

Electronic Supplementary Information (ESI)

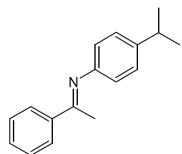
Lewis acid double metal cyanide catalysts for hydroamination of phenylacetylene

Annelies Peeters, Pieterjan Valvekens, Frederik Vermoortele,
Rob Ameloot, Christine Kirschhock and Dirk De Vos

*Centre for Surface Chemistry and Catalysis, Department of Microbial and
Molecular Systems, K.U.Leuven, Kasteelpark Arenberg 23, 3001 Leuven,
Belgium.*

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; $\text{CuK}\alpha_1$, 1.54060 \AA) using a linear position sensitive detector. *Infrared measurements (IR)* were performed on a Nicolet 6700 spectrometer. Thin self-supporting wafers ($\pm 10 \text{ mg cm}^{-2}$) were prepared and placed in an *in situ* cell. The cell was placed under vacuum ($p < 10^{-4} \text{ Pa}$) 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 AS1WinTM 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 $10^\circ\text{C}/\text{min}$ 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)

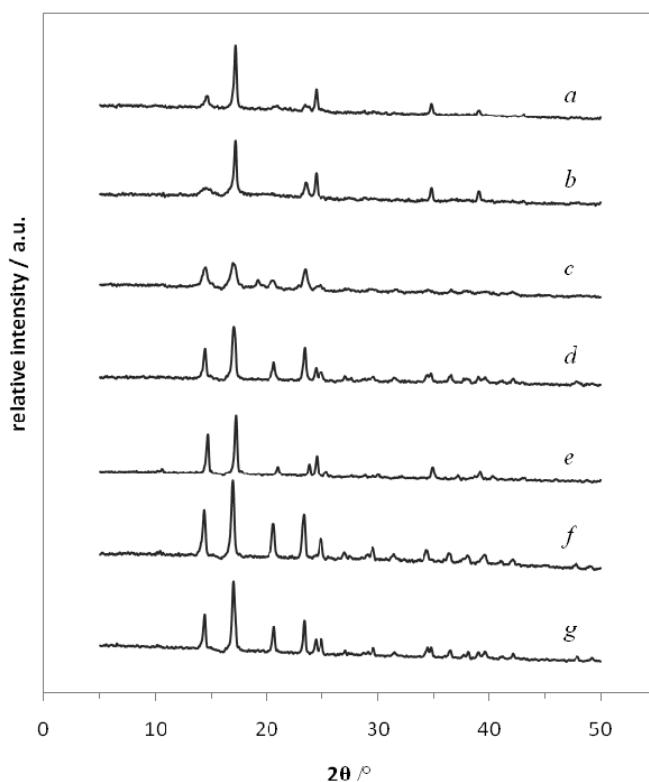


Fig. S1 Powder X-ray diffraction patterns of (a) Zn-Co-DMC-PTMEG, (b) Zn-Co-DMC-P123, (c) Zn-Co-DMC-PEG (PEG: MW 2000 g/mol), (d) Zn-Co-DMC-/ (only tBuOH as CA, no co-CA), (e) Zn-Co-DMC-pure (no CA or co-CA), (f) Zn-(SO₄)-Co-DMC-PTMEG and (g) Zn-(CF₃SO₃)₂-Co-DMC-

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

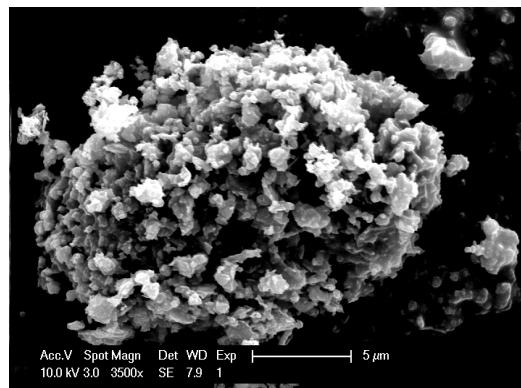


Fig. S2 SEM picture of Zn-Co-DMC-PTMEG

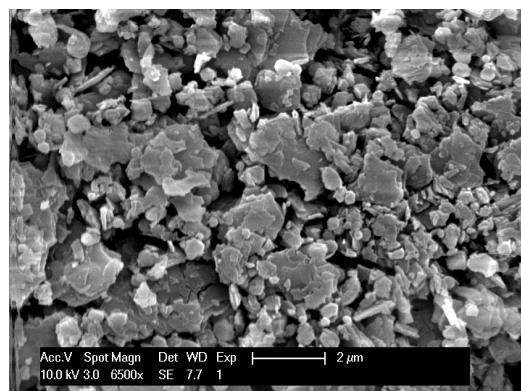


Fig. S3 SEM picture of Zn-Co-DMC-/-: *t*BuOH as complexing agent, no co-complexing agent was used.

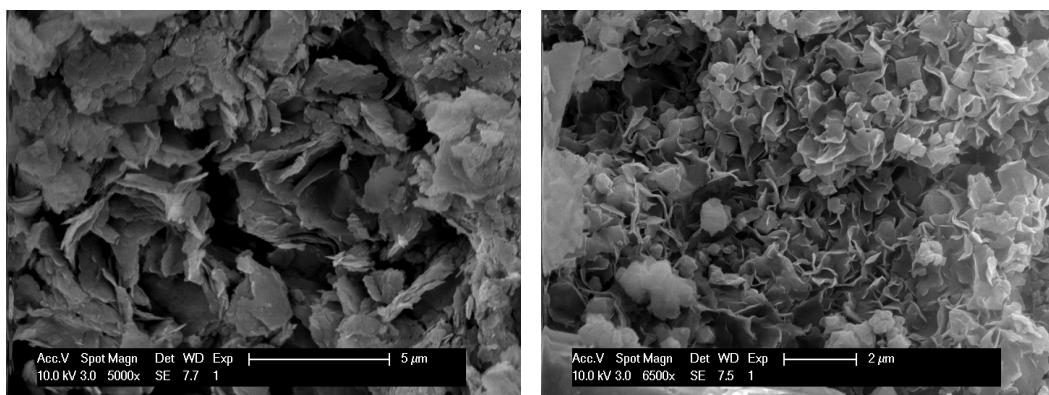


Fig. S4 SEM picture of Zn-Co-DMC-PEG (*left*) and Zn-Co-DMC-P123 (*right*)

2.4 Thermogravimetric analysis (TGA)

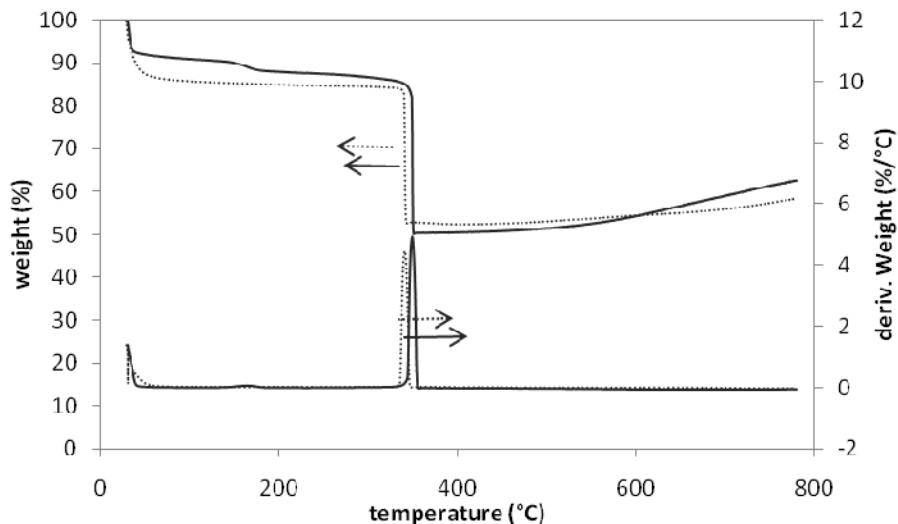


Fig. S5 TGA analysis of Zn-Co-DMC-PTMEG (full lines) and Zn-Co-DMC-pure (dashed lines). The first weight loss is due to loss of adsorbed water. The large loss at ca. 350 °C is due to decomposition of the CN-bridges in the structure.

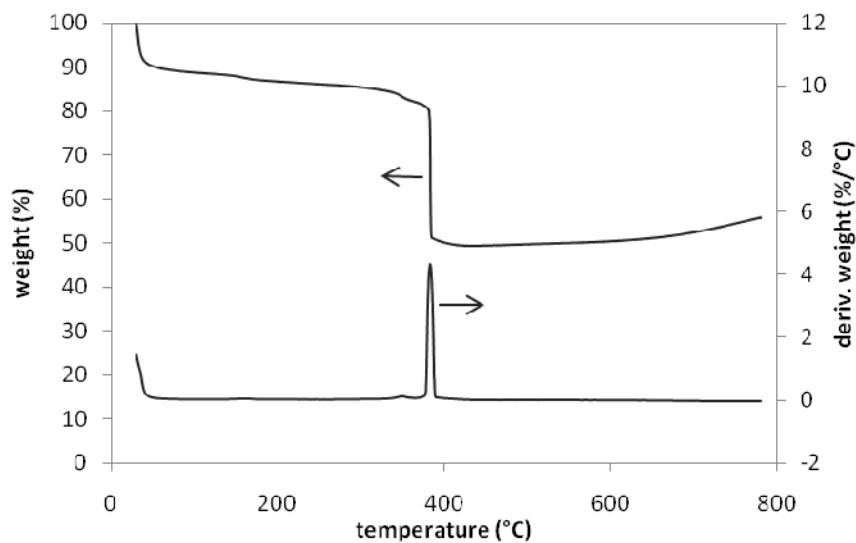


Fig. S6 TGA analysis of Zn-Co-NDMC-Igepal.

2.5 Infrared measurements

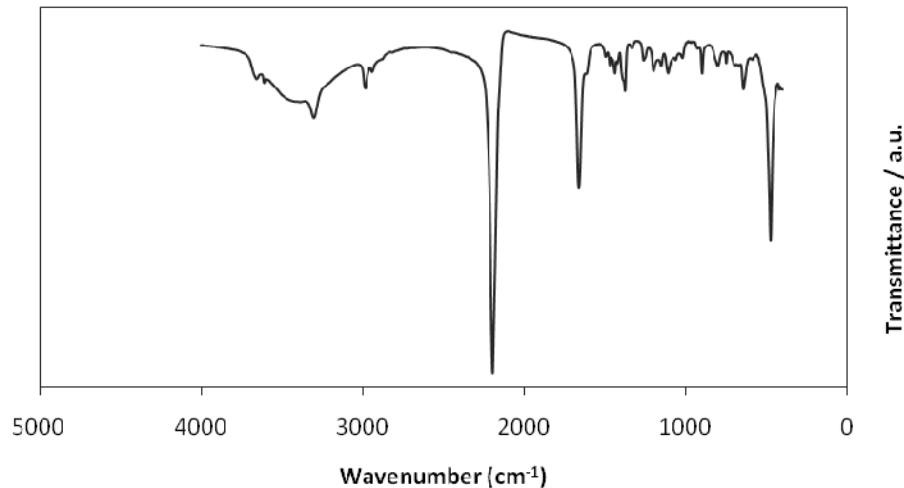


Fig. S7 IR spectrum of Zn-Co-DMC-PTMEG; typical $\nu(\text{CN})$ bond can be observed at 2194 cm^{-1} .

2.6 Hot filtration test

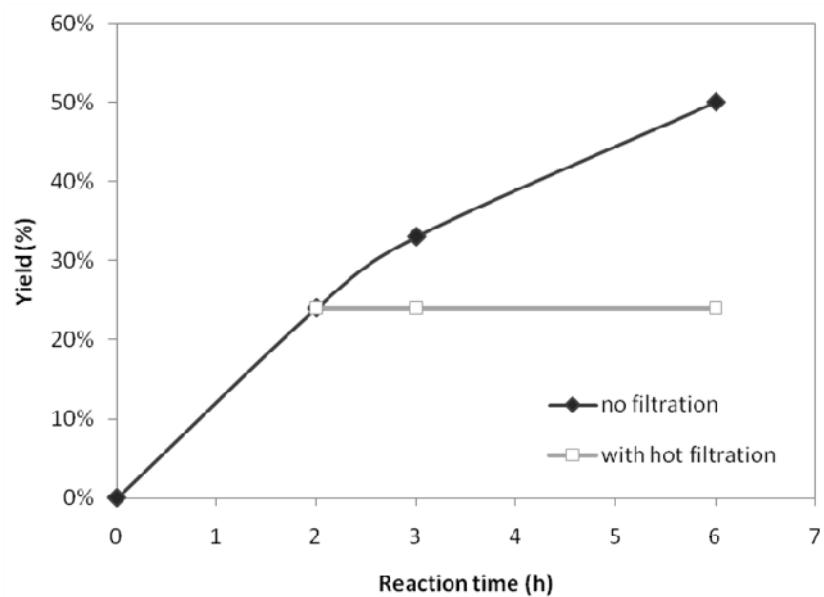


Fig. S8 Reaction of phenylacetylene and 4-isopropylaniline with Zn-Co-DMC-PTMEG; yield (%) of the hydroamination product, before and after hot filtration. Conditions as in Table 1, entry 5.

2.7 Nitrogen sorption measurements

	Zn-Co-DMC-PTMEG <i>Standard synthesis</i>	Zn-Co-NDMC-Igepal <i>Reverse emulsion synthesis</i>
<i>BET surface area</i>	464 m ² /g	552 m ² /g
<i>HK-model pore radius</i>	2.3 Å	2.3 Å
<i>Micropore volume</i>	0.224 cc/g	0.166 cc/g
<i>Micropore area</i>	443 m ² /g	382 m ² /g
<i>External surface area</i>	21 m ² /g	170 m ² /g

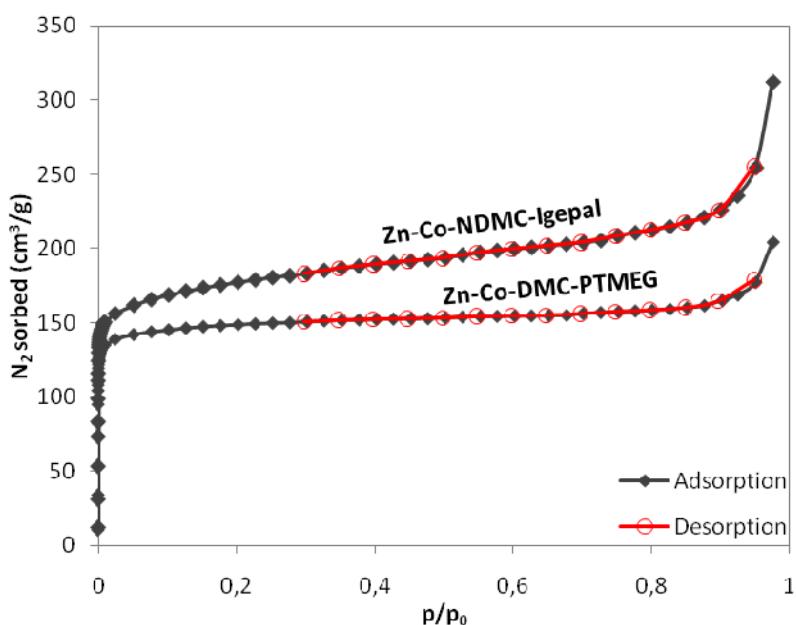


Fig. S9 Nitrogen sorption isotherm of Zn-Co-NDMC-Igepal (top) and Zn-Co-DMC-PTMEG (bottom) recorded at 77 K. The micropore volume, micropore area and external surface area were obtained by the T-plot method of Lippens and de Boer.