Electronic Supplementary Information (ESI)

Lewis acid double metal cyanide catalysts for hydroamination of phenylacetylene

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1. General procedures and instrumental analysis

*Typical hydroamination procedure:* 50 mg of the DMC catalyst was activated under vacuum at 80 °C overnight. Toluene (1 ml), phenylacetylene (0.5 mmol, 55 µl) and 4-isopropylaniline (1 mmol, 137 µl) were added under N₂-atmosphere. The reaction was stirred at 500 rpm and heated in a copper heating block at 110 °C. After reaction, the samples were kept on ice, centrifuged and analyzed by GC (Shimadzu 2014 GC equipped with a FID detector and an apolar CP-Sil 5 CB column). The identity of the reaction products was verified by GC-MS (Agilent 6890 gas chromatograph, equipped with a HP-5MS column, coupled to a 5973 MSD mass spectrometer). Purification of reaction product was carried out by filtration of the reaction mixture to remove the heterogeneous catalyst. The toluene solvent was removed by drying under reduced pressure, followed by purification on a silica column with petroleum ether – ethyl acetate using a Biotage® Flash purification system with UV/Vis detector. 104 mg of the purified product was obtained. NMR spectra were recorded on a Bruker AMX-300 spectrometer at ambient temperature.

(4-isopropylphenyl)(1-phenylethylidene)amine ¹H-NMR (300 MHz, CDCl₃): δ (ppm) 7.90 (m, 2H, Ph), 7.36 (m, 3H, Ph), 7.13 (d, J = 8.1 Hz, 2H, Ph), 6.65 (d, J = 8.1 Hz, 2H, Ph), 2.83 (m, 1H, CH), 2.18 (s, 3H, CH₃), 1.18 (d, J = 6.95 Hz, 6H, 2 CH₃); ¹³C-NMR (75.5 MHz, CDCl₃): δ (ppm) 165.3 (C=N), 149.4 (C(-iPr)), 143.8, 139.7, 130.4, 128.4, 127.1, 126.8, 119.5 (all in the aromatic rings), 33.6 (CH), 24.1 (2 CH₃), 17.4 (CH₃(C=N)). m/z 237 (M⁺, 37%), 222 (100%), 206 (4%), 180 (8%), 160 (3%), 144 (7%), 115 (5%), 103 (27%), 91 (15%), 77 (33%), 65 (4%), 51 (11%).
2. Characterization of double metal cyanides

2.1 Instrumentation

Powder X-ray diffraction (PXRD) reflection patterns were recorded on a STOE STADI MP in Bragg-Brentano mode ($2\theta-\theta$ geometry; CuK$_\alpha_1$, 1.54060 Å) using a linear position sensitive detector. Infrared measurements (IR) were performed on a Nicolet 6700 spectrometer. Thin self-supporting wafers ($\pm$ 10 mg cm$^{-2}$) were prepared and placed in an in situ cell. The cell was placed under vacuum ($p < 10^{-4}$ Pa) at 175 °C and an IR spectrum was recorded. Pyridine was adsorbed at 323 K and the weakly physisorbed pyridine was evacuated at 448 K. Nitrogen sorption measurements were performed at 77 K on Quantachrome AS1Win™ equipment. Before N$_2$ adsorption, the sample was evacuated at 373 K overnight. Thermogravimetric analyses (TGA) on DMCs were recorded on a TA Instruments Q500 thermogravimetric analyzer with a heating rate of 10 °C/min under O$_2$-atmosphere. Scanning electron microscopy (SEM) micrographs were recorded using a Philips XL30 FEG after coating with Au, coupled with Energy dispersive X-ray spectroscopy (EDX) at 15kV.

2.2 Powder X-ray diffraction (PXRD)

![Fig. S1 Powder X-ray diffraction patterns of (a) Zn-Co-DMC-PTMEG, (b) Zn-Co-DMC-P123, (c) Zn-Co-DMC-PEG (PEG: MW 2000 g/mol), (d) Zn-Co-DMC-$\dagger$ (only tBuOH as CA, no co-CA), (e) Zn-Co-DMC-pure (no CA or co-CA), (f) Zn-(SO$_4$)$_2$-Co-DMC-PTMEG and (g) Zn-(CF$_3$SO$_3$)$_2$-Co-DMC.](image)
PTMEG. The additional reflections in comparison with the patterns shown in Fig. 1 (left) are due to a related rhombohedral phase (see Wojdel et al., J. Mol. Model., 2007, 13, 751-756)

2.3 Scanning electron microscopy

Fig. S2 SEM picture of Zn-Co-DMC-PTMEG

Fig. S3 SEM picture of Zn-Co-DMC-/: tBuOH as complexing agent, no co-complexing agent was used.

Fig. S4 SEM picture of Zn-Co-DMC-PEG (left) and Zn-Co-DMC-P123 (right)
2.4 Thermogravimetric analysis (TGA)

**Fig. S5** TGA analysis of Zn-Co-DMC-PTMEG (full lines) and Zn-Co-DMC-pure (dashed lines). The first weight loss is due to loss of adsorbed water. The large loss at ca. 350 °C is due to decomposition of the CN-bridges in the structure.

**Fig. S6** TGA analysis of Zn-Co-NDMC-Igepal.
2.5 Infrared measurements

**Fig. S7** IR spectrum of Zn-Co-DMC-PTMEG; typical $\nu$(CN) bond can be observed at 2194 cm$^{-1}$.

2.6 Hot filtration test
**Fig. S8** Reaction of phenylacetylene and 4-isopropylaniline with Zn-Co-DMC-PTMEG; yield (%) of the hydroamination product, before and after hot filtration. Conditions as in Table 1, entry 5.

2.7 Nitrogen sorption measurements

<table>
<thead>
<tr>
<th></th>
<th><strong>Zn-Co-DMC-PTMEG</strong></th>
<th><strong>Zn-Co-NDMC-Igepal</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>BET surface area</strong></td>
<td>464 m²/g</td>
<td>552 m²/g</td>
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<tr>
<td><strong>HK-model pore radius</strong></td>
<td>2.3 Å</td>
<td>2.3 Å</td>
</tr>
<tr>
<td><strong>Micropore volume</strong></td>
<td>0.224 cc/g</td>
<td>0.166 cc/g</td>
</tr>
<tr>
<td><strong>Micropore area</strong></td>
<td>443 m²/g</td>
<td>382 m²/g</td>
</tr>
<tr>
<td><strong>External surface area</strong></td>
<td>21 m²/g</td>
<td>170 m²/g</td>
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**Fig. S9** Nitrogen sorption isotherm of Zn-Co-NDMC-Igepal (top) and Zn-Co-DMC-PTMEG (bottom) recorded at 77 K. The micropore volume, micropore area and external surface area were obtained by the T-plot method of Lippens and de Boer.