Supporting Information

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

Brunilde Castano,[a] Paolo Zardi,[a] Yvonne Honneman,[a,b] Anne Galarneau,[c] Emma Gallo,[a] R. Psaro,[b] Alessandro Caselli,*[a] Vladimiro Dal Santo, *[b]

[a] *Dipartimento di Chimica, Università di Milano, and ISTM-CNR; Via Golgi 21, 20133 Milano, Italy. Fax: (+39)02 5031 4405; Tel: (+39)02 5031 4372; E-mail: alessandro.caselli@unimi.it*

[b] *CNR – Istituto di Scienze e Tecnologie Molecolari, Via C. Golgi 19, 20133 Italy. Fax: +39-02-50314405; Tel: +39-02-50314428; E-mail: v.dalsanto@istm.cnr.it*

[c] *CNRS ICGM ENSCM, 8 Rue de l’Ecole Normale 34296 Montpellier France.*

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_2SO_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 CaH_2 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 reported[1] 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 SiO_2, 0.1 CTAB, 0.27 NaOH, 32 H_2O. 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 m^2/g.

Aerosil_2 (Aerosil 380): surface area 262 m^2/g.

MCM-41_A (6124): pore diameter 3.6 nm; pore volume 0.61 mL/g; surface area 827 m^2/g.

MCM-41_B (6170): pore diameter 3.6 nm; pore volume 0.73 mL/g; surface area 967 m^2/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 m^2/g.

SBA-15_B (MFDC065, prepared at 130 °C): pore diameter 9.6 nm; pore volume 1.02 mL/g; surface area 525 m^2/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**[4] and **2**[5] were previously reported. The collected analytical data for *cis* and *trans* ethyl-2-methyl-2-phenylcyclopropanecarboxylate,[6], *cis* and *trans* *tert*-butyl-2-methyl-2-phenylcyclopropanecarboxylate,[7] *cis* and *trans* ethyl-2-phenylcyclopropanecarboxylate,[8] *cis* and *trans* ethyl-2-*p*-tolyl-cyclopropanecarboxylate,[9] *cis* and *trans* ethyl 2-(4-chlorophenyl)cyclopropanecarboxylate,[9] ethyl-2,2-diphenylcyclopropanecarboxylate,[8] *cis* and *trans* ethyl 2,2-dimethyl-3-(2-methylpropenyl)cyclopropanecarboxylate (ethyl chrysanthemate),[7] dimethyl-2-oxabicyclo[3.1.0]hex-3-ene-3,6-dicarboxylate[10] and *cis* and *trans* ethyl-2-hexylcyclopropanecarboxylate[11] are in agreement with those reported in the literature.

Grafting of [Cu^I(Pc-L*)]CF_3SO_3 complex, 1, on silica. Typical procedure.

Method 1: complex **1** (0.0461 g, 0.0629 mmol) was dissolved in CH_2Cl_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_2Cl_2 (3 x 5 mL) and dryed overnight to yield the immobilized copper(I) complex.

Method 2: $[Cu(OTf)]_2\cdot(C_6H_6)$ (0.140 g, 0.277 mmol) was added to a $C_2H_4Cl_2$ (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 $C_2H_4Cl_2$ (3 x 10 mL) and dryed overnight to yield the immobilized copper(I) complex.

Table S1. Impregnation method and Cu loadings (determined by ICP-OES), of [Cu^I(Pc-L*)]CF_3SO_3/SiO_2 samples

Entry	SiO_2 support	Impregnation method	Cu loading [wt %]
1 / MCM-41_A_1	MCM-41_A	1	0.62
1 / MCM-41_B_1	MCM-41_B	1	0.54
1 / Davisil_1	Davisil LC150	1	0.66
1 / Aerosil_2	Aerosil 380	2	0.45
1 / SBA-15_A_2	SBA-15_A	2	1.09
1 / SBA-15_B_2	SBA-15_B	2	1.59
1 / SBA-15_B_1	SBA-15_B	1	0,45
2 / Davisil_1	Davisil LC150	1	0.66

Cu loadings between 0.32 and 1.79 wt % were obtained. In general, higher loadings could be achieved using [Cu^I(Pc-L*)]CF_3SO_3 directly after its synthesis in the dissolved form, without isolation from the solvent.

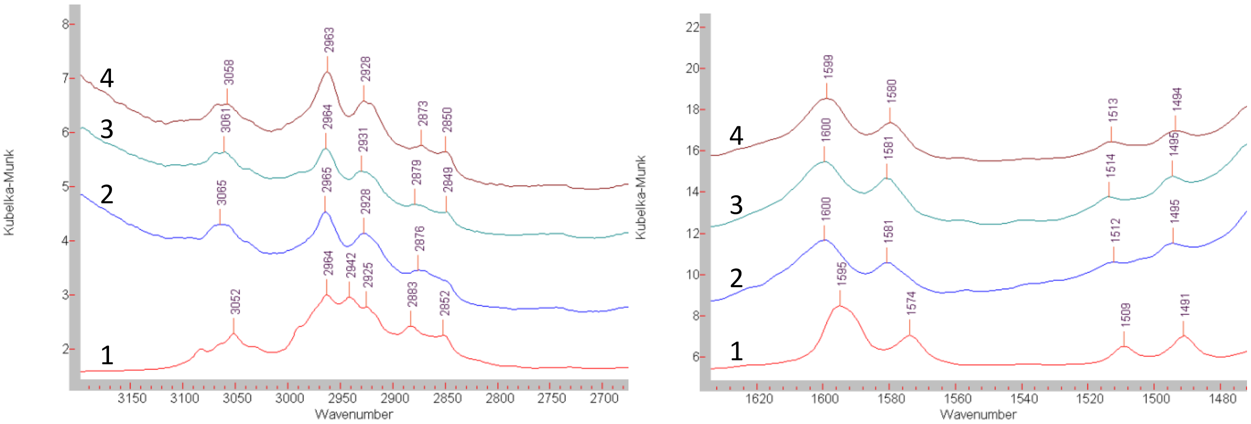

Figure S1. DRIFT spectra of [Cu^I(Pc-L*)]CF_3SO_3 pure complex (**1**) in solid state (mixed with KBr), trace 1; **1** / Davisil_1 sample, trace 2; **1** / SBA-15_B_2 sample, trace 3; **1** / MCM-41_A_1 sample, trace 4.

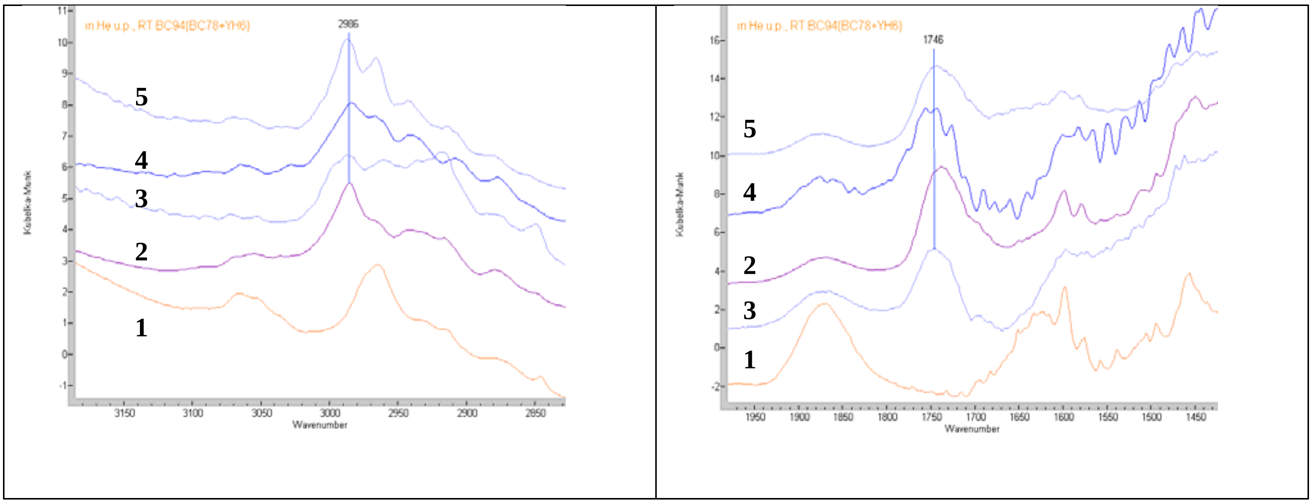

Figure S2. DRIFT spectra of [Cu^I(Pc-L*)]CF_3SO_3/Davisil_1 samples before (**1**) and after catalysis: **2**, 4-chloro styrene + EDA; **3**, 4-methyl styrene + EDA; **4**, α-methyl styrene + EDA; **5**, α-methyl styrene + EDA (after 3 cycles and washing in 1,2-dichloroethane); characteristic bands of cyclopropanation products (pure cyclopropanes) at 2980 and 1730 cm^{-1}.

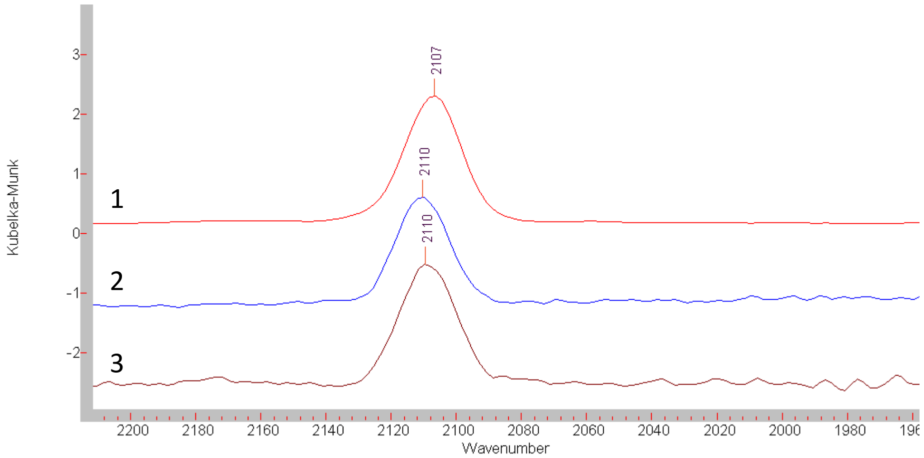

Figure S3. CO-DRIFT spectra of: 1**, 1** / Davisil_1; 2, **1** / MCM-41_A_1; 3, **1** / SBA-15_B_2 samples after catalysis.

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