



# Covalent attachment of a biomimetic Ru-(terpy)(bpy) complex on silica surface: Catalytic potential

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Dedicated to Alfred Werner on the 100th Anniversary of his Nobel prize in Chemistry in 1913.

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## ABSTRACT

The Ru-containing modified silica  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-Me bpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_m \cdot z\text{SiO}_2$  has been prepared by covalent attachment on silica surface of biomimetic  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H-4'-Me bpy})\text{Cl}]^+$  complex through the formation of a pseudo-peptide bond. The catalytic ability of bio-derived silica for alkene oxidation with  $\text{HOO}^t\text{Bu}$  has been evaluated exhibiting significant efficiency and, in some cases, showing increased activity compared vs. the corresponding 'net'  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H-4'-Me bpy})\text{Cl}]^+$  complex. The data supported that the covalently attached ruthenium complex preserves the catalytic behaviour of the 'net' ruthenium complex indicating that the presented grafting process was successful.

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## 1. Introduction

Covalently anchoring of bio-inspired metal complexes on silica surface through the side chain functionalities offers alternative processes to develop bio-derived silica frameworks that can be utilized as catalytic materials for specific transformation in fine chemical production [1]. This synthetic strategy is grounded on the evidence that the active sites of metalloenzymes involve metal complexes which are efficient and selective catalysts *in vivo* as well as *in vitro*, in oxidation reactions of organic compounds [2–5]. Among the different oxidation reactions, the epoxidation of olefins is of major importance for organic synthesis. Nevertheless, the synthesis of epoxides catalyzed by transition metal complexes is still important on laboratory as well as on industrial scale [3,6–8]. Based on our recent work on catalytic epoxidations using manganese and iron biomimetic complexes 'net' and covalently attached on inorganic matrices [9–15], we were interested in using ruthenium-based catalytic materials in these reactions. The potential of ruthenium as epoxidation catalyst arises from its extensive redox chemistry and its propensity to form high-valent oxo complexes [16].

Ruthenium complexes as homogeneous catalysts offered interesting results, e.g. such as high yield and chemoselectivity [16–23], however, they become more useful if the separation process is targeted to recover them at the end of reaction. Metal-based catalysts can be covalently anchored on the surface of porous materials most

effectively by post-grafting method [1,24,25] through anchoring of the organic ligands present [26–28]. This covalent route to immobilisation of homogeneous catalysts is believed to be the most suitable, since adsorption and ionic methods lead to a decrease in catalyst stability [1].

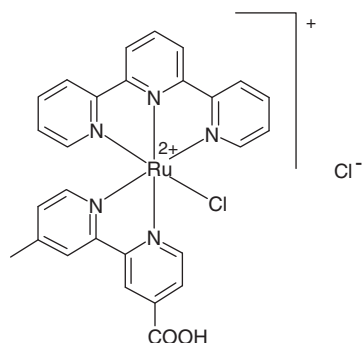
Although ruthenium complexes with Schiff bases or polypyridine ligands have been thoroughly studied, rather few reports are available on immobilised ruthenium complexes and their application in oxidation catalysis. As example, we refer the work of Ram and co-workers [29–31], Reedijk and co-workers [32] and Che and co-workers [33]. More recently, ruthenium-salophen, and ruthenium-bipyridine complexes supported on polystyrene, or mesoporous silica FSM have been prepared and evaluated as oxidation catalysts of alkenes with  $\text{NaO}_4$  and TBHP respectively [34,35].

The biomimetic ruthenium complex,  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H-4'-Me bpy})\text{Cl}]\text{Cl}$  (Scheme 1), has been designed and served as precursor of polypyridylruthenium conjugated peptide/amino acid complexes [36]. This class of compounds has been shown remarkable photoinduced nucleolytic activity cleaving the DNA phosphodiesteric bonds [37].

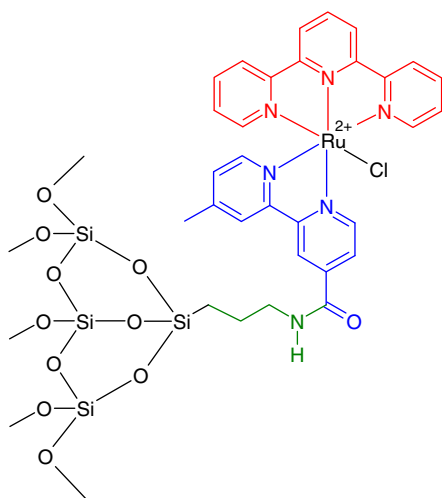
In the present study, this Ru-complex has been immobilised on silica surface (Scheme 2). The applied method, depicted in Scheme 3, builds up the ruthenium complex on preformed silica. Thus, the ligand 4'-Me bpy-4-COOH (4'-methyl-2,2'-bipyridine-4-carboxylic acid) was attached onto a modified amino-propyl-silica *via* pseudo-peptide bond formation, then reaction with  $\text{Ru}(\text{terpy})\text{Cl}_3$  yielded the supported ruthenium complex,  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-Me bpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_m \cdot z\text{SiO}_2$ . The developed Ru-based material as well as the ruthenium complex  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H-4'-Me bpy})\text{Cl}]\text{Cl}$ , was

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**Scheme 1.** The structure of biomimetic complex  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H-4'-Meppy})\text{Cl}]\text{Cl}$ .



**Scheme 2.** The developed bio-functionalized silica  $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{-Mebpy/4-CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_m \cdot z\text{SiO}_2$ .

tested for their catalytic ability in the oxidation of various olefins using *tert*-butylhydroperoxide (TBHP), as oxidant.

## 2. Experimental

### 2.1. General

The ligand 4'-Mebpy-4-COOH (4'-methyl-2,2'-bipyridine-4-carboxylic acid), and the complexes  $\text{Ru}^{\text{III}}(\text{terpy})\text{Cl}_3$  and  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H-4'-Meppy})\text{Cl}]\text{Cl}$  were synthesized according to literature [36,38–39]. All reagents were purchased from Aldrich Chemical Co. and were used as received. Silica gel K100 was purchased from Merck and was activated at 200 °C for 12 h before use. All used substrates were purchased from Aldrich, in their highest commercial purity, stored at 5 °C and purified by passage through a column of basic alumina prior to use. TBHP used was also purchased from Aldrich (~5.5 M solution in decane).

Elemental analyses (C, H, N) were obtained using a Perkin Elmer Series II 2400 elemental analyzer. The ruthenium amount was determined by flame atomic absorption spectroscopy on a Perkin-Elmer AAS-700 spectrometer. Infrared spectra were recorded on a Spectrum GX Perkin-Elmer FT-IR System. UV-Vis spectra were recorded using a UV/VIS/NIR JASCO Spectrophotometer and a Perkin-Elmer Lambda 35 with a diffuse reflectance setup. Thermogravimetric analyses were carried out using Shimadzu DTG-60 analyser. GC analysis was performed using an 8000 Fisons chromatograph

with a flame ionization detector and a Shimadzu GC-17A gas chromatograph coupled with a GCMS-QP5000 mass spectrometer.

### 2.2. Catalyst preparation and characterization

#### 2.2.1. Synthesis of amino-propyl-modified silica $[\text{NH}_2(\text{CH}_2)_3\text{SiO}_{3/2}]_p \cdot y\text{SiO}_2$

Amino-propyl-modified silica was synthesized according to [40]. *Anal. Calc.* Found: C, 4.68; N, 1.82%; organic weight loss (%) 7.9. DRIFTS-IR ( $\text{cm}^{-1}$ , selected peaks of the organic functionality): 3658:  $\nu(\text{N-H})$ ; 1661:  $\delta(\text{N-H})$ ; 1591:  $\nu(\text{C-N})$ ; 1480:  $\delta(\text{C-C})$ . The loading achieved is ca. 1.3  $\text{mmol g}^{-1}$  determined by thermogravimetric and elemental analysis.

#### 2.2.2. Synthesis of $[4'\text{-Mebpy/4-CONH}(\text{CH}_2)_3\text{SiO}_{3/2}]_n \cdot x\text{SiO}_2$

The conjugation of the ligand 4'-Mebpy-4-COOH (340 mg) to the amino-propyl-modified silica (200 mg) was achieved with the coupling agents benzotriazol-1-yl-oxytris(pyrrolidino)phosphonium hexafluorophosphate (pyBOP, 852 mg) and diisopropylethylamine (DIPEA, 528  $\mu\text{l}$ ) in *N*-methyl-2-pyrrolidone (NMP, 1 ml). After 24 h reaction at room temperature, the solid material was filtered and washed carefully with NMP, EtOH and MeOH. *Anal. Calc.* Found: C, 5.82; N, 2.79%; organic weight loss (%) 13.8. DRIFTS-IR ( $\text{cm}^{-1}$ , selected peaks of the organic functionality): 3456:  $\nu(\text{N-H})$ ; 1705:  $\nu(\text{C=O})$ ; 1653:  $\nu(\text{C=C})$ ; 1522:  $\nu(\text{C-N})$ . Elemental and thermogravimetric analysis indicated a post-modification degree of 0.23 mmol attached ligand/g modified support.

#### 2.2.3. Synthesis of $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{-Mebpy/4CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_m \cdot z\text{SiO}_2$

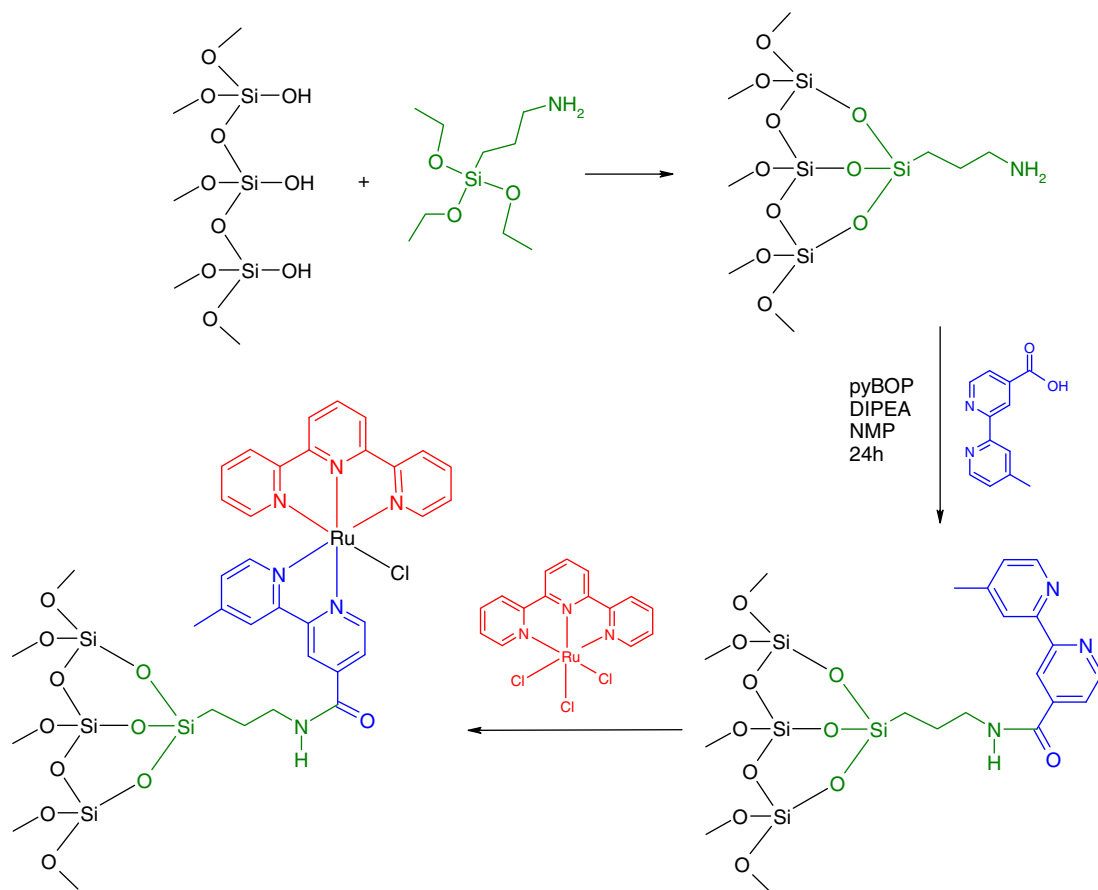
The post-modified silica  $[4'\text{-Mebpy/4-CONH}(\text{CH}_2)_3\text{SiO}_{3/2}]_n \cdot x\text{SiO}_2$  (200 mg) was refluxed with  $\text{Ru}^{\text{III}}(\text{terpy})\text{Cl}_3$  (110 mg), LiCl (15 mg) and  $\text{Et}_3\text{N}$  (60  $\mu\text{l}$ ), in DMF/EtOH (4.5/1.5 ml v/v) for 24 h. The solid product was filtered and washed thoroughly with DMF, EtOH and MeOH. *Anal. Calc.* Found: C, 12.90; N, 3.67%; Ru, 2.22; organic weight loss (%) 19.5. DRIFTS-IR ( $\text{cm}^{-1}$ , selected peaks of the organic ligand): 3063:  $\nu(\text{N-H})$ ; 1705:  $\nu(\text{C=O})$ ; 1659:  $\nu(\text{C=C})$ ; 1598:  $\nu(\text{C-N})$ . Metal loading: 0.22  $\text{mmol g}^{-1}$ . The further organic loading achieved is ca. 0.21  $\text{mmol g}^{-1}$  determined by thermogravimetric and elemental analysis. DR-UV-Vis ( $\lambda_{\text{max}}$ , nm): 274:  $\pi \rightarrow \pi^*$  (intraligand); 329, 350 and 400:  $d_{\pi}(\text{Ru}) \rightarrow \pi^*$  (ligand) (MLCT); 580:  $d_{\pi}(\text{Ru}) \rightarrow \pi^*$  (ligand) (MLCT) [41].

### 2.3. Catalytic evaluation

TBHP was slowly added (within a period of 5 min) to a *tert*-BuOH solution (0.9 ml) containing the catalyst and the substrate under Ar atmosphere, at room temperature (26 °C). As an internal standard, acetophenone or bromobenzene were used. Catalytic reactions were started by adding the oxidant into reaction mixture. The ratio of [catalyst: oxidant: substrate] was equal to [1:100:1000]  $\mu\text{mol}$ . We underline that in catalytic reactions taking place under air,  $\text{O}_2$  affected both yield and selectivity of the oxidation products. Thus, in the data shown herein all the catalytic reactions were studied under strict inert Ar atmosphere.

The progress of the reaction was monitored by GC-MS, by removing small samples of the reaction mixture. The yields reported herein are based on the amount of oxidant added. Reactions were complete within 24 h. To establish the identity of the products unequivocally, the retention times and spectral data were compared to those of commercially available compounds. Blank experiments showed that without catalyst the oxidative reactions do not take place.

Control for metal leaching from the heterogeneous catalyst during the catalytic experiments was accomplished (a) by ruthenium analysis into the catalytic medium and (b) by the 'filtration method'



**Scheme 3.** Synthetic procedure for the bio-derived silica  $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{-Mebpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_m \cdot z\text{SiO}_2$ .

[10,42]. Both methods indicated that no metal-leaching occurred during the catalytic process.

### 3. Results and discussion

#### 3.1. Covalent attachment of the ruthenium complex

The synthesis of bio-derived silica  $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{-Mebpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_m \cdot z\text{SiO}_2$  was performed in three steps (Scheme 3). In the first step, 3-aminopropyltriethoxysilane was immobilized on a silica surface resulting in  $[\text{NH}_2(\text{CH}_2)_3\text{SiO}_{3/2}]_p \cdot y\text{SiO}_2$  modified silica with 1.3 mmol organic content/g modified silica. Subsequently, the attachment of the ligand 4'-Mebpy-4-COOH to the modified support occurred *via* formation of a pseudo-peptide bond between the carboxy-terminal of the ligand and the amino-functional group of the modified silica. This conjugation was achieved by the coupling agents pyBOP and DIPEA in N-methyl-2-pyrrolidone forming the  $[4'\text{-Mebpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2}]_n \cdot x\text{SiO}_2$  modified material. Approximately, 18% of the  $\text{NH}_2$ -groups of the amino-propyl-modified silica reacted with the ligand. Finally, the post-modified silica  $[4'\text{-Mebpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2}]_n \cdot x\text{SiO}_2$  was reacted with  $\text{Ru}^{\text{III}}(\text{terpy})\text{Cl}_3$  by refluxing in DMF/EtOH yielding the ruthenium complex supported on silica  $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{-Mebpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_m \cdot z\text{SiO}_2$ . The ruthenium loading on the silica was found 0.22 mmol ruthenium/g modified silica.

#### 3.2. Catalytic evaluation of the modified material

The catalytic properties of the  $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{-Mebpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_m \cdot z\text{SiO}_2$  modified silica as heterogeneous

**Table 1**

Alkene oxidation catalyzed by  $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{-Mebpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_m \cdot z\text{SiO}_2$  modified silica with TBHP.<sup>a</sup>

Substrate	Products	Yield (%) <sup>b</sup>
Cyclohexene	<i>cis</i> -Epoxide	5.0 (5.0) <sup>c</sup>
	2-Cyclohexenol	22.0 (12.7)
	2-Cyclohexenone	46.0 (27.0)
1Methylcyclohexene	<i>cis</i> -Epoxide	21.0 (32.0)
	3-Methyl-2-cyclohexen-1-ol	24.0 (12.0)
	3-Methyl-2-cyclohexen-1-one	8.0 (14.0)
Cyclooctene	<i>cis</i> -Epoxide	70.0 (20.0)
	2-Cyclooctenone	18.0 (5.0)
Styrene	Epoxide	24.0 (30.0)
	Benzaldehyde	19.0 (13.0)
Methyl-styrene	<i>trans</i> -Epoxide	20.5 (50.0)
	Benzaldehyde	21.5 (13.0)
<i>cis</i> -Styrene	<i>cis</i> -Epoxide	54.0 (16.5)
	<i>trans</i> -Epoxide	15.0 (6.6)
	Benzaldehyde	20.0 (25.0)
Limonene	1,2-Epoxides ( <i>Z</i> - and <i>E</i> -)	15.0 (20.0)
	Limonene alcohol <sup>d</sup>	31.1 <sup>e</sup> (32.0) <sup>f</sup>
	Limonene ketone <sup>g</sup>	23.0 (22.0)

<sup>a</sup> Conditions: ratio of catalyst:TBHP:substrate = 1:100:1000. Reactions were completed within 24 h.

<sup>b</sup> Yield based on oxidant added.

<sup>c</sup> Data given in parenthesis ( ) were provided by homogeneous  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H}-4'\text{-Mebpy})\text{Cl}]\text{Cl}$  catalyst.

<sup>d</sup> Limonene alcohols were found to be a mixture of 1-ol, 2-ol and 6-ol.

<sup>e</sup> 31.1% Yield corresponds to 8.0% for 1-ol, 5.1% for 2-ol and 18.0% for 6-ol.

<sup>f</sup> 32% Yield corresponds to 6% for 1-ol, 10.0% for 2-ol and 16.0% for 6-ol.

<sup>g</sup> The only observed ketone is the 6-one.

catalyst for alkene oxidation with TBHP have been evaluated. The oxidation reactions were carried out at room temperature (26 °C)

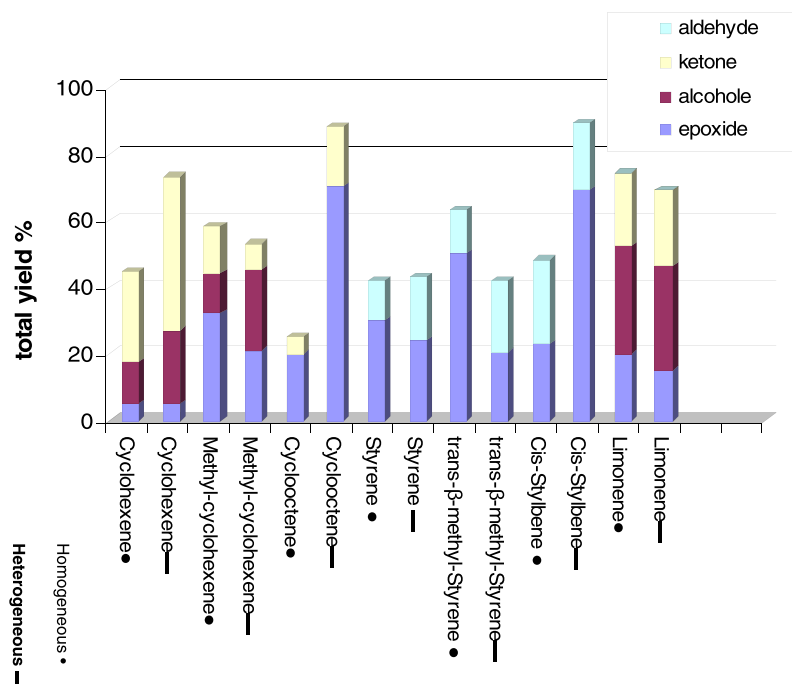


Fig. 1. Distribution of oxidation products catalyzed by grafted on silica or 'net' biomimetic ruthenium complexes in the presence of TBHP. See Table 1 for further details.

under inert Ar atmosphere. For comparison reasons, the catalytic behaviour of the 'net'  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H-4'-Mebpy})\text{Cl}]\text{Cl}$  complex as homogeneous catalyst, under the same experimental conditions, has been also investigated. The catalytic results are summarized in Table 1. Fig. 1 provides a histogram plot of the data in Table 1.

Based on Table 1, the Ru-containing modified silica was efficient in alkene oxidations providing significant yields. More specifically, cyclohexene and limonene oxidation provided oxidation products with a combined yield of 73.0% and 69.1% respectively. Cyclohexene undergoes mainly allylic oxidation forming 2-cyclohexene-1-ol and 2-cyclohexene-1-one with yield 22.0% and 46.0% respectively. However cyclohexene epoxidation was also observed, providing low epoxide yield of 5.0%. Overall, cyclohexene was oxidised by  $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{Mebpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_{\text{m}}\text{zSiO}_2$  providing 73.0% total oxidation yield. The major products detected from limonene oxidation were (i) two epoxides (*Z*- and *E*-) derived from epoxidation of the electron-rich double bond in 1,2-position, (ii) alcohols derived from hydroxylation in 1-, 2- and 6-positions of limonene ring. Oxidation products from the more accessible, but less electron-rich, double bond at 8,9-position were not observed. Additionally, considerable amounts of the corresponding ketone at 6-position was also formed. In summary, the total yield were (a) epoxides (*Z*-1,2 and *E*-1,2) 15.0%, (b) alcohols (1-ol, 2-ol and 6-ol) 31.1% and (c) ketone (only at 6-position) 23.0%. These results provide a total oxidation yield of 69.1% achieved by ruthenium complex grafted on silica.

In the case of methyl-cyclohexene, the detected oxidation products were *cis*-epoxide (21.0%), 3-methyl-2-cyclohexen-1-ol (24.0%) and 3-methyl-2-cyclohexen-1-one (8.0%) with a total yield of 53.0%. *cis*-Cyclooctene as substrate afforded two reaction products giving *cis*-cyclooctene epoxide and 2-cyclooctenone with 70.0% and 18.0% yield respectively. Styrene oxidation provided epoxide (24.0%) and benzaldehyde (19.0%) as oxidation products formed by direct oxidation and oxidative cleavage respectively of the exo-cyclic double bond. Overall, styrene was oxidised by  $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{Mebpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_{\text{m}}\text{zSiO}_2$  with total oxidation yield 43.0%. The methyl-substituted styrene, *trans*-β-methyl styrene provided total oxidation yield 42.0%. The identified products

were *trans*-epoxide (20.5%) and benzaldehyde (21.5%) as oxidation cleavage adduct. In the oxidation of *cis*-stilbene, the major products were epoxides: *cis*-stilbene epoxide with yield 54.0% and *trans*-stilbene epoxide with yield 15.0% respectively. Considerable amounts of benzaldehyde as oxidative cleavage product (20.0%) have been also detected.

Comparing the ruthenium complex covalently attached on silica surface  $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{Mebpy}/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_{\text{m}}\text{zSiO}_2$  with the corresponding 'net' complex  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H-4'-Mebpy})\text{Cl}]\text{Cl}$  (see Table 1 and Fig. 1), we observe that the attached system leads to considerable reactivity with TBHP presenting analogous profile of oxidation products with those of the 'net' homogeneous system. However, in some cases, i.e., in cyclohexene, cyclooctene and *cis*-stilbene oxidation, the Ru-containing modified silica showed increased activity providing total oxidation yield 73.0%, 88.0% and 89.0% respectively vs. 44.7%, 25.0% and 48.1% yielded by the 'net' homogeneous catalyst. That is, the applied grafting process preserves the catalytic activity of the 'net' complex and, in some cases increases its reactivity. Moreover, the inorganic support does not introduce any steric hindrance preventing the substrate access to the active metal sites.

Alkene oxidations catalyzed by both attached and 'net' ruthenium complex with TBHP present comparable selectivity and distribution of oxidation products with those catalyzed by iron-non-heme catalysts with  $\text{H}_2\text{O}_2$  [9]. In these systems, the major oxidation products of alkenes were alcohols and ketones, mainly derived by an allylic oxidation reaction; however, considerable amounts of epoxides have been also formed. This behavior could indicate similar mechanistic path in the catalysis as in the iron-catalyzed-oxidations [9], i.e., the formation here of a  $\text{Ru}^{\text{III}}\text{-OO}^t\text{Bu}$  intermediate which undergoes homolytic O–O bond cleavage providing  $\text{Ru}^{\text{IV}}=\text{O}$  and  $\cdot\text{O}^t\text{Bu}$  species [22,35].

#### 4. Conclusion

The biomimetic ruthenium complex  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H-4'-Mebpy})\text{Cl}]^+$  has been covalently attached on silica surface through the formation of a pseudo-peptide bond providing the bio-derived

silica,  $[\text{Ru}^{\text{II}}(\text{terpy})(4'\text{-Me}bpy/4\text{CONH}(\text{CH}_2)_3\text{SiO}_{3/2})\text{Cl}]^+_m\text{-zSiO}_2$ . The Ru-containing modified silica, which was evaluated as heterogeneous catalyst, was efficient in alkene oxidations with TBHP as oxidant providing significant yields and, in some cases, it showed increased activity compared to 'net' ruthenium complex. The catalytic data indicate that the used grafting process was appropriate and able to preserve the catalytic behaviour of the 'net' active ruthenium complex  $[\text{Ru}^{\text{II}}(\text{terpy})(4\text{-CO}_2\text{H-4'-Me}bpy)\text{Cl}]^+$ . This is a very interesting and useful approach for tailoring homogeneous catalysts *via* their immobilisation. The chemical behaviour of ruthenium complexes in solution and covalently attached on silica is quite similar and we suggest that they probably function *via* the formation of ruthenium-peroxo-species with a dominant radical mechanistic path.

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.poly.2012.07.094>.

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