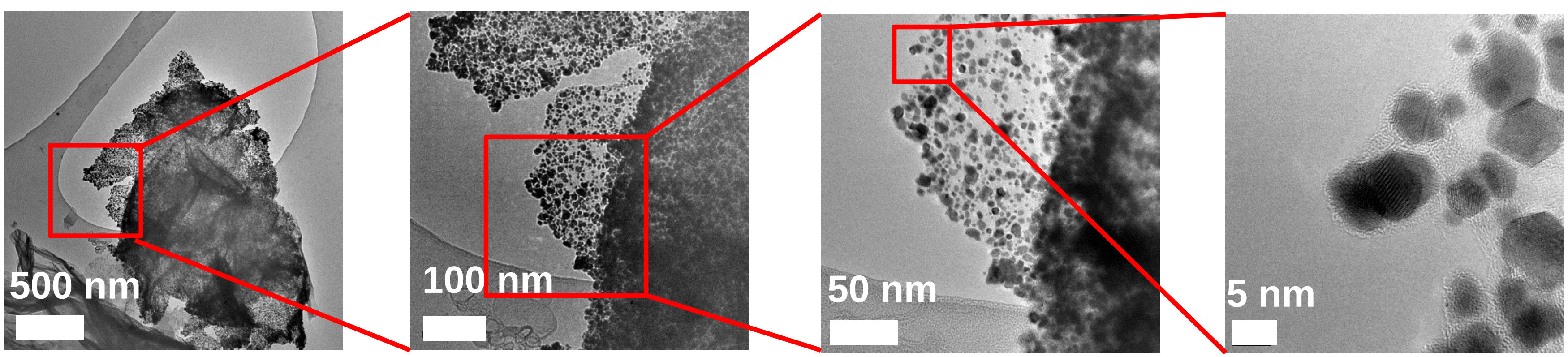
ring opening of propylene sulfide (2-methylthiirane)



(a) LDA (lithium diisopropylamide)





Ø 9 ± 4 nm, 3.2 wt% Pt-NP@TRGO

Marquardt, D., Beckert, F., Pennetreau, F., Tölle, F., Mülhaupt, R., Riant, O., Hermans, S., Barthel, J., Janiak, C., *Carbon* **2014**, *66*, 285-294.

M-NP@TRGO as re-usable hydrogenation catalysts under organic-solvent-free conditions

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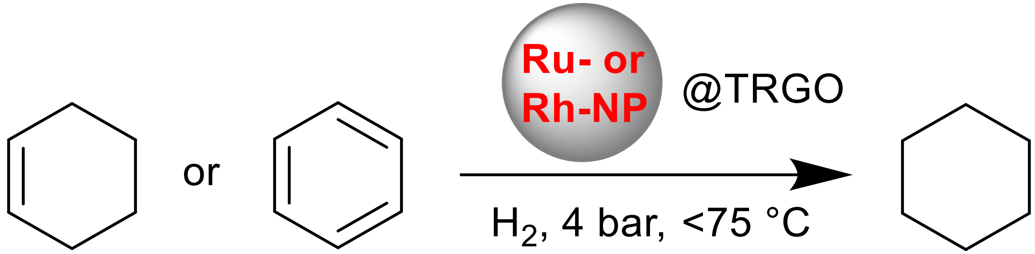
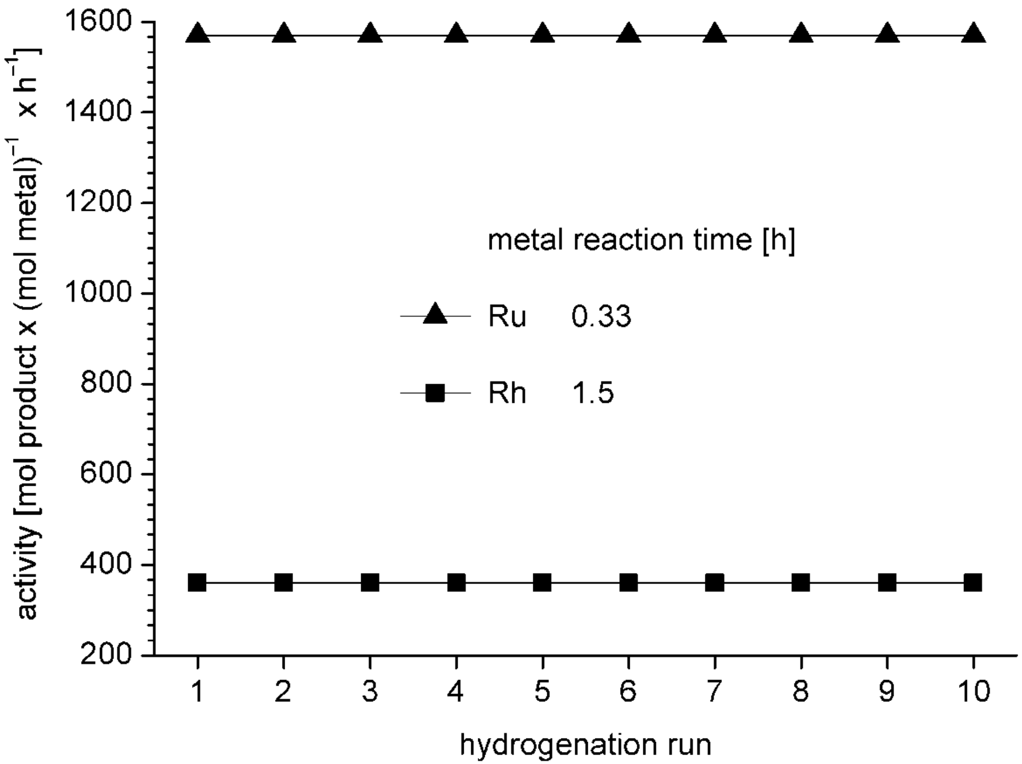
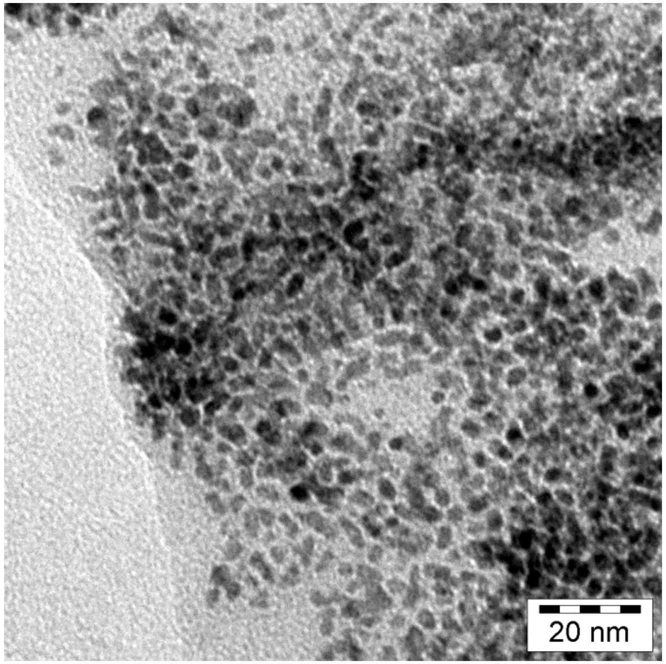


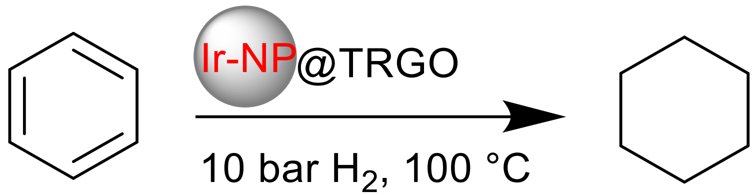


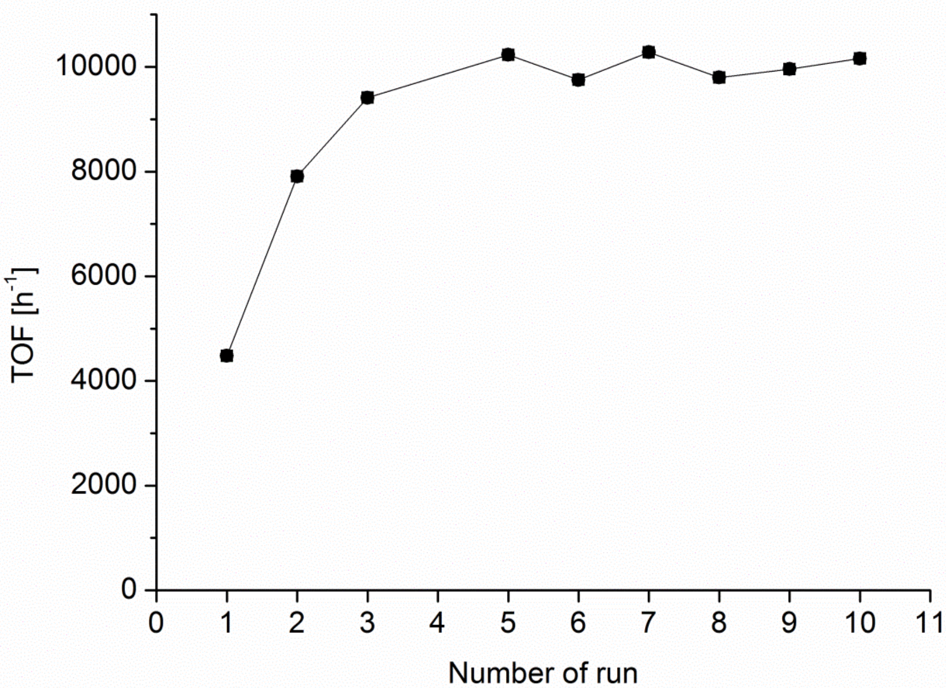


Rh-NP@TRGO after 10th run

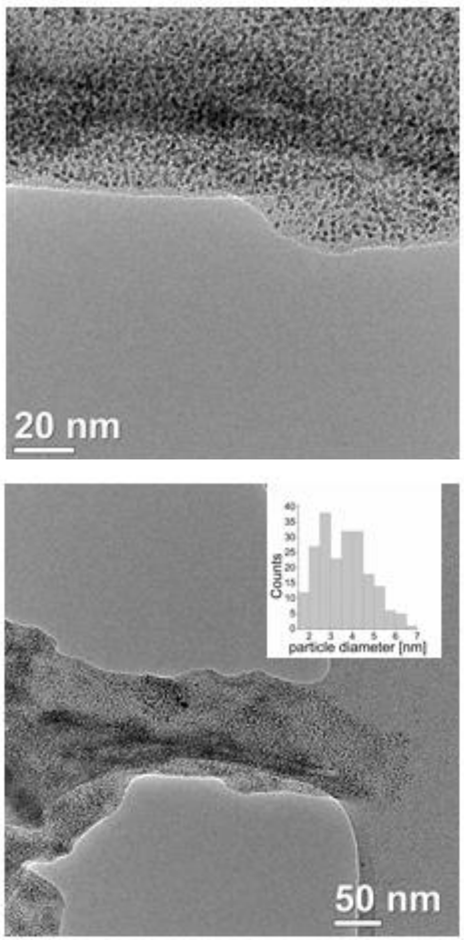
Carbon **2011**, *49*, 1326-1332.

Ir-NP@TRGO as re-usable hydrogenation catalysts under organic-solvent-free conditions



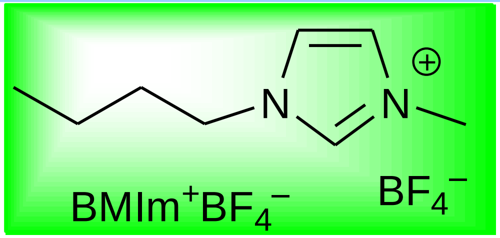


after 10th run



Marcos-Esteban, R., Schütte, K., Brandt, P., Marquardt, D., Meyer, H., Beckert, F., Mülhaupt, R., Kölling, H., Janiak, C., *Nano-Structures & Nano-Objects* **2015**, *2*, 11-18

Deposition of metal nanoparticles on Teflon!

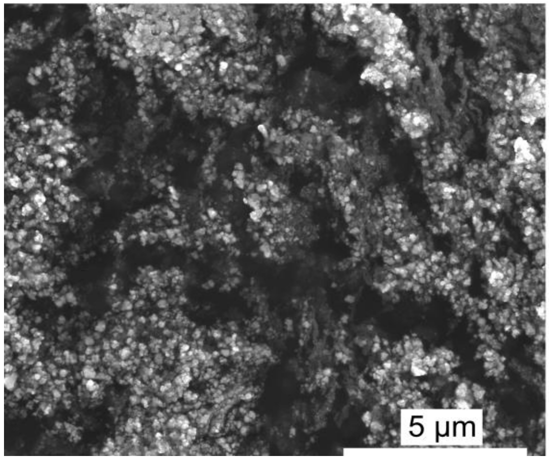


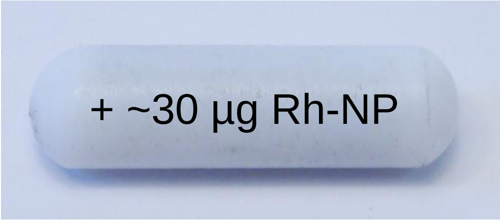
$Rh_6(CO)_{16}$

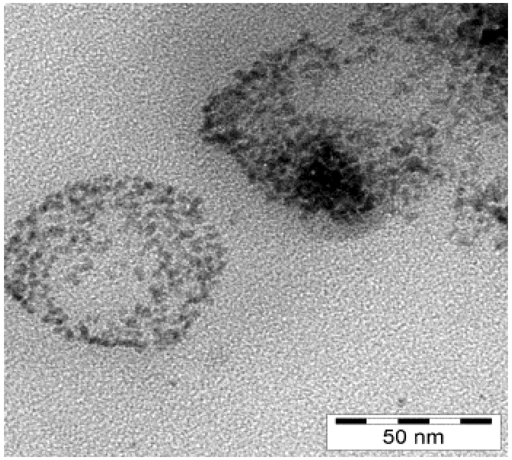
microwave irradiation
(MWI)
10 W, 6 min

(unused new stirring bar)

20 × 6 mm



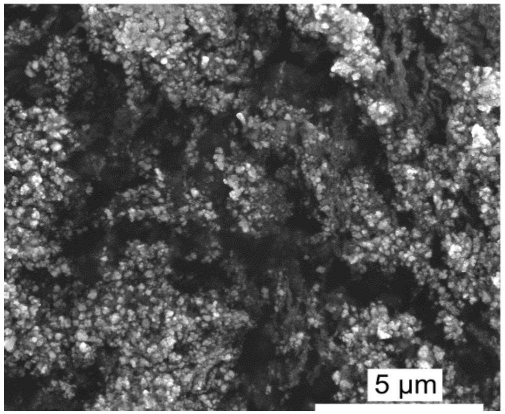


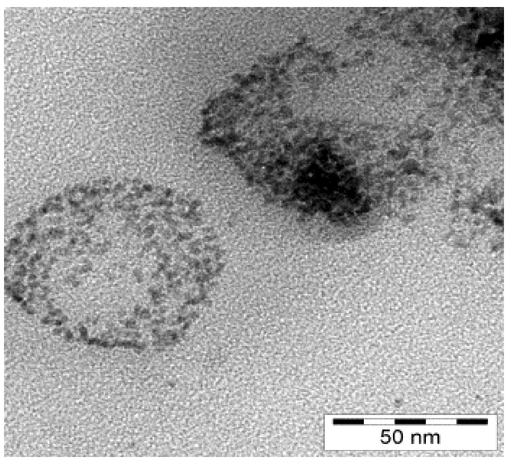


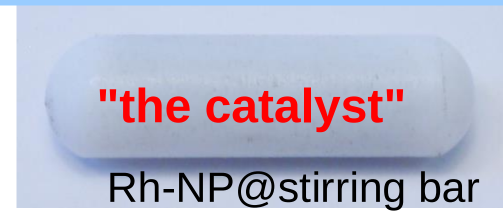
Rh-NP@stirring bar, Ø 2.1(5) nm

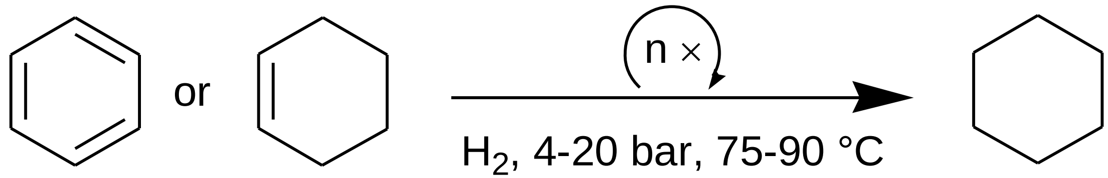
Appl. Catal. A **2012**, *425-426*, 178.

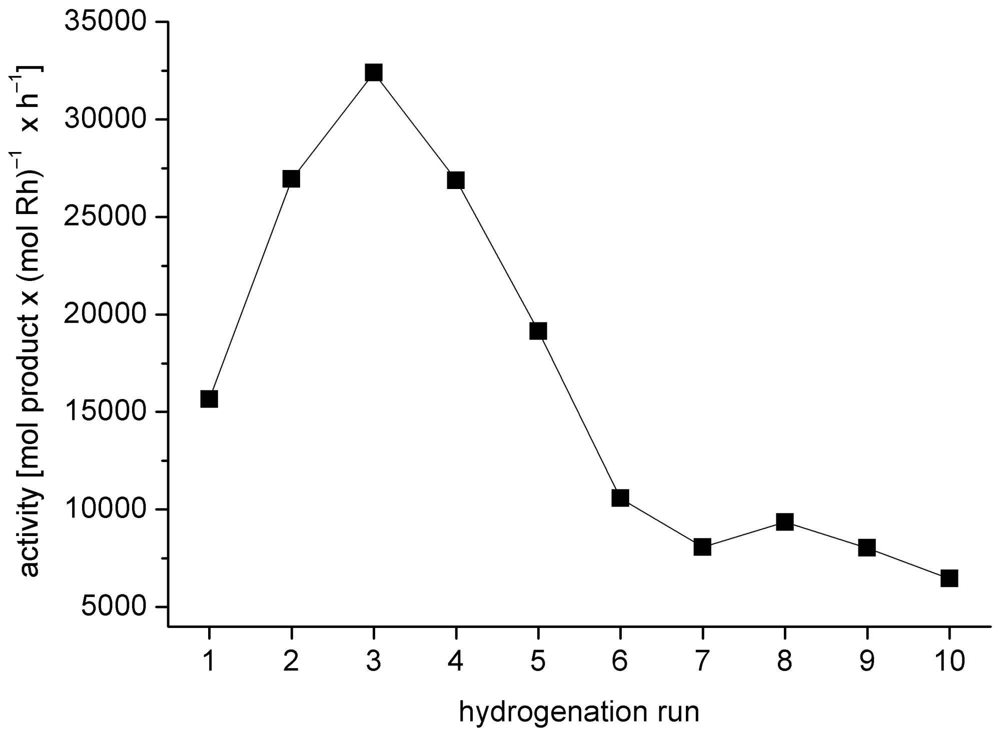
Deposition of metal nanoparticles on Teflon!











Appl. Catal. A **2012**, *425-426*, 178-183

Summary

Precursors

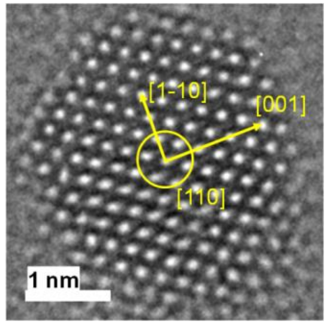
$Zn/Cd(R_2N\text{---}Se)_2$

$M_x(CO)_y$
$Cp'PtMe_3$

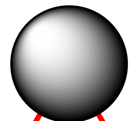
$M(R_2\text{-Me-amidinate})_x$
$Ni(COD)_2$, GaCp*

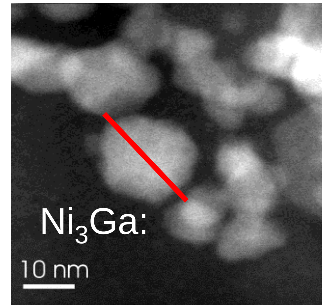
$Au(CO)Cl$
$KAuCl_4$

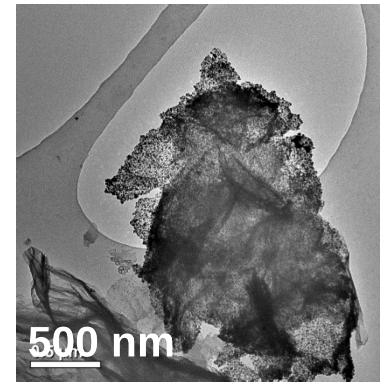
no capping ligands necessary!



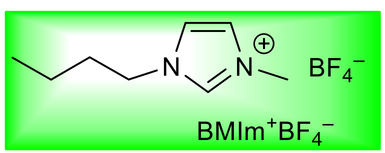
nano-particles





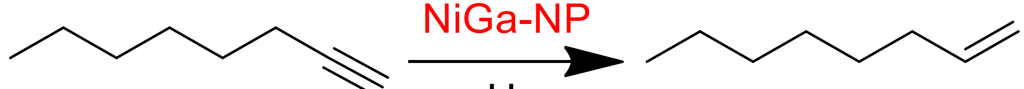


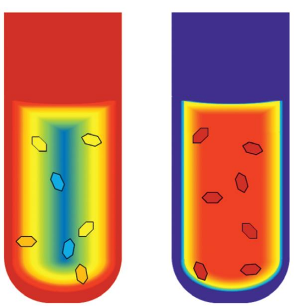
methods:
PXRD,
HR-(S)TEM,
EDX, XPS
DLS



ionic liquids

$$H_2 + CO + CO_2 \xrightarrow{\text{Cu/ZnO-NP}} CH_3OH$$





µ-wave heating

Acknowledgements
- the Team counts

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Karsten Klauke
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Tian Zhao

SPP 1708

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RuSn precursors — Prof. M. Saito, Saitama Univ. Japan
Modified graphene: — Prof. R. Mülhaupt, Univ. Freiburg, Prof. S. Hermans, UC Louvain
TEM, HRTEM: — Dr. J. Barthel, FZ Jülich

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