Synthesis of Cu, Zn and bimetallic Cu/Zn brass alloy nanoparticles from metal amidinate precursors in ionic liquid or propylene carbonate with relevance to methanol synthesis

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Cu/Zn phase diagram
NMR spectrum and thermal stability of {[Me(C(NiPr)2)Cu]2 (1)
Cu-NP dispersion in propylene carbonate (PC)
Zn-NP dispersion in IL [BMIm][BF4]
Zn-NP dispersion in propylene carbonate (PC)
Bimetallic Cu/Zn nanoparticles
Catalytic MeOH synthesis
Calibration XPS
Fig. S1  Copper-Zinc binary alloy phase diagrams from ASM International Database, *ASM-253638-tlo3-CuZn.*
$^1$H NMR spectra:

![H NMR spectrum](image)

**Fig. S2** $^1$H NMR spectrum ($\text{C}_6\text{D}_6$, 500.131 MHz, 298 K) of $\{\text{Me}(\text{N}^3\text{Pr})_2\text{Cu}\}_2$ (I).
Thermal stability of $\{[\text{Me}(\text{N}^\text{Pr})_2]\text{Cu}_2\}$ (1):

Fig. S3 Selected $^1$H NMR spectra ($C_6D_6$, 200.771 MHz, 298 K) of a decomposition series of $\{[\text{Me}(\text{N}^\text{Pr})_2]\text{Cu}_2\}$ (1) at 220 °C in [BMIm][BF$_4$] upon 150 W microwave irradiation for the given time.

* residual proton solvent signal of $C_6D_6$

# signal of the N–C(CH$_3$)$_3$–N methyl group.

The $\{[\text{Me}(\text{N}^\text{Pr})_2]\text{Cu}_2]/[\text{BMIm}][\text{BF}_4]$ solution was sealed in microwave-tubes and heated up to 220 °C by microwave irradiation. The tubes were periodically removed from the microwave oven every 30 s and their $^1$H NMR spectra were recorded by dissolving a 50 mg sample in 0.65 mL deuterated benzene. The intensity of the well separated peak with chemical shift $\delta = 1.91$ ppm was recorded relative to the residual proton peak ($\delta = 7.3$ ppm) in the $C_6D_6$ solvent.
Fig. S4  Thermal stability of $\{\text{Me}(\text{NPr})_2\}\text{Cu}_2$ (1) according to Li, Barry und Gordon in an oven at 200°C (graphics prepared from data given in ref.1).

Cu-NP dispersion in propylene carbonate (PC), 0.5 wt% Cu-NP/PC:

Fig. S5 HAADF-STEM (top), EDX (middle) and PXRD (bottom, Cu reference peaks in red from JCPDS data bank, No. 4-0836) of 0.5 wt% Cu-NPs in PC from [{Me(C(NiPr)2)Cu}2] (microwave irradiation for 10 min, 150 W, 220 °C). (STEM-EDX: FEI Technai f20, 200 or 136 kV, respectively; PXRD: 4 h, Cu-Kα, 35 kV).

Table S1 Cu-NP size and size distribution in 0.5 wt% Cu-NP dispersion. 

<table>
<thead>
<tr>
<th></th>
<th>TEM Ø (σ) [nm]</th>
<th>DLS Ø (σ) [nm]</th>
<th>PXRD Ø (σ) [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>dec. in [BMIm][BF4]</td>
<td>9 (± 4)</td>
<td>13 (± 7)</td>
<td>7 (± 3)</td>
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<tr>
<td>dec. in propylene carbonate</td>
<td>85 (± 16)</td>
<td>102 (± 11)</td>
<td>55 (± 7)</td>
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a precursor [{Me(C(NiPr)2)Cu}2], dispersions obtained by MWI with 50 W for 10 min at 220°C. BSc Thesis of Mrs. Christin Grunow, University of Düsseldorf, 2012, p. 32.

b Median diameter (Ø) and standard deviation (σ).

c from Scherrer equation $\varepsilon = \frac{K\lambda}{B\cos\theta_B}$ with $\varepsilon =$ average diameter of nanocrystallites [Å], $K =$ Scherrer factor (1); $\lambda =$ X-ray wavelength (Cu-Kα = 1.5406 Å), $B =$ half-width of reflection (rad); $\theta_B =$ angle at peak-maximum [degree], with analysis here at the (111) reflection.
Zn-NP dispersion in [BMIm][BF₄], 0.5 wt% M-NP/IL:

Fig. S6 HAADF-STEM of 0.5 wt% Zn-NPs in [BMIm][BF₄] from [Me(C(NiPr)₂)₂Zn (2) (microwave irradiation for 10 min, 150 W, 220 °C). (TEM-EDX: FEI Technai f20, 200).

Table S2  Zn-NP size and size distribution in 0.5 wt% Zn-NP dispersion. a

<table>
<thead>
<tr>
<th></th>
<th>TEM Ø (σ) [nm]b</th>
<th>DLS Ø (σ) [nm]b</th>
<th>PXRD Ø (σ) [nm]b,c</th>
</tr>
</thead>
<tbody>
<tr>
<td>dec. in [BMIm][BF₄]</td>
<td>3.5 (± 1.5)</td>
<td>6 (± 4)</td>
<td>2.9 (± 0.2)</td>
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<tr>
<td>dec. in propylene carbonate</td>
<td>5.5 (± 3.5)</td>
<td>11 (± 6)</td>
<td>----</td>
</tr>
</tbody>
</table>

a precursor [Me(C(NiPr)₂)₂Zn (2), dispersions obtained by MWI with 50 W for 10 min at 220°C. BSc Thesis of Mrs. Christin Grunow, University of Düsseldorf, 2012, p. 35.
b Median diameter (Ø) and standard deviation (σ).
c from Scherrer equation $\varepsilon = \frac{k\lambda}{B\cos\theta}$ with $\varepsilon$ = average diameter of nanocrystallites [Å], $K =$ Scherrer factor (1); $\lambda =$ X-ray wavelength (Cu-Kα=1.5406 Å), $B =$ half-width of reflection (rad); $\theta_B =$ angle at peak-maximum [degree], with analysis here at the (111) reflection.
Bimetallic Cu/Zn nanoparticles

CuZn from PC (1.0 wt%)

Fig. S7 HAADF-STEM for β-CuZn nanoparticles (1.0 wt% in PC).
CuZn from [BMIm][BF$_4$] (1.0 wt%)
Cu$_3$Zn from [BMIm][BF$_4$] (1.0 wt%)
Fig. S10 HAADF-STEM (top) and EDX (bottom, averaged over 10-15 particles) of $\gamma$-Cu$_3$Zn nanoparticles in PC.
Catalytic MeOH synthesis

**Fig. S7** ^1^H NMR Spectrum (CDCl\textsubscript{3}, 500.13 MHz, 265 K) of the reaction solution from the catalytic methanol synthesis with β-CuZn-NP/IL dispersion (1.0 wt% CuZn in *\[BMMim][BF_4]\* at 220 °C and 30 bar after 3 h).

**Calibration XPS**
Spectra have been recorded, using Al K\textsubscript{alpha} X-rays, from clean samples of copper, silver and gold, at 20 eV and 10 eV pass energies and compared with reference values. The results are shown below.

### 20 eV Pass Energy

<table>
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<th></th>
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<th>Experiment</th>
<th>Difference</th>
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<tbody>
<tr>
<td>Au 4f7/2</td>
<td>83.98 ± 0.02</td>
<td>84.00</td>
<td>+ 0.02</td>
</tr>
<tr>
<td>Ag 3d5/2</td>
<td>368.26 ± 0.02</td>
<td>368.25</td>
<td>- 0.01</td>
</tr>
<tr>
<td>Cu 2p3/2</td>
<td>932.67 ± 0.02</td>
<td>932.71</td>
<td>+ 0.04</td>
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### 10 eV Pass Energy

<table>
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<th>Reference</th>
<th>Experiment</th>
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<td>Au 4f7/2</td>
<td>83.98 ± 0.02</td>
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