Supporting Information

Silica “SHB” chiral Pc-L* copper complexes for halogen-free solvent cyclopropanation reactions.

Brunilde Castano, Paolo Zardi, Yvonne Honneman, Anne Galarneau, Emma Gallo, R. Psaro, Alessandro Caselli, Vladimir Dal Santo

General. NMR spectra were recorded on Bruker Avance 300-DRX or Avance 400-DRX spectrometers. Chemical shifts (ppm) are reported relative to TMS. The $^1$H NMR signals of the compounds described in the following have been attributed by COSY and NOESY techniques. Assignments of the resonance in $^{13}$C NMR were made using the APT pulse sequence and HSQC and HMBC techniques. Infrared spectra were recorded on a BIO-RAD FTS-7 spectrophotometer. Elemental analyses and mass spectra were recorded in the analytical laboratories of Milan University. GC-MS analysis were performed on a Shimadzu GCMS-QP5050A instrument. Optical rotation were measured on a Perkin Elmer instruments model 343 plus; $[\alpha]_D$ values are given in 10$^{-1}$ deg cm$^2$ g$^{-1}$. The water and air sensitive compounds were handled in a dry-box, model “MB-10-Compact”. Metal loadings are determined by ICP-OES using a Thermo X Series II apparatus. 15 mg of each sample are mineralized by adding 3 mL of 37% HCl, 1 mL of concentrated HNO$_3$, 1 mL of 98% H$_2$SO$_4$. CO-DRIFT spectra of the samples were recorded using a FTS-60A spectrophotometer consisting of a homemade reaction chamber. After purging the apparatus with ultra-pure He, spectra of the samples were recorded at RT in He and CO flow, before and after catalysis. HPLC analyses were performed on a Hewlett-Packard 1050 instrument equipped with DAI-CEL CHIRALCEL, IB, OJ and AD chiral columns.
Solvents were dried prior use by standard procedures and stored under dinitrogen. α-Methyl styrene was distilled over CaH₂ and stored under dinitrogen. Davisil_1 (Grace Davison, LC 150 Å, 35-70 micron) and Aerosil_2 (380, Evonik) are commercially available. All other starting materials were commercial products and were used as received. Unless otherwise specified, all the reactions were carried out in a dinitrogen atmosphere employing standard Schlenk techniques and magnetic stirring.

MCM-41 materials were prepared accordingly as already reported¹ in large scale in 4 L and 2 L autoclaves, for MCM-41_A and MCM-41_B, respectively, starting from 240 and 120 g Aerosil 200 (Degussa) as source of silica, with a temperature of 105 °C for 1h, following the ratio: 1 SiO₂, 0.1 CTAB, 0.27 NaOH, 32 H₂O. The characteristic (pore diameter, pore volume, surface area) are listed below:

**Davisil_1 (Davisil LC150 Å, 35-70 micron):** pore diameter 13.3 nm; pore volume 1.1 mL/g; surface area 279 m²/g.

**Aerosil_2 (Aerosil 380):** surface area 262 m²/g.

**MCM-41_A (6124):** pore diameter 3.6 nm; pore volume 0.61 mL/g; surface area 827 m²/g.

**MCM-41_B (6170):** pore diameter 3.6 nm; pore volume 0.73 mL/g; surface area 967 m²/g.

SBA-15 were prepared accordingly to references.²,³ The characteristic (pore diameter, pore volume, surface area) are listed below:

**SBA-15_A (MFDC061, prepared at 60 °C):** pore diameter 6.7 nm; pore volume 0.69 mL/g; surface area 786 m²/g.

**SBA-15_B (MFDC065, prepared at 130 °C):** pore diameter 9.6 nm; pore volume 1.02 mL/g; surface area 525 m²/g.
Before use, MCM.41 and SBA-15 were calcinated at 550 °C for 8 h in air.

Activation of all silicas was performed in a Schlenk flask at 300 °C for 2-3 h in air, subsequently in high vacuum (at least 10^{-5} mbar) overnight.

The synthesis and characterization of copper(I)(Pc-L*) complexes 1\textsuperscript{4} and 2\textsuperscript{5} were previously reported. The collected analytical data for cis and trans ethyl-2-methyl-2-phenylcyclopropanecarboxylate,\textsuperscript{6} cis and trans tert-butyl-2-methyl-2-phenylcyclopropanecarboxylate,\textsuperscript{7} cis and trans ethyl-2-phenylcyclopropanecarboxylate,\textsuperscript{8} cis and trans ethyl-2-p-tolyl-cyclopropanecarboxylate,\textsuperscript{9} cis and trans ethyl 2-(4-chlorophenyl)cyclopropanecarboxylate,\textsuperscript{9} ethyl-2,2-diphenylcyclopropanecarboxylate,\textsuperscript{8} cis and trans ethyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate (ethyl chrysanthemate),\textsuperscript{7} dimethyl-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate\textsuperscript{10} and cis and trans ethyl-2-hexylcyclopropanecarboxylate\textsuperscript{11} are in agreement with those reported in the literature.

**Grafting of [CuI(Pc-L*)]CF_{3}SO_{3} complex, 1, on silica. Typical procedure.**

**Method 1:** complex 1 (0.0461 g, 0.0629 mmol) was dissolved in CH_{2}Cl_{2} (10 mL). The resulting colourless solution was added to activated Davisil B (0.400 g), the mixture was stirred at RT for 4 h under inert atmosphere, filtered, washed with CH_{2}Cl_{2} (3 x 5 mL) and dried overnight to yield the immobilized copper(I) complex.

**Method 2:** [Cu(OTf)]_{2}·(C_{6}H_{6}) (0.140 g, 0.277 mmol) was added to a C_{2}H_{4}Cl_{2} (28 mL) solution of Pc-L* (0.371 g, 0.555 mmol). The resulting colorless solution was stirred for 1 h., than it solution was added to activated Davisil B (3.5 g), the mixture was stirred at RT for 4 h under inert atmosphere, filtered, washed with C_{2}H_{4}Cl_{2} (3 x 10 mL) and dried overnight to yield the immobilized copper(I) complex.
Table S1. Impregnation method and Cu loadings (determined by ICP-OES), of [Cu\(^{1}\)(Pc-L\(^{*}\))]CF\(_3\)SO\(_3\)/SiO\(_2\) samples

<table>
<thead>
<tr>
<th>Entry</th>
<th>SiO(_2) support</th>
<th>Impregnation method</th>
<th>Cu loading [wt %]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 / MCM-41_A_1</td>
<td>MCM-41_A</td>
<td>1</td>
<td>0.62</td>
</tr>
<tr>
<td>1 / MCM-41_B_1</td>
<td>MCM-41_B</td>
<td>1</td>
<td>0.54</td>
</tr>
<tr>
<td>1 / Davisil_1</td>
<td>Davisil LC150</td>
<td>1</td>
<td>0.66</td>
</tr>
<tr>
<td>1 / Aerosil_2</td>
<td>Aerosil 380</td>
<td>2</td>
<td>0.45</td>
</tr>
<tr>
<td>1 / SBA-15_A_2</td>
<td>SBA-15_A</td>
<td>2</td>
<td>1.09</td>
</tr>
<tr>
<td>1 / SBA-15_B_2</td>
<td>SBA-15_B</td>
<td>2</td>
<td>1.59</td>
</tr>
<tr>
<td>1 / SBA-15_B_1</td>
<td>SBA-15_B</td>
<td>1</td>
<td>0.45</td>
</tr>
<tr>
<td>2 / Davisil_1</td>
<td>Davisil LC150</td>
<td>1</td>
<td>0.66</td>
</tr>
</tbody>
</table>

Cu loadings between 0.32 and 1.79 wt % were obtained. In general, higher loadings could be achieved using [Cu\(^{1}\)(Pc-L\(^{*}\))]CF\(_3\)SO\(_3\) directly after its synthesis in the dissolved form, without isolation from the solvent.

Figure S1. DRIFT spectra of [Cu\(^{1}\)(Pc-L\(^{*}\))]CF\(_3\)SO\(_3\) pure complex (1) in solid state (mixed with KBr), trace 1; 1 / Davisil_1 sample, trace 2; 1 / SBA-15_B_2 sample, trace 3; 1 / MCM-41_A_1 sample, trace 4.
Figure S2. DRIFT spectra of [Cu'(Pc-L*)]CF₃SO₃/Davisil_1 samples before (1) and after catalysis: 2, 4-chloro styrene + EDA; 3, 4-methyl styrene + EDA; 4, α-methyl styrene + EDA; 5, α-methyl styrene + EDA (after 3 cycles and washing in 1,2-dichloroethane); characteristic bands of cyclopropanation products (pure cyclopropanes) at 2980 and 1730 cm⁻¹.

Figure S3. CO-DRIFT spectra of: 1, 1 / Davisil_1; 2, 1 / MCM-41_A_1; 3, 1 / SBA-15_B_2 samples after catalysis.

References