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Silica "SHB" chiral Pc-L* copper complexes for halogen-free solvent cyclopropanation reactions†

Brunilde Castano,[a] Paolo Zardi,[a] Yvonne C. Hönemann,[ab] Anne Galarneau,[c] Emma Gallo,[a] Rinaldo Psaro,[b] Alessandro Caselli*[a] and Vladimiro Dal Santo*[b]

The grafting of the preformed Pc-L* (pyridine containing macrocyclic ligands) copper(I) complexes on different ordered and non-ordered silicas, and their use, under heterogeneous batch conditions, as catalysts for the olefin cyclopropanation are reported. High yields (up to 99%) and good recyclability in halogen-free solvent reactions were obtained, together with negligible copper leaching (0.1% of total copper).

Introduction

Immobilized heterogenous catalysts present several inherent advantages, such as stability and recyclability, compared to their homogeneous counterparts. However, when chiral catalyst are immobilized onto solid surfaces, the interaction between the active metal complex and the surface may reduce the obtained stereoselectivities.[1] Anchoring chiral complexes through covalent bonds has been one of the most used methods to immobilize chiral ligands on silica materials, however the structural modification needed to graft the ligand to the support has often a detrimental effect on the observed enantioselectivities.[2] Conversely, supported hydrogen-bonded (SHB) catalysts (a class of non-covalent bound homogeneous catalysts) show some peculiar advantages, with respect to the covalent bound ones, such as remarkably mild grafting protocols and the possibility to easily recover the bound complex for further studies by standard liquid-phase techniques.[3,4] Moreover, the SHB methodology can be profitably applied to cationic metal complexes, with minimal or no ligand modifications of the parent homogeneous complex (only the presence of $CF_3SO_3^-$ counter-anion is necessary).[5]

Copper complexes SHB catalysts found interesting applications in several reactions, like cyclopropanations,[6] Diels–Alder additions,[7,8] and epoxidations.[9]

On the other hand, Cu(I) complexes based on functionalised pyridine-containing macrocyclic ligands[10] show excellent performances in asymmetric cyclopropanation reactions.[11,12] The macrocyclic ligands confer to the complex additional

stability, which is highly recommended if separation and recovery of the catalyst are to be pursued.

The advantages of highly active and selective homogeneous catalysts coupled with the ease of separation typical of heterogeneous systems is also highly recommended to implement such catalysis. Moreover, by using nanostructured supports, like mesoporous silicas or clays, it is also possible to exploit the positive confinement effects[13–16] on activity, diastereo-, and enantio-selectivity.

Here we report on the use of SHB copper catalysts in cyclopropanations by using bare alkanes as reaction solvents in place of the less desirable halogeno–alkanes.

Results and discussion

Synthesis and characterisation of the supported catalyst

The copper(I) complex **1** (Fig. 1) was chosen as a model complex to be supported on different silicas to be studied as a catalyst in cyclopropanation reactions. The presence of a naphthyl substituent confers a good stability to this copper(I) complex and, although the synthesis is better performed under protecting atmosphere, compound **1** could be manipulated in air for limited period of time without any appreciable decomposition. The reason of this major stability is due to the presence of the naphthyl group that can act as a further coordination site for the metal (Fig. 1). Four different silicas were investigated as a support: two commercial ones, Davisil LC150 (Grace) and Aerosil 380 (Evonik), and two popular and often applied mesoporous silica support materials, MCM-41[17,18] and SBA-15[19] (see ESI† for details). The adopted SHB methodology allowed the easy and very mild preparation of the supported **1**/SiO₂ catalyst showing a copper loading in a range of 0.3–1.8 Cu wt%, depending on the used silica (see Table 1 in ESI†). The interaction, *via* H-bonding, was confirmed by a perusal of DRIFT spectra: upon the Cu complex grafting the strong and sharp band located at 3740 cm⁻¹, ascribable to isolated silanols,

[a]Dipartimento di Chimica, Università di Milano, Via C. Golgi 19, 20133 Italy. E-mail: alessandro.caselli@unimi.it; Fax: +39-02-50314405; Tel: +39-02-50314372

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

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

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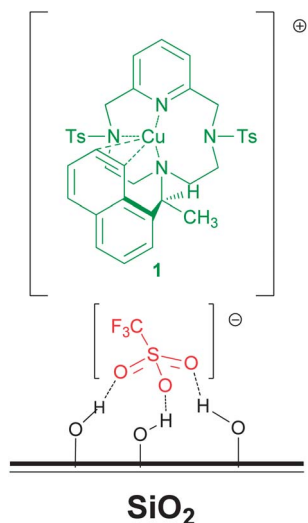
Fig. 1 Supported copper(ɪ) complex **1**.

disappeared almost completely, and a new broad band, located between 3500 and 3400 cm^{-1} (originated by O–H stretching vibration of silanols H-bonded with triflate counteranion) appeared in the spectra (Fig. 2). Moreover, DRIFT spectra showed also that the Cu complex is grafted without any modification of the ligand structure, since the IR absorption bands did not show any appreciable modification with respect to solid **1**, nor in location, nor in intensity (see ESI, Fig. S1†).

Spectroscopic properties

The nature of the grafted Cu complex was further investigated by CO–DRIFT spectroscopy, since CO is a very good probe molecule for Cu(ɪ) sites. In fact, stretching vibrations of a copper bound CO, ν(C≡O), is very sensitive to the coordination and electronic density on Cu site.[20,21]

Cu complex in the solid state (diluted in KBr, trace E in Fig. 3) did not adsorb CO under mild pressure (up to 2 bar), while, when CuL was dissolved in dichloroethane, an intense band located at 2111 cm^{-1} readily appeared in solution (Scheme 1, trace D in Fig. 3).[11] The observed frequency of the coordinated CO was slightly higher than those reported for the CO adsorbed on tetra coordinated Cu(ɪ) of [bis(2-pyridylmethyl) amine] copper complexes (2097 cm^{-1})[22] probably due to the lower efficiency of aliphatic amines in transferring electron density to the metal centre compared to pyridine.

Notably also the grafted complex exposed to CO flow showed the presence of a strong CO band, slightly red-shifted and broadened, located in the range 2115–2119 cm^{-1}, (traces A–C in Fig. 3) that suggests a "solution like" complete accessibility to the Cu sites of the supported complex to small molecules (like CO).

Catalytic cyclopropanation of olefins

The catalytic activity of copper complexes supported on silica in cyclopropanation reactions has been investigated. As model reaction we chose the cyclopropanation of α-methyl styrene by EDA (EDA = ethyl diazoacetate). Catalytic reactions were run by

Table 1 Cu(ɪ)/Pc-L* (*S* configuration) supported complexes for asymmetric cyclopropanation of α-methyl styrene[a]

Entry	Run	Catalyst[b]	Yield[c] (%)	cis : trans[c]	ee[d] (%)	
					cis	*trans*
1	1	**1**	81	62 : 38	55	62
2	1	**1**/Davisil_1	72	72 : 28	35	26
3[e]	1	**1**/Davisil_1	<1	—	—	—
	1		74	76 : 24	35	27
4	1	**1**/Davisil_1	65	72 : 28	40	31
	2		68	72 : 28	39	32
	3		56	71 : 29	41	30
5	1	**1**/SBA-15_A_2	45	71 : 29	35	25
	2		43	72 : 28	42	33
	3		40	70 : 30	38	29
6	1	**1**/SBA-15_B_2	91	67 : 33	35	24
	2		78	72 : 28	39	30
	3		52	71 : 29	40	30
7	1	**1**/SBA-15_B_1	57	70 : 30	36	29
	2		73	73 : 27	38	29
	3		58	72 : 28	46	38
8	1	**1**/MCM-41_B_1	53	68 : 32	29	22
	2		77	71 : 29	34	23
	3		75	72 : 28	23	20
9[f]	1	**1**/MCM-41_B_1	97	63 : 37	39	34
	2		88	62 : 38	37	31
	3		99	63 : 37	33	33
10	1	**1**/MCM-41_A_1	67	69 : 31	36	26
	2		71	70 : 30	37	27
	3		78	71 : 29	37	26
	6		65	70 : 30	37	26
	7[g]		37	70 : 30	34	25
11[e,f]	1	**1**/MCM-41_A_1	<10	59 : 41	46	58
	1		64	64 : 36	58	54
12[f]	1	**1**/MCM-41_A_1	69	64 : 36	58	54
	2		99	63 : 37	53	47
	3		96	63 : 37	n.d.	n.d.
13	1	**1**/Aerosil_2	73	67 : 33	39	31
	2		99	69 : 31	39	30
	3		91	68 : 32	39	30
14[f]	1	**1**/Aerosil_2	99	63 : 37	33	33
	2		95	63 : 37	50	51
	3		98	62 : 38	46	48
15[h]	1	**3**/Davisil_1	63	68 : 32	−59	−60
	2		71	65 : 35	−65	−56
	3		65	63 : 37	−67	−60

[a] Reactions were performed with [Cu(ɪ)] (3.0 × 10^{-2} mmol) in *n*-hexane (5 mL). Slow addition of EDA (1 mmol) in *n*-hexane (1 mL) over 100 min at 0 °C. [b] Support materials: letter A or B refer to different materials, number 1 or 2 refers to different grafting procedures, see Table S1.† [c] Determined by GC and ^{1}H NMR, with 2,4-dinitrotoluene as internal standard. [d] Determined by chiral HPLC; absolute configurations: *cis*-cyclopropanes were (1*R*,2*S*), *trans*-cyclopropanes were (1*R*,2*R*); The opposite enantiomers were obtained in the same ee when employing Pc-L* with a *R* configuration. [e] Sheldon test (upper row). [f] Reaction performed in 1,2-dichloroethane. [g] In the 7th run reaction was slower and further 45 minutes after the addition were needed to reach completion. [h] Opposite enantiomers were obtained.
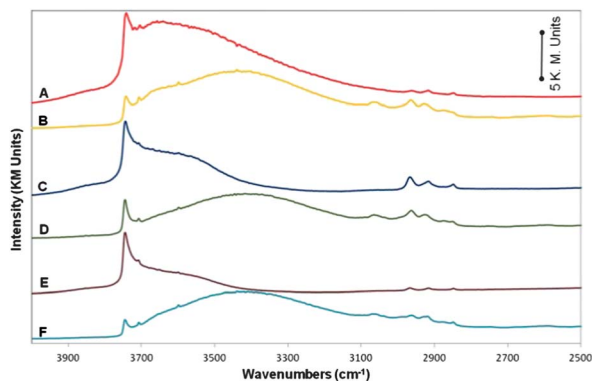
Fig. 2 DRIFT spectra showing the interaction *via* H-bonding; (A) bare Davisil; (B) **1**/Davisil_1; (C) bare MCM-41_A; (D) **1**/MCM-41_A_1; (E) bare SBA-15_B; (F) **1**/SBA-15_B_2.
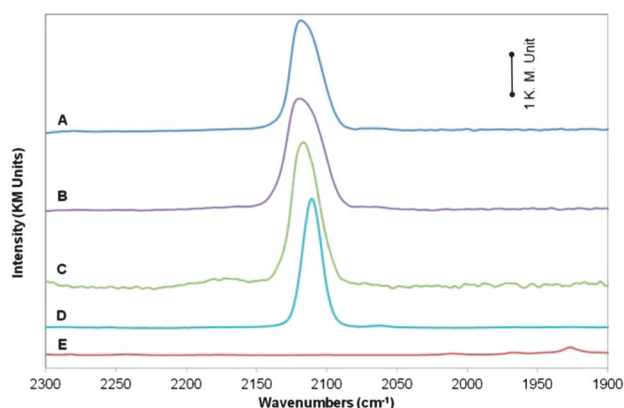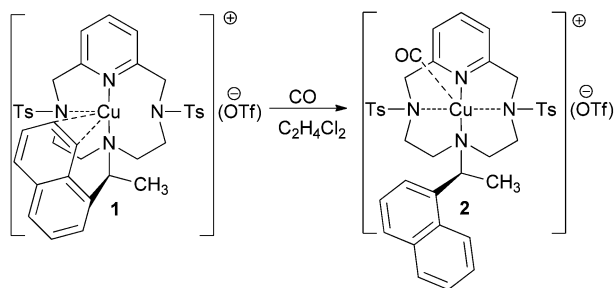

Fig. 3 CO–DRIFT spectra of Cu(I) Pc-L* supported complex. (A) **1**/Davisil_1; (B) **1**/MCM-41_A_1; (C) **1**/SBA-15_B_2; (D) **1** in dichloroethane solution; (E) **1** solid state (KBr pellet).

Scheme 1 Reaction of complex **1** with CO.

syringe pump slow addition of a EDA solution to a suspension containing the olefin and the catalyst (Cu–EDA–olefin ratio 1 : 35 : 170); the disappearance of the band due to the stretching of the N_2 moiety ($\nu = 2114$ cm^{-1}) was followed by IR spectroscopy. These conditions are very close to those used in the homogeneous phase[12] and allow for a direct comparison of the obtained results. The major difference is that the solvent used in the homogeneous phase, 1,2-dichloroethane, was replaced with the more eco-friendly *n*-hexane. Although the latter is a

volatile organic solvent, its use should be intended only as a proof of concept. In fact, for practical applications it may be easily substituted with other hydrocarbons with higher boiling point. All reactions were carried out at 0 °C, since this was the optimal temperature for cyclopropanation reactions catalysed by complex **1** in the homogeneous phase. We first tested the reaction by changing the employed silica support. The results are summarised in Table 1, compared with a typical result for the cyclopropanation reaction in the homogeneous phase by using the same copper(I) complex **1** as catalyst. All reported yields have been determined by GC and confirmed by quantitative ^{1}H NMR and based on EDA. In all tested cases we observed a complete conversion of the starting EDA after the end of the addition (100 min) and cyclopropanes were obtained as major products; fumarate and maleate, the homo-coupling products of EDA, were the only other compounds detected and accounted for the reaction mass balance.

The catalyst activity was almost unchanged in the heterogeneous phase with respect to the homogeneous one, although in some cases (entry 5, Table 1) the yield in cyclopropanation products is somewhat lower, due both to a slight increase in the coupling product fumarate and maleate and to a partial absorption of the cyclopropanes on silica (see next section). Actually, in selected cases, especially when employing *n*-hexane as the solvent, reaction yields in cyclopropane products increase in the second run. This can be explained with a better release of the formed product from the silica (see entries 6, 9, 10 and 13, Table 1). Experimental data show only a very weak dependence of the reaction efficiency from the surface area characteristics of the employed silica. In particular, we have obtained almost indistinguishable diastereo- and enantio-selectivities using either commercial Davisil or Aerosil 380, either ordered mesoporous silicas MCM-41 or SBA-15. The possibility to use commercially available silica as a support in the present system is very interesting and pave the way to the employment of this immobilization technique also in laboratories not equipped for the synthesis of mesoporous materials. Other authors, using covalently bonded bis(oxazoline)–copper complexes on silicas, recently reported that in those conditions commercially available silica were not suitable materials, probably due to its acidity.[2]

The Sheldon test[23] showed that the catalyst is strongly bound to the support and that the filtered solution has no catalytic activity, while the filtrate keeps the same catalytic activity as the original material (compare entries 2 and 3, Table 1). After the catalytic run, the filtrate solution was analyzed by ICP-OES to determine the copper content and the results (0.1% of total Cu originally present in the catalyst) confirmed that leaching is negligible when employing *n*-hexane as the reaction solvent. A blank test (MCM-41 not loaded with copper complex) showed that the silica has no catalytic activity in the present reaction.

As often observed for heterogeneous catalysts, the ees are in any case slightly lower if compared to the homogeneous system, especially for the *trans* isomer.[2] Compared to the homogeneous reaction (entry 1, Table 1), better diastereomeric excesses in favor of the *cis* isomer were obtained in *n*-hexane, a fact that is in agreement with those reported for clay-immobilized copper

complexes.[24] In a low polarity solvent, in fact, tight ion pairs are to be expected and it is reasonable to assume that in this case, the steric hindrance of the support must favor the preferential formation of the *cis* isomer.[15] It should be pointed out that complex **1** is not soluble in *n*-hexane and thus the reaction cannot be performed in this solvent under homogeneous conditions. On the other hand, reactions in 1,2-dichloroethane yielded to better enantioselectivities, especially for the *trans* isomer (entries 9, 11, 12 and 14, Table 1). This may well be due to the enhancement of the polarity of the medium that will affect the strength of ion pairs and ions–silica interactions,[25] finally leading to the observed differences in enantioselectivity (it should be pointed out how cyclopropanation reactions can be affected by several parameters in a complex way).[14]

The improvement in the yield of the first run in these last cases can be explained with the better solubility of the cyclopropanes in chlorinated solvents. However, in this last solvent, some leached catalyst could be active in solution, as shown by the Sheldon test performed in 1,2-dichloroethane (entry 11, Table 1). This may explain the higher enantiomeric excesses obtained in the second and third run of the reaction when employing Aerosil 380 as a support (entry 14, Table 1), while ee obtained in *n*-hexane remains constant during all the consecutive runs (entry 13, Table 1). To further asses eventual leaching of the catalyst employing dichloroethane as reaction solvent, also in this case the filtered reaction mixture after catalysis was analyzed by ICP-OES, showing Cu concentrations below 12.4 ppm, corresponding to a maximum leaching of 4.3% of copper present in the catalysts. It should be pointed out that in such low concentration in solution, complex **1** is a poor cyclopropanation catalyst, especially at 0 °C. Copper leaching in chlorinated solvents should be promoted by the presence of EDA.[2,26]

Given the efficacy of the supported catalysts in the cyclopropanation reaction, we tested their reusability both using *n*-hexane and 1,2-dichloroethane as single solvents. As mentioned previously, *n*-hexane appears as a valuable greener solvent with respect to chlorinated ones. It is noticeable that quantitative conversions were still observed and cyclopropanes were obtained in almost unchanged yields, diastereo- and enantio-selectivities in all consecutive runs. All catalysts were recycled at least three times, without any noticeable deactivation. In particular, in the case of catalyst **1**/MCM-41_A_1 the reaction was repeated for several consecutive runs and only after the seventh recycle (two days) a decrease in activity was observed. It is well known that silica can act as ligand for copper leading to non-enantioselective catalytic processes.[27] We guess that this must not be the case in the present system, since if that were truth we should expect a progressive decrease in the enantioselectivity after consecutive runs. To further exclude this hypothesis, in order to remove eventual free copper species from the reaction mixture, the catalyst was washed with 1,2-dichloroethane after the first run in *n*-hexane. Then, the reaction was repeated using the hydrocarbon solvent and no change in yield, diastereo- and enantioselectivity was observed.

When employing the bulkier *tert*-butyl diazoacetate, *t*BuDA, (conditions as in the caption to Table 1, **1**/Davisil_1 as supported catalyst) together with lower yields (35% average of three

runs) we observed a decrease in the enantioselectivities (ee *cis* 19%, *trans* 20%) and a complete drop of the diastereoselectivity (*cis* : *trans* = 50 : 50). Similar negative effects related to the diazoacetate steric hindrance have been observed also in the homogeneously catalysed reaction[12] and have been explained in terms of overcrowding of the transition state.[28]
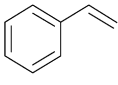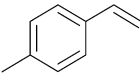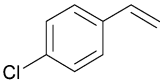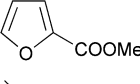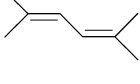
Under optimal conditions, other alkenes were employed to determine the substrate scope of the copper catalysed cyclopropanation reactions. Since the results in terms of diastereo- and enantioselectivity were comparable for all tested materials, the less expensive commercial Davisil silica was chosen as support. At a Cu(ɪ)–EDA–alkene ratio of 1 : 35 : 170, the formed complex catalysed the reaction of all the tested substrates yielding the cyclopropanes in acceptable yields and enantioselectivities. It should be pointed out that for these substrates, reported yields have been determined by quantitative ^{1}H NMR and based on EDA. However, the high volatility of some cyclopropane products requires a careful removal of the reaction solvent. Fumarate and maleate were again the only detected side products. The absence of α-substituents on the styrene affected the diastereoselectivity of the reaction, although also in this case a slight *cis* preference was observed compared to the results obtained in the homogeneous phase.[12] We have obtained almost indistinguishable diastereo- and enantioselectivities using styrene (entry 1, Table 2), 4-methyl styrene (entry 2) and 4-chloro styrene (entry 3). Enantioselectivities obtained for the *cis* cyclopropane products with those substrates were higher than those observed in the homogeneous reactions.[12] Low yields and enantioselectivities were obtained with diphenylethylene (entry 4, Table 2). Interestingly, benzophenone (less than 10% with respect to starting diphenylethylene) was found in this case amongst the reaction products.

To explore the scope of the reaction, we next studied the cyclopropanation of two different dienes. Excellent diastereoselectivity to yield the desired *trans* isomer (attack only at the non-substituted double bond), was obtained with methyl-2-furoate (entry 5, Table 2).[29] The cyclopropane obtained from this reaction is an important building block in the synthesis of bioactive compounds.[30]

With 2,5-dimethyl-2,4-hexadiene, an important precursor to the chrysanthemic acid synthesis,[31] the catalytic reaction yielded the desired cyclopropanes (cyclopropanation of only one double bond was observed[32]) although in modest yields (37%, isolated yield), if a large excess of the olefin (Cu–EDA–olefin = 1 : 35 : 500) is employed (entry 6, Table 2). Worth to note, slightly higher ees with respect to the homogeneously catalysed reaction were observed. Even aliphatic alkenes that are generally less reactive in cyclopropanation reactions,[33] gave very good results. For instance, the cyclopropanation occurs also with reasonable yields with the non-activated double bond of *n*-octene, although in this case the olefin has been used as the solvent (entry 7, Table 2).

Finally, since the Cu(ɪ) complex, **3** (Fig. 4), of the more sterically hindered ligand, possessing two further stereocenters on the ring skeleton (6-[(*R*)-1-naphthylethyl]-3,9-ditosyl-3,8-[(*S,S*)-iso-propyl]-3,6,9,15-tetraazabicyclo[9,3,1]pentadeca-1(15),11,13-triene), gave the best results in term of enantioselectivity

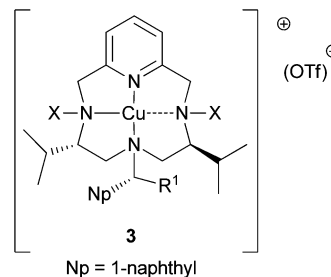**Table 2** Asymmetric cyclopropanation of alkenes by **1**/Davisil_1[a]

Entry	Alkene	Yield[b] (%)	cis : trans[b]	ee[c] (%) cis	trans
1	styrene	36	61 : 39	45	35
		33	61 : 39	37	29
		35	61 : 39	38	30
2	4-methylstyrene	59	58 : 42	42	35
		65	60 : 40	39	35
		68	57 : 43	39	35
3	4-chlorostyrene	48	56 : 44	42	38
		61	56 : 44	42	38
		50	56 : 44	42	38
4	Ph₂C=CH₂	33	—	21	
		36	—	23	
		29	—	25	
5	methyl 2-furoate acrylate	46	>1 : 99	n.d.	49
		43	>1 : 99	n.d.	49
		44	>1 : 99	n.d.	44
6[d]	diene	37	60 : 40	38	33
		37	60 : 40	38	33
7[e]	n-octene	50	56 : 44	40	35

[a] Reactions were performed with [Cu(I)] (3.0 × 10⁻² mmol) in n-hexane (5 mL). Slow addition of EDA (1 mmol) in n-hexane (1 mL) over 100 min at 0 °C. [b] Determined by ¹H NMR, with 2,4-dinitrotoluene as internal standard. [c] Determined by chiral HPLC; absolute configurations: for entries 1–3 cis-cyclopropanes were (1R,2S), trans-cyclopropanes were (1R,2R); entry 4: the absolute configuration was (1R), entry 5: trans-cyclopropane was (1S, 2S, 6S). For entries 6 and 7 were not determined. [d] Cu(I)–EDA–olefin = 1 : 35 : 500; isolated yield. [e] n-Octene as the solvent: Cu(I)–EDA–olefin = 1 : 35 : 1060; isolated yield.

in the homogeneous phase,[11] we next studied its reactivity when supported on silica. Again commercial Davisil LC150 was chosen as support.

A complete conversion of the starting EDA was observed also in this case (entry 15, Table 1), although we should point out that the reaction in the third run was slightly slower and further 15 minutes after the addition were needed to reach completion. Remarkably, **1**/Davisil_1 and **3**/Davisil_1 gave cyclopropane products in very similar yields (compare entry 4 with entry 15, Table 1). It should be pointed out that complex **3** under homogeneous conditions gave equal amounts of both isomers whilst, when supported on Davisil, a slight preference for the cis isomer is again obtained. As expected, observed enantiomeric excesses were higher (67% for the trans, 60% for the cis isomer).

Grafted complexes were investigated at the end of the catalysis. The intact Cu complex structure was confirmed by means of IR spectroscopy, showing the presence of all the bands in the skeletal range of the spectrum typical of **1**. These results confirmed that the grafted complex is stable under the reaction conditions. The presence of bands at 2986 and 1746 cm⁻¹ suggests the presence of adsorbed –COOR compounds (IR spectra of reaction products pure cyclopropanes show similar bands located at 2980 and 1730 cm⁻¹) (see ESI, Fig. S2†). The state of Cu(I) site was further investigated by CO–DRIFT and, in

Fig. 4 Copper(I) complex **3**.

general, CO bands undergo a small redshift to lower wavenumbers at around 2113 cm⁻¹ (see ESI, Fig. S3†), possibly due to the reversible coordination of reaction products on copper site. Coordination of by-products[34] (diethyl maleate and fumarate) and formation of diazoacetate polymers[35] have been proposed in the literature as possible deactivation processes for bis(oxazoline) copper complexes. Also in the present system slightly longer reaction times, after the third run, were observed. However, high yields and constant stereoselectivities were obtained in all consecutive runs.

Conclusions

In summary, we have developed new supported hydrogen-bonded (SHB) chiral copper(I) complexes showing good performances in cyclopropanation reactions allowing the use of more environmentally friendly n-hexane as solvent in place of 1,2-dichloroetane. Although a fivefold excess of the olefin has to be used to keep low the side products derived from EDA self-condensation, it can be easily recovered at the end of the reaction by simple distillation and re-used for further reactions. The heterogeneous systems showed higher or comparable activities than the homogeneous counterpart and a good recyclability. In all cases, the diastereoselective outcome of the reaction is strongly affected by the catalyst grafting on the silica support and we observed an inversion of the selectivity in favour of the less sterically hindered cis cyclopropane derivative. This is an interesting result, since cis cyclopropanes are present in several compounds biologically active. The catalyst can be easily recycled (up to 6 times) without any change in the obtained stereoselectivity. We did not observe any significant Cu leaching when employing n-hexane as a reaction medium and the catalytic system is of truly heterogeneous nature, since the filtered solution is not catalytically active. The observed effects on stereoselectivity are more dependent on the employed solvent (non-polar vs. halogenated) than to the kind of support (ordered or non-ordered). Worth to note is the fact that even commercial silica can be used as a support, without any need of structural modification of the ligand in order to strongly graft the complex.

Cyclopropanes were obtained in good to excellent yields and enantiomeric excesses up to 67%. The high stability showed by the copper(I) Pc-L* complexes will be the basis for more work in the direction of their use as supported catalysts and we are currently moving towards the use of these catalysts in reactors.

Experimental procedures

Materials

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 (Grace Davison, LC 150 Å, 35–70 micron) and Aerosil 380 (Evonik) are commercially available.

All other starting materials were commercial products and were used as received.

Instrumentation and measurements

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.

Preparations

Unless otherwise specified, all the reactions were carried out in a argon or dinitrogen atmosphere employing standard Schlenk techniques and magnetic stirring.

The copper(I) complex **1** and **2** were synthesized as already reported.[11]

MCM-41 (ref. 36) and SBA-15 (ref. 37 and 38) were synthesized as already reported. The characteristic (pore diameter, pore volume, surface area) are listed below:

MCM-41_A 6124: pore diameter 3.6 nm; pore volume 0.61 mL g^{-1}; surface area 827 m^2 g^{-1}.

MCM-41_B 6170: pore diameter 3.6 nm; pore volume 0.73 mL g^{-1}; surface area 967 m^2 g^{-1}.

SBA-15_A (prepared at 60 °C): pore diameter 6.7 nm; pore volume 0.69 mL g^{-1}; surface area 786 m^2 g^{-1}.

SBA-15_B (prepared at 130 °C): pore diameter 9.6 nm; pore volume 1.02 mL g^{-1}; surface area 525 m^2 g^{-1}.

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.

Grafting of [Cu^I(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_2Cl_2 (10 mL). The resulting colourless solution was added to activated Davisil LC150 (0.400 g), the mixture was stirred at RT for 4 h under inert atmosphere, filtered, washed with CH_2Cl_2 (3 × 5 mL) and dryed overnight to yield the immobilized copper(I) complex.

Method 2. [Cu(OTf)]$_2$·(C_6H_6) (0.140 g, 0.277 mmol) was added to a $C_2H_4Cl_2$ (28 mL) solution of Pc-L* ligand (0.371 g, 0.555 mmol). The resulting colorless solution was stirred for 1 h, than 5.5 mL of solution was added to activated SBA-15_A (0.340 g), the mixture was stirred at RT for 4 h under inert atmosphere, filtered, washed with $C_2H_4Cl_2$ (3 × 5 mL) and dryed overnight to yield the immobilized copper(I) complex.

General procedure for the catalytic cyclopropanation reactions

In a typical experiment, [Cu^I(Pc-L*)]·(CF$_3$SO$_3$)/SiO$_2$ ([Cu] = 3.0 × 10^{-2} mmol) and α-methyl styrene (0.650 mL, 5.0 mmol) were suspended in *n*-hexane (5 mL) and the reaction mixture was cooled at 0 °C. Then a *n*-hexane solution (1 mL) of EDA (0.114 g, 0.105 mL, 1 mmol) was slowly added by a syringe pump during 100 minutes. The reaction was monitored by IR, following the disappearance of the band due to the stretching of N_2 moiety at 2114 cm^{-1}. The reaction was considered to be finished when the absorbance of the EDA was below 0.03 (by using a 0.1 mm thick cell). The solution was filtered by cannula, the solid catalyst was washed with *n*-hexane (3 × 5 mL), then 2,4-dinitrotoluene was added as internal standard and the solution was analysed by GC. The solution was then evaporated to dryness *in vacuo* and analysed by ^{1}H NMR. The residue purified by silica gel chromatography (eluant ethyl acetate–*n*-hexane = 0.3 : 10). Enantiomeric excess were determined by HPLC.

The solid catalyst could be recycled for further reactions employing the same reagent amounts. In all cases (with few exceptions reported in the tables captions) a quantitative conversion of the starting EDA was observed.

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Notes and references

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